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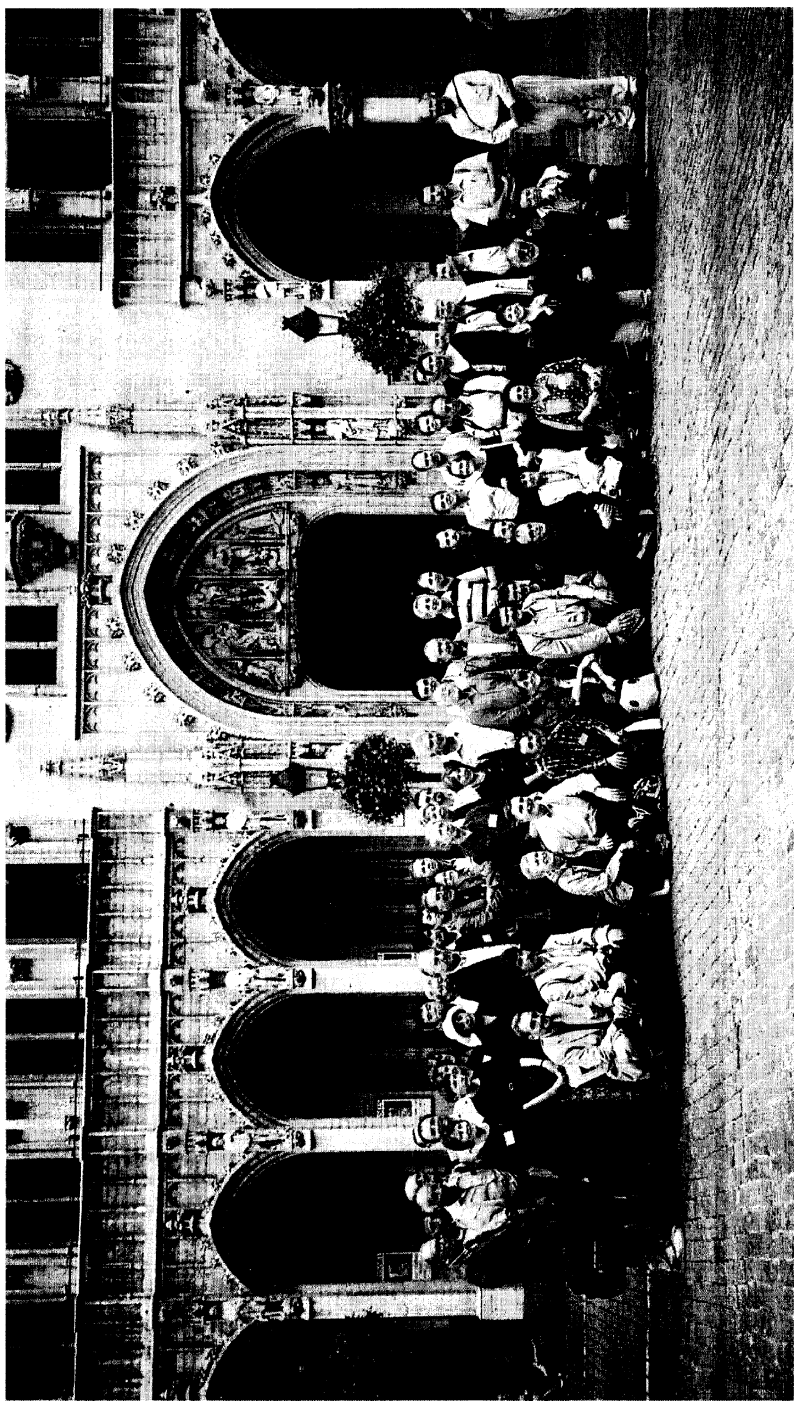
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Preface

From August 26 till September 1, 2002 the ancient college of The Falcon in Leuven was the scene of the sixteenth edition of the International Jahn–Teller conference. This series of meetings started in Bad Honnef in 1976, first as an annual symposium, later on since 1983 as a biannual international conference. Conference locations alternated between Western and Eastern Europe, but in 2000 the conference moved to Boston, to come back to Europe now and find hospitality at the Catholic University of Leuven, Belgium. Over the years the theme of the conference has broadened to cover all aspects and possible manifestations of vibronic interactions. In this evolution the Jahn–Teller effect itself acts as a kind of paradigmatic core, describing the symmetric case of electronic degeneracy. In the conference in Leuven, the whole spectrum of applications in chemistry and physics was amply demonstrated through 12 invited plenary lectures, 25 oral presentations, and some 40 posters. The present volume offers a detailed account of all this work.

In spite of the long history of the Jahn–Teller effect new fundamental perspectives were also presented at this sixteenth edition: they were in part inspired by the developing studies of icosahedral systems, mainly in fullerene science, which require advanced group theoretical and topological techniques. One of the important fundamental themes during the conference was the theoretical description of nonadiabatic effects. Strong debates were held over the role of the geometric phase in connection with the topology of the seam of conical intersections. Participants left the conference with the idea that serious further work must be done on the clarification of the nonadiabatic effect. There should come an unambiguous answer to the question of how to describe the dynamics in the crossing region of two adiabatic potential energy surfaces. From the chemical point of view we discovered the firm statement that so far detailed analysis of some twenty photochemical processes has revealed that the photochemical reaction always proceeds through a conical intersection. This aspect has important consequences both for the study of chemical reactions and the role of Woodward–Hoffmann selection rules, and for the study of the Jahn–Teller effect itself. We hope that these two lines of research will converge towards each other in the near future. Traditionally the Jahn–Teller effect in physics is connected to the study of impurity centres and cooperative phenomena in the solid state, and the current proceedings contains accounts of several new developments in this area. One new aspect involves the concept of an ‘orbiton’, an orbital excitation in a lattice which can travel as a wave, and may couple to Jahn–Teller active vibrations and to spin magnons. Fullerenes and the hot topic of their potential



Participants of the 16th JT symposium in front of Brussels Hôtel de Ville.

superconductivity in positively charged states mark another area of continuing emphasis, where the Jahn–Teller effect is prominently present in current physics.

We hope that the participants and the larger scientific community, interested in vibronic effect, may find in the present volume a reference text on the current status of the study of the Jahn–Teller effect, and a source of inspiration for future work. At the end we express our profound gratitude to the conference secretary, Mrs. R. Jungbluth-Hendrickx, for the perfect organisation, to the international organizing committee, chaired by Prof. Colin Bates for the full support with the programme, and to our sponsors: K.U. Leuven, the research community of the Flemish Quantum Chemists, and the National Science Fund, F.W.O. Vlaanderen.

While the proceedings of the sixteenth conference went into press, news agencies around the world announced the decease of Dr. Edward Teller at the age of 95. The Jahn–Teller community commemorates him as author, together with Jahn, of the seminal paper that gave birth to the entire subject of symmetry breaking and vibronic coupling.

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Obituary Frank Ham (1928–2002)

Frank S. Ham died on Thursday, 12 December 2002, at the age of 74.
He is survived by his wife Joan and two sons William and Peter.



Frank Ham – The Theoretician for Experimentalists

If there were to be a celestial dinner party of the greatest physicists, most participants would request to be seated next to Frank Ham. Frank was a gifted conversationalist, who could command the attention of an audience on a variety of topics. His passing will come as a shock to many, as the vivacity of his personality drove away the thoughts of death from any association with him.¹

¹I had the pleasure of playing host to Frank for several days in the summer of 1999, when he gave a series of lectures in Switzerland, and I would often invite friends and colleagues to join us for dinner. Frank relished meeting people. One evening I informed him that I had invited a professor from our department, who was also a colonel in the Swiss army. This found Frank expatiating on military history, WWII in particular. On another occasion, he would astound our Swiss guests with his repertoire of German folk songs. At the weekend I took him on a walk which I thought suitable for those over seventy. This did not suit him at all. Rather than go *around* the mountain, Frank insisted on going *over* it. I must confess that though Frank was over twice my age, I had difficulty in keeping up with him.

Frank Slagle Ham was born in Bronxville, New York on August 15, 1928, the only child of William T. Ham and Virginia Slagle. He grew up in Washington, D.C. and obtained both a B.A. and a Ph. D. in physics from Harvard. After a year at the University of Illinois working with John Bardeen, he moved to the General Electric Research and Development centre in 1955. “They told me that it doesn’t matter what you do or how long it takes, just do some good science”, and indeed he did.

He quickly demonstrated his aptitude for solid state physics, and his early work attests to a broad range of interests. In 1964 Frank had an idea that led him to write two papers and a review article on the dynamical Jahn–Teller effect that are widely recognised as classics. He was puzzling over some rather interesting EPR data for various transition metal ions doped into silicon, and binary oxides; systems where the ground term is orbitally degenerate, and hence a Jahn–Teller effect is to be expected. Contrary to common belief at that time, the spectra were characteristic of a cubic rather than a low symmetry structure, but with a significant reduction in the orbital Zeeman effect. Frank thought about orbital angular momentum in the presence of $T \otimes e$ Jahn–Teller coupling, and then pronounced ebulliently, “It’s being quenched!” His work on the dynamic Jahn–Teller effect instigated an explosion of research into Jahn–Teller systems. Experimentalists loved Frank’s theory as the concept was simple and it gave them something to measure. “The Ham Effect”, “Ham-Quenching”, and “Ham-Factors” soon became common parlance amongst spectroscopists.

In the 1970s Frank continued to work on the Jahn–Teller effect, but now the philosophy at G. E. was changing. Frank told me that he would write an article but not submit it, as this would expose what he was working on. He said he could empathise with L. A. Boatner, whom he quotes as saying, “They [the authorities at LTV Aerospace Corporation] were interested in the work I had been doing until they found out that they couldn’t put a Jahn–Teller on an aeroplane”. In the early 1980s Frank wished to work on Quantum dots whereas G. E. wanted him to work on computer-assisted molecular modelling. I could not help but smile when Frank told me this. Whilst Frank was a brilliant theoretician, who could conjure up a simple analytical expression to describe very complex phenomena, computers were not his forte. To the very end, Frank hand-wrote all his papers, preparing the final version with a typewriter. Frank is the only person to have ever sent me an e-mail with the express purpose of asking me for my e-mail address. In 1983 Frank took early retirement from G. E. and became a consultant at the department of Physics at Lehigh University, in close collaboration with George Watkins. 1987 saw the publication of his seminal paper on “Berry’s geometrical phase and the sequence of states in the Jahn–Teller effect”, which once again is recognised as a harbinger of a spate of subsequent philosophical enquiry.

The Lisha Kill Natural Area was one of the passions and delights of his life. He raised the funds to buy the land for the Nature Conservancy, laid out, marked and maintained the trails, and supervised the project for over forty years.

During his visit to our department in 1999, I was quite taken by his interest in the work of synthetic inorganic chemists and spectroscopists. Frank told me he regarded himself as a theoretician for experimentalists, and hence the title of this obituary. His heart beat a little bit faster when shown a beautiful spectrum, and he could communicate; this was an integral factor in his success. His series of lectures met with such applause that many entreated him, with much importunity, to write a book on the Jahn–Teller effect. He said he would give serious consideration to the matter. Sadly, this endeavour was never undertaken. In 1997, his intellectual soul-mate Mary O’Brien had died. On 13 April 2001, he wrote to me thus, “I surely do miss Mary, as I’m sure you do too. After her death, I found that my interest in many of the questions we had pursued more or less in parallel simply crashed, and I have not been able to do much to reinvigorate them since.”

Frank was a master at providing clear, straightforward explanations to problems of great complexity. His articles had the rare combination of perspicuity and perspicacity. As a measure of the perennial impact of Frank’s work consider this: Throughout his career Frank S. Ham was the author, or co-author, of 64 articles; in the last four years alone, these papers have been cited 343 times – a remarkable achievement. I frequently sought his opinion on articles that I had written and more often than not received a reply, which, I think, epitomised his approach to problem solving: “Nice work, but I am sure this could be solved analytically”.

Philip L.W. Tregenna-Piggott,
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University of Bern,
Switzerland.

Frank Ham and the Jahn–Teller Community

The Jahn–Teller community has lost one of our illustrious members with the death of Frank Ham on December 12, 2002. Phrases such as ‘The Ham effect’, ‘Ham factors’ and ‘Ham quenching’ are terms that frequently appear in any article in which the Jahn–Teller effect or vibronic coupling is involved. I would like to record my own personal thoughts about Frank and on behalf of the whole Jahn–Teller community.

I was in contact with Frank Ham for over 30 years through his several visits to Nottingham, our meetings at conferences and from a large amount of correspondence initially by letter and then latterly via e-mail. I always found his comments on my work and those of my students and colleagues extremely valuable and particularly constructive. Frank attended many of the 16 Jahn–Teller symposia, which began in 1976 in Bad Honnef, Germany and it is fitting that the last one he attended was in Boston USA, very close to Frank’s home in Schenectady. This venue was also significant because this was the first time that any of the Symposia had left the confines of its European homeland and gone to the U.S. It is a testimony to Frank’s support for the symposia that he attended many of them at his personal

expense as G. E., who employed Frank, was not supporting research on the Jahn–Teller Effect!

I first heard of Frank, although I had not then met him, when I was a research (graduate) student at Nottingham University when my supervisor (Ken Stevens) passed me a copy of his PhD thesis. This was probably in either 1958 or 1959 but I still have the thesis! Ken and Frank had been friends a few years before at Harvard. The thesis is entitled “Electronic Energy Bands in Metals” and Ken probably passed it on to me as my own thesis was based on the band structure of iron. It describes a procedure called the Quantum Defect Method that Frank studied under his supervisor Harvey Brooks. I have searched the thesis for the names ‘Jahn’ and ‘Teller’ without success! However, there are many pages devoted to the WKB approximation which I have recently used with my colleagues Janette Dunn and Victor Polinger in analysing possible tunnelling paths in particular Jahn–Teller systems. I have always been impressed by the way that Frank could pick out the essential facts in any experiment, report, theory (such as the WKB method) or argument and replace them with his own carefully considered views. This ability was already apparent in his thesis. The appendices contain many numerical and analytical expressions of his results from his quantum defect calculations including errata of tables published by others. It is hard to realise that all such calculations were probably undertaken with just hand-operated mechanical calculators. Although Frank was a theoretician, he was always very keen to find out how any experimental data was obtained and how the results could be interpreted. He made much use of group theory in his calculations at a time when there were virtually no textbooks in English on the subject. He had the task of giving a physical gloss to the subject, which existed almost entirely through a mathematical framework often described in German.

Frank’s research career began at a time when Solid State Physics was a new topic in Physics. He contributed very much to what became an all-embracing topic in both basic physics and in its numerous applications in chemistry as well as physics in areas now frequently described as ‘Condensed Matter’. He pointed out how random strains can force a dynamic Jahn–Teller system to reflect distorted static behaviour in certain cases particularly in EPR spectra. This involved considerations of the orbital angular momentum of the magnetic ions present in these systems and he showed how the ‘Ham Effect’, as it became known, could explain why the electronic angular momentum could be quenched in many systems.

Frank had a long and very fruitful collaboration with Mary O’Brien, which lasted until Mary died in 1997. It is perhaps fitting to add that the last e-mail I had from Frank in November 2000 talked about his plans to make some minor corrections to Mary’s manuscript describing her calculations of tunnelling paths in two Jahn–Teller systems which she never had time to publish before she died. Frank said that my correspondence with him had given him the incentive to correct the few errors in the paper previously identified by Mary and submit this for publication under both their names. Sadly, Frank died before this could be done.

‘Frank was a gifted conversationalist.’ This leads me to mention another side to Frank that is perhaps even more important than his life as a physicist. It has always

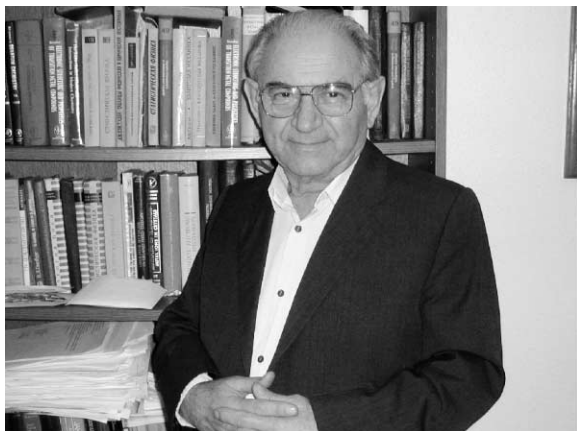
been my practice to take my research students to conferences whenever possible so that they could meet and talk to the leading figures in the field and hear them talking about their work. Frank was an excellent person to meet research students. For example, Janette recalls the many long discussions she had with Frank when she was a research student (and many times since then!) at conferences and in private meetings. Like others before her and other research students after her, she found him so very easy to talk to. He would spend as much time with a young student as he would with a leading senior professor in the field. He was always interested in what they were doing and would pass on his views whether they were supportive or not, in a constructive way. Victor Polinger told me that, just before he was about to leave Kishinev for the US, he sent a brief note to Frank telling him of his plans. By return, Frank sent Victor a five-page hand written letter pointing out the pros and cons of such a decision.

Probably the last time I saw Frank was towards the end of the symposium in Boston. During the ‘free’ afternoon, he offered to drive my wife Margaret, Janette and me to Concord. This is a very nice historic town including Hawthorne’s Old Manse and other old homes, but most famously known for the bridge that was the site of the last battle between the English and Americans! I will always treasure the photograph taken by Margaret of the three of us standing on this bridge.

Frank was not only a Great Scientist but also a delightful man to meet and to talk to, and it was always a pleasure to be in his company.

Colin A. Bates,
School of Physics and Astronomy,
University of Nottingham.

Anniversary Isaac Bersuker 75



Isaac B. Bersuker is 75. Hard to believe! This is because he's not changed since the late sixties when we, young and enthusiastic students, met him for the first time at the Institute of Chemistry in Moldova. Well, he's changed a little: he has more grey hair on his head. The rest, his boiling academic activity, his restless lifestyle, his ability to go to the roots of new ideas, has not changed a bit. Although Bersuker doesn't like to waste time on biographical memories and reminiscences, we learned something about his life.

He was born in 1928 to a family of a carpenter. He was 13 years old when tragic events of the World War II forced his Jewish family to run from the Nazis to an Azerbaijan village where he spent a year as a shepherd boy. In the best meaning of this expression, Isaac Bersuker is a self-made man. After the war, fluent in Yiddish and Romanian but with a limited ability to speak Russian, he completed a four-year program of a Russian-speaking high school in two years and then graduated from Kishinev State University in Moldova with an excellent GPA. Several years later he earned his PhD in physics from Leningrad (now Saint-Petersburg) State University in Russia at the laboratory of Prof. V. Fock, under the guidance of Prof. M. Veselov.

His early works on adiabatic separation of valence electrons from fast moving core electrons in atoms attracted much attention a few years later, when the time came for the theory of pseudopotentials. These papers are still being referred to, more than forty years after their publication.

In the late fifties, he moved back to Kishinev where, in the Institute of Chemistry, he created his famous Laboratory of Quantum Chemistry. At that time Isaac Bersuker turned his attention to the Jahn–Teller effect and, more generally, to the theory of vibronic interactions in molecules and solids. He was among the first to realize that the Jahn–Teller effect is something more important than just a source of distortions in symmetric molecules and that it plays a determinant role in numerous physical and chemical properties of polyatomic systems. As a result, his studies expanded to a larger field of systems and topics. Besides the general theory of the Jahn–Teller effect, Bersuker considered its manifestations in impurity centers in solids, chemical reactivity and catalysis, different spectral ranges in molecular spectroscopy, cooperative phenomena in solids, etc. In early sixties he published several pioneering works that explained the physics of Jahn–Teller tunneling and its averaging role in symmetry breaking phenomena. In addition, he developed the most general method of evaluating tunneling splitting energy gaps that includes anisotropy of potential wells. In 1966 Bersuker suggested a pseudo Jahn–Teller effect as the physical mechanism of ferroelectricity in titanates. About 15 years later predictions of his vibronic theory of ferroelectricity were brilliantly confirmed. In the late eighties Kishinev was called “the capital of the Jahn–Teller effect” by some.

After the disintegration of the Soviet Union, Bersuker’s team spread to many parts of the world. In 1993 he moved to the United States. As at the very beginning, Bersuker found himself alone, without his lab and without the software for electronic structure calculations he developed in Kishinev. So he started everything from the scratch. Today, in his seventies he is surrounded by young students ignited by his contagious ideas, as we were thirty years ago. Bersuker’s recent publications on the crossover problem in the theory of Jahn–Teller effect demonstrate his inexhaustible ability to generate new ideas. Working for years in a chemical institution, he was motivated to solve some chemical problems as well. As everything else he did, Bersuker’s contribution to quantum chemistry was full of new ideas and ingenious approaches. He was the initiator of a new and very promising trend in theoretical chemistry that combines methods of quantum chemistry with statistics of large samples of molecules having a certain biochemical activity. In this field he is most active today.

Our brief review of Bersuker’s academic life won’t be complete, without mention to his excellent reviews and books on the Jahn–Teller effect and vibronic interactions in molecules and solids, on vibronic theory of ferroelectricity, on electron properties of coordination compounds, and on the electron-conformational approach to the problem of identification of biologically active units in a large set of molecules. However, the most important creation of Isaac Bersuker is his school, the world-known group of scholars that hold his system of views and follow his high

criteria of a true academic style. We are proud to belong to this school. Happy birthday, Isaac Borisovich!

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Encounters with Isaac Bersuker

In 1969 the conference commemorating the 25th anniversary of the discovery of Electron Paramagnetic Resonance (EPR) by E.S. Zavoisky took place at the Kazan State University. We were both interested in the Jahn–Teller effect of single ions; Isaac mainly in understanding the dynamic ground state with theory, and I with EPR relaxation, in investigating the excited state including the existence of Slonewski modes. The excursion of the conference was organized to be on a large ship on the river Volga, where the possibility for scientific discussions in cabins was arranged. Isaac and I took advantage of this possibility and reviewed our knowledge on the subject. However, we did not restrict the ample time at disposition to our common scientific interests but found quite other topics where our views matched. This included our time in the Second World War, where he was saved by being evacuated from Kishinev by his government, and I by living in Switzerland surrounded but not occupied by national socialistic Germany. This encounter on the Volga River marked the beginning of the many years of friendship.

We met at most of the Conferences AMPERE, devoted to magnetic resonance phenomena, which purposely took place consecutively one time in the west and next time in the east of Europe. I had the pleasure to invite Isaac to the Research IBM laboratory in Rüschlikon, my permanent work place and our home in Hedingen, and later also to the IBM T.J. Watson Research Center in Yorktown Heights, New York, where I was active for two years at the end of the seventies.

Thanks to his success in vibronic theory and his organizational capabilities, Isaac had by then become head of a large research institute in Kishinev and member of the Moldavian Academy of Sciences of the former USSR. In this position he invited me in 1986 for three weeks, with first an extended stay in Kishinev, and interesting tours to Odessa and other fascinating places. There I met his main collaborators and his family. Then my tour continued to Kazan and Leningrad, ending in Moscow. In order to help me with the unfamiliar administrative requirements in Soviet Russia, he assigned Victor Polinger to travel with me. We had of course substantial scientific debates together but also the fun of participating at the famous Leningrad first white night.

At the time I had shown, using EPR of four-valent manganese as an impurity in ferroelectric BaTiO_3 , that the Ti ions were primarily displaced along body diagonals, proving the theoretical vibronic predictions of Isaac correct. In 1986, Georg Bednorz and I already had the resistivity data indicating our discovery of high-temperature superconductivity (HTSC) in Ba doped La_2CuO_4 . However, we had not yet confirmed our findings with susceptibility measurements. Therefore I did not disclose our possible breakthrough during my visit to Russia.

After the end of the Soviet Union, Isaac moved to the University of Austin Texas because of lack of funding for his institute in Kishinev, and we only corresponded but did not meet for a quick while. Then at his proposition, Prof. Kaplan, a former collaborator of his in Kishinev, invited me to the Jahn–Teller conference in Boston in the Mid-August of 2000. The reason was the increasing experimental evidence that my concept for HTSC, which had led to the discovery of the cuprate superconductors, i.e. a vibronic Jahn–Teller ground state, was correct. There he invited me and my wife to Austin in the following spring. We were both so glad to meet his wife, and the family of his son, and musically very gifted grandson. Isaac was in full swing at the university, writing books, discussing with great wit, and quick to understand – as I had known him for well over thirty years.

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A Unique Jahn–Teller Mechanism of all the Symmetry Breakings in Molecular Systems and Condensed Matter

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Abstract

An attempt is made to present all the symmetry breakings (SB) in molecular systems and condensed matter from a unique point of view as controlled by the electronic structure, degeneracy and pseudodegeneracy, via the Jahn–Teller (JT) vibronic coupling effects [JT, Renner–Teller (RT), and pseudo Jahn–Teller (PJT) effects]. For chemically bonded systems in high-symmetry configurations and transition states of chemical reactions, as proved earlier, the JT effects are the only possible source of spontaneous distortion, which is the necessary condition of SB. It is shown that the JT (and related RT and PJT) effects are directly applicable to chemically nonbonded systems: formation of molecules from atoms (chemical bonding), as well as intermolecular interaction, can be regarded as particular cases of JT effects. This closes the gap in considering all the SB in molecular systems as triggered by JT effects. It stimulated also a general (extended and more rigorous) formulation of the JT theorem to include all the vibronic coupling effects and recent achievements in the JT effect theory. Added to the JT origin of structural phase transitions and liquid–solid transition, considered earlier, and gas–liquid transition shown to be in principle of the same JT origin, the results above lead us to a general conclusion that spontaneous SB in molecular systems and condensed matter are always associated with degeneracy or pseudodegeneracy and realized *via* JT vibronic coupling effects. Together with the concept of SB in particle physics as associated with degeneracy, we can speculate about a general picture of consecutive transformations of matter *via* similar in nature degeneracy-based SB, beginning with the *Big Bang*.

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1. INTRODUCTION

The problem of symmetry breaking (SB) is well known and multiply discussed in literature. Briefly, we can formulate it as follows. The Hamiltonian of any system of particles forming the Universe is totally symmetric with respect to rotations and reflections in the isotropic space–time, as well as transmutations of identical and equivalent particles, whereas the real objects of the material world composed by these particles do not possess such symmetry. This is seen already from the examples that we live in a world of particles, not antiparticles, and in condensed matter, we have mostly low-symmetry structures. This circumstance can be expressed by the statement that the world is in a state of *broken symmetry*. An obvious explanation of the contradiction between the totally symmetric Hamiltonian and the broken symmetry of the real world is that the latter is not a solution of its Schrödinger equation.

The picture of formation of states with broken symmetry is of significant interest. Approximately 15 billion years ago, immediately after the *Big Bang* at the temperature of $T \sim 10^{45}$ K the Universe system was in a quite symmetric state with respect to all its elementary particles. By expansion and cooling, a series of consequent spontaneous SB took place resulting in states with consequently decreasing symmetry. At $T \sim 10^4 - 10^3$ K the first elements of condensed matter – atoms—were formed. Further cooling lead to the next consequent spontaneous SB resulting in new phases of condensed states with lower symmetry. However, the mechanism of formation of these SB states and its relation to the structure of matter is not fully explored.

The SB are obviously temperature dependent and have the features of (and can be treated as) spontaneous phase transitions that lower the symmetry of the system (many SB in condensed matter *are* phase transitions). At the temperature of phase transition T_0 , the free energy $E = U - T_0 S$ (U is the internal energy and S is the entropy) of the two phases 1 (at higher symmetry) and 2 (at lower symmetry) should coincide: $U_1 - T_0 S_1 = U_2 - T_0 S_2$. The entropy of the system in the higher symmetry configuration *ceteris paribus* is always higher than in its less disordered state of lower symmetry, $S_1 > S_2$. Therefore, the SB takes place when $U_1 > U_2$ and the difference $U_1 - U_2$ compensates the contribution of entropy change $T_0(S_1 - S_2)$,

$$T_0 = (U_1 - U_2)/(S_1 - S_2) \quad (1)$$

In other words, SB may take place when there is a mechanism that spontaneously lowers the internal energy of the system together with its symmetry.

There are several obvious mechanisms that lower both the internal energy and symmetry. These are first of all electron–nuclear bonding and interatomic and intermolecular interactions. They underlie the formation of condensed matter (atoms, molecules, and solids) by cooling which takes place in a series of typical SB. Beside these cases there are many SB that are at first sight not associated with bonding, but with spontaneous distortions of high-symmetry configurations (which

are ultimately due to bonding alterations too). These are the so-called Jahn–Teller (JT), Renner–Teller (RT), and pseudo-JT (PJT) effects, jointly JT vibronic coupling effects [1–3], which are associated with degeneracy and pseudodegeneracy.

The presence of degeneracy or pseudodegeneracy is crucial in JT symmetry breaking. Qualitatively, the proper JT SB in these cases can be explained by the fact that the two or more states with equal energy required by degeneracy have necessarily different, anisotropic distribution in space. Therefore, in the presence of any anisotropic interaction (including internal interaction) the degenerate level splits, and one of its states becomes lower in energy than others thus producing a configuration with lower symmetry (in accordance with its anisotropic distribution). The case of pseudodegeneracy is in principle similar: the energy gap between the close-in-energy states increases and the ground state energy lowers by lowering the symmetry of the system.

The intention of this paper is to show that the JT, RT, and PJT mechanisms of SB are in fact of general validity for all the SB in molecular systems and condensed matter. For this purpose, after brief formulation of the basics of JT SB, we show first that the simultaneous decrease of energy and symmetry (required by SB) by formation of molecules from atoms and intermolecular interactions is either a JT or a PJT effect associated with, respectively, degeneracy or pseudodegeneracy. This allows for an extended (more general) and more rigorous formulation of the JT theorem. Then we mention the results on structural phase transitions, melting, vaporization, and enantiomer formation as SB triggered by the JT effect, and we come to the conclusion that “any SB in molecular systems and condensed matter is associated with degeneracy or pseudodegeneracy and realized via the Jahn–Teller vibronic coupling effects”. Some aspects of this problem were discussed earlier [1,4–6].

Note that a similar statement, *SB is always associated with a degeneracy* [7] is widely accepted in particle physics. We extend the analogy with particle physics to include pseudodegeneracy and speculate about a global rule of formation of matter in the Universe.

2. JAHN–TELLER, RENNER–TELLER, AND PSEUDO-JAHN–TELLER SYMMETRY BREAKING

As noted above, the necessary condition of SB by cooling is spontaneous decrease of internal energy with decrease of the symmetry of the system. For high-symmetry configurations of polyatomic systems, this requirement is wonderfully fulfilled by the JT, RT, and PJT effects [1–3]. Indeed, in systems with JT vibronic coupling effects the high-symmetry configuration is unstable, and the stable configurations at the minima of the adiabatic potential (AP) correspond to structures with lower symmetry.

Figure 1 illustrates the three cases of JT vibronic coupling effects in the simplest situation of a double degenerate or pseudodegenerate state interacting with only one

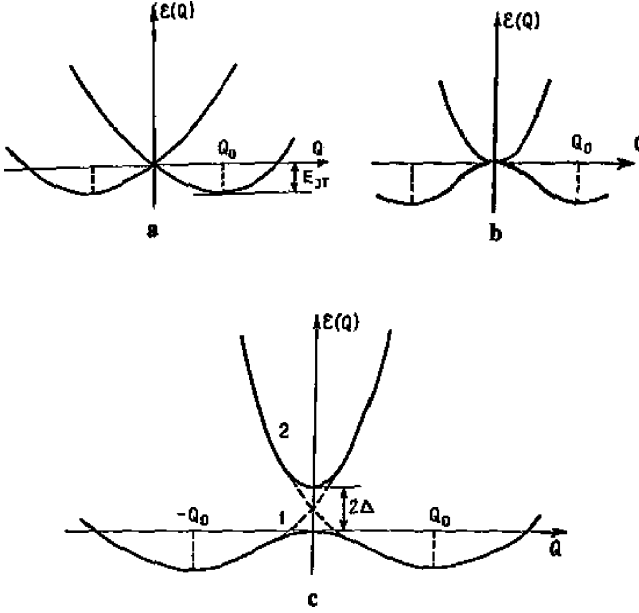


Fig. 1. The adiabatic potentials (AP) in the Jahn–Teller (a), Renner–Teller (b), and pseudo-Jahn–Teller (c) effects for systems with a double degenerate electronic term interacting with one coordinate Q ($E \otimes b_1$ problem in the JT case). In all three cases the ground state is unstable in the high-symmetry configuration $Q = 0$, while the stable configurations at $\pm Q_0$ are at lower symmetry. The differences between these cases are in the behavior of the AP at $Q = 0$.

coordinate of distortion (in the JT case it corresponds to the $E \otimes b_1$ problem [2,3]). The common feature of all these cases is decreasing energy at lower symmetry ($Q = 0$ is the point of highest symmetry) favoring spontaneous distortion that may lead to SB. The differences between these cases are in the nature of the AP splitting at $Q = 0$: in the JT case the AP branches are linear in Q , in the RT effect they are quadratic, while in the PJT effect the AP is quadratic too, but with an energy gap between the two states.

In a general description of all these cases we start with the solution at $Q = 0$, which is a 2-fold degenerate or pseudodegenerate state and include the Q -dependent interaction $V(r, Q)$ as a perturbation. The two-level problem for the electronic states yields (H is the Hamiltonian):

$$\begin{vmatrix} H_{11} - \varepsilon' & H_{12} \\ H_{21} & H_{22} - \varepsilon' \end{vmatrix} = 0 \quad (2)$$

with

$$\varepsilon'_{1,2} = \frac{1}{2} \{ H_{11} + H_{22} \pm [(H_{11} - H_{22})^2 + 4|V_{12}|^2]^{1/2} \} \quad (3)$$

For degenerate states at $Q = 0$ we have $H_{11} = H_{22}$ and with an appropriate energy read off and the basic repulsion term $\frac{1}{2}K_0Q^2$ included we get:

$$\varepsilon_{1,2} = \frac{1}{2}K_0Q^2 \pm |V_{12}| \quad (4)$$

where

$$K_0 = \langle 1 | (\partial^2 V / \partial Q^2)_0 | 1 \rangle \quad (5)$$

is the so-called primary force constant [2].

By expanding the potential $V(r, Q)$ in a series of small Q values one finds that the first nonzero matrix element V_{12} is linear in the JT case (nonlinear systems) and quadratic for the RT effect (linear molecules) [1–3]. In the case of proper JT effect the minima positions in the linear approximation are at $Q_0 = \pm F/K_0$ (Fig. 1a), where $F = \langle 1 | (\partial V / \partial Q)_0 | 2 \rangle$ is the vibronic coupling constant, while the JT stabilization energy is

$$E_{JT} = F^2 / 2K_0 \quad (6)$$

If there is no exact degeneracy, i.e. there is an energy gap 2Δ between the two states at $Q = 0$ (pseudodegeneracy), the two states after equation (2) are (the energy read off is in the middle of the energy gap at $Q = 0$):

$$\varepsilon_{1,2} = \frac{1}{2}K_0Q^2 \pm [\Delta^2 + |V_{12}|^2]^{1/2} \quad (7)$$

and the instability of the ground state occurs only if

$$\Delta < |V_{12}|^2 / K_0 \quad (8)$$

In spite of lower energy in the distorted configuration, the JT effects in a single molecular system do not mean SB. Indeed, there are two equivalent minima of the AP complementing each other, thus preserving, in principle, the symmetry of the initial high-symmetry configuration. However, in the interaction with other systems in the ensemble the equivalency of the two minima is lost and the instant distorted configurations become determinant in producing a broken symmetry state. In particular, at the temperature T_0 after equation (1) an ordering of the distortions at the minima of the AP may take place resulting in a lower symmetry phase of the system as a whole, in which the local distortions are stabilized in mutually oriented positions. Denoting high- and low-symmetry states by h and l , respectively, we have for the change of internal energy $U_h - U_l = E_{JT}$ and entropy $S_h - S_l = S_{JT}$, where E_{JT} is the JT stabilization energy of the whole system that includes the interaction of the local distortions, and by analogy S_{JT} may be called JT stabilization entropy.

Determination of the critical temperature after equation (1), $T_0 = E_{JT}/S_{JT}$, is considered in the cooperative JT and PJT effects [2,3,8,9]. In particular, the origin of structural ferroelectric phase transitions as due to the PJT effect (the vibronic theory of ferroelectricity) was suggested first in the sixties [10] (see also Ref. [9]). JT structural phase transitions are reviewed in Ref. [8].

A special feature of these JT-induced SB is that they emerge directly from the electronic structure of the system that determines the degeneracy and pseudodegeneracy and the parameters of instability (which in turn determine the SB), and it is quite clear how these SB are controlled by the electronic structure.

An important question is whether the JT vibronic coupling (JT, RT, and PJT) mechanism of SB is unique, or it is applicable to a limited number of special cases and hence there may be other mechanisms of SB that are in principle different from the JT one. The answer is that the JT mechanism of spontaneous distortions of high-symmetry configurations (chemically stable systems and transition states of chemical reactions) that leads to SB is unique, and there is no other in principle different mechanism that produces such distortions [1,2,5,11]. It was also shown that in ensembles of systems (e.g. local centers in crystals), just the interaction between them (e.g. mutual polarization) cannot produce SB without local (JT) distortions of each system [12]. The JT effects provide thus the necessary and sufficient condition of SB in the systems under consideration.

3. CHEMICAL BONDING AS A PARTICULAR CASE OF THE JAHN–TELLER EFFECT: RIGOROUS FORMULATION OF THE JT THEOREM

In a simplified formulation (for more elaborate formulations see Refs. [1–3]) the JT theorem states that “the nuclear configuration of any nonlinear polyatomic system in a degenerate (except spin 2-fold degeneracy) electronic state is unstable with respect to nuclear displacements that lower the symmetry and remove the degeneracy”. For linear systems analogous formulation is known as the RT effect (Fig. 1b), while for nondegenerate states the PJT formulation (Fig. 1c) is valid (see below). The authors of these formulations (see in Refs. [1–3]) implied that the degenerate or pseudodegenerate electronic states are inherent to the nuclear configuration of a polyatomic system formed by a set of *bonded* atoms. Meanwhile, in the proof of the statements above the set of atoms of the reference configuration are *not* required to be necessarily bonded. The only essential requirement in the proof of the JT (and related RT and PJT) theorems is the presence of two or more electronic states, which become mixed under nuclear displacements from the reference configuration.

However, so far all the applications of the JT effect theory were realized only for chemically bonded systems in their high-symmetry configuration and transition states of chemical reactions. We show here that this is an unnecessary restriction: the JT type instability is inherent to all the cases of degeneracy or pseudodegeneracy in molecular systems and condensed matter including nonbonded states in molecule formation from atoms, intermolecular interaction, and chemical reactions.

Consider first chemical bonding, i.e., the formation of molecules from atoms. In the formation of a homonuclear molecule, the two electronic states of the two identical atoms at large interatomic distances R have the same energy, and hence

they form a double degenerate state. Introducing for convenience the coordinate $Q_M = 1/R$, we get for the interaction between the atoms treated by perturbation theory the same secular equation (2) as in the JT $E \otimes b_1$ problem in which $V(r, Q)$ is the operator of interatomic interaction. The solution of this equation yields the two states with energies after equation (4) (with $K_0 = 0$), one of which is lower and the other is higher than the corresponding energies at $Q = 0$ (Fig. 2a). The lower level describes the bonding that lowers the symmetry from that of spherical atoms to the symmetry of diatomics. This reasoning can be easily expanded to the bonding of more than two identical atoms or groups of atoms and to chemical reactions. Bonding is thus a typical JT effect in nonbonded ($K_0 = 0$) systems.

For the bonding in heteronuclear diatomics we start from a pseudodegenerate term of the two different atoms at $Q = 0$ and get the same secular equation (2) with the solutions (7) as in any other cases of the PJT effect. Again, one of the solutions leads to bonding with the same decrease in symmetry, as in the homonuclear case (Fig. 2b), and this picture can be easily extended to the bonding of several different atoms or groups of atoms.

We see that there is a full similarity between the JT (or RT) and PJT distortions of stable polyatomic systems, considered in the previous section, and the formation of, respectively, homonuclear and heteronuclear diatomics, as well as bonding in extended systems. The formation of molecules from atoms (or bonding of groups of atoms) is thus another particular case of spontaneous symmetry reductions controlled by the JT vibronic coupling effects as formulated above at the beginning of this section. The differences between the particular cases of JT instability are in the details of the AP behavior at the point of degeneracy: in the proper JT case the level crossing, as mentioned above, is linear in Q (Fig. 1a), in the RT effect it is quadratic (Fig. 1b), in the PJT effect it is quadratic with an energy gap between

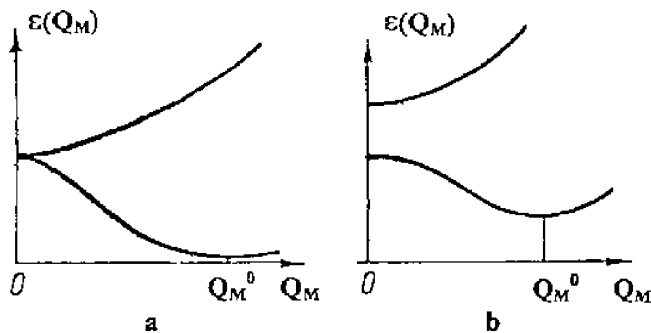


Fig. 2. Illustration to the JT and PJT effect in diatomic molecule formation. In the homonuclear case (a) the two atomic states at large interatomic distances $Q_M = 1/R = 0$ form a double degenerate term which at larger Q_M (smaller R) splits due to bonding, thus reducing the energy and symmetry quite similar to any other JT $E \otimes b_1$ problem (cf. Fig. 1a at $Q > 0$); for heteronuclear diatomics (b) the bonding picture is that of the pseudo JT effect (cf. Fig. 1c at $Q > 0$).

the two states (Fig. 1c), in homonuclear bonding it is rather exponential with $K_0 = 0$ (Fig. 2a), and in the heteronuclear bonding it is exponential too with a PJT energy gap and $K_0 = 0$ (Fig. 2b). In the latter case, there is also another distinction from the general PJT case: because of $K_0 = 0$ there is no limiting threshold of the type (8) in heteronuclear diatomics formation; instead the formation of bonding states gradually disappears with increasing energy gap 2Δ .

In chemical reactions with a transition state the later is a typical JT or (in most cases) PJT situation with the instability coordinate leading to the products formation [13]. For pure van der Waals interaction of closed-shell systems the polarization and correlation effects that lead to intermolecular bonding can in principle be described by involving excited states via the mixing of the ground state of one system with the excited state of the other one that form together the pseudodegenerate situation of the PJT effect.

Thus the SB produced by chemical bonding, intermolecular interactions, and chemical reactions can be regarded as triggered by the same mechanism of JT vibronic coupling effects as in the SB of structural phase transitions in crystals.

Based on the discussion above in this section and involving the recent achievements in the JT effect theory, especially the proof of the uniqueness of the JT origin of molecular high-symmetry configuration instability, mentioned above, we can give a more general (extended and more rigorous) formulation of the fundamental JT theorem that forms the basis of all the JT vibronic coupling effects:

“The necessary and sufficient condition of instability (lack of minimum of the AP) of high-symmetry configurations of any polyatomic system is the presence of two or more electronic states, degenerate (except 2-fold spin degeneracy) or pseudodegenerate, which interact sufficiently strong under the nuclear displacements in the direction of instability”.

4. JAHN–TELLER INDUCED SYMMETRY BREAKINGS IN STRUCTURAL PHASE TRANSITIONS, MELTING, VAPORIZATION, AND ENANTIOMER FORMATION

The JT origin of structural phase transitions in crystals with JT centers was realized at very early stages of the study of the JT effect. It is obvious that the interaction of JT local distortions in crystals, as mentioned above, under certain conditions, at temperatures T_0 in equation (1) may lead to their ordering resulting in crystal structures of lower symmetry (cooperative JT effect; for review see Ref. [8]).

Not so obvious is the JT origin of structural phase transitions in crystals without JT centers. For them it was shown that local PJT distortions may serve, in principle the same role as the JT distortions in JT crystals [2,4,9,10]. Since it was proved that the PJT is the only possible source of instability of polyatomic systems, the PJT local distortions come out to be the only source of structural phase transitions in such crystals. It was also shown that just the long-range interactions without local distortions cannot produce structural phase transitions [12].

All the SB in crystals are thus of some kind of order–disorder transitions with JT or PJT origin of the ordering distortion units. Order–disorder transitions in crystals with rigid dipole molecules may be considered as an extreme case of such SB when two or more possible positions of the molecule in the lattice are regarded as due to corresponding PJT distortions from their averaged high-symmetry hypothetical formation (similar to enantiomers, see below).

Even less obvious is the JT origin of first-order phase transitions. The liquid-crystal phase transition (melting) as triggered by the JT effect was considered first in Ref. [14]. The authors start with the idea that, in accordance with literature data, the instant local ordering in, for instance, monoatomic liquids is of high (icosahedral) symmetry. High symmetry results in high electronic degeneracy or pseudodegeneracy, and hence in JT vibronic instability with several equivalent minima of lower (e.g. cubic) symmetry of the AP. At high temperatures the local order in the liquid state is short-lived and the distorted configurations at the minima are oriented arbitrarily with a complicated dynamics of transition between them. At the critical temperature T_0 , an ordering of these distortions takes place due to their interaction, and the system transforms into a crystal with the symmetry determined by the local distorted configurations and their interaction, quite similar to phase transitions in crystals. Another possibility is that the liquid state transforms into an amorphous state if, dependent on the interaction between the centers, the frozen of the randomly oriented distortions takes place before their ordering [14].

The parameters of the JT distortions were calculated by the X_α -method for a series of crystals in good agreement with experimental melting temperatures [14]. The details of the theory and specific calculations seemingly require additional refinements, but the main idea of the JT origin of the liquid-crystal phase transition seems to be quite reasonable. This work thus makes an important next step toward a better understanding of the relation between the macroscopic property of SB and the microscopic electronic structure, the JT effect parameters.

With the melting explained as a JT-induced SB in addition to the SB in atom–molecule, molecule–molecule transitions and structural phase transitions in crystals, only the transition gas–liquid remains not considered from the JT vibronic coupling point of view. In Ref. [14] this possibility is mentioned, but not realized. Let us discuss this problem in some more detail (see also Ref. [4]).

Consider a simple system of a monoatomic gas. Assume first that the atoms are at sufficiently large interatomic distances at which their interaction can be neglected. The symmetry of such a system is very high, its Longuet–Higgins group of symmetry being $G = R(3)\pi(N)C_i$, where $R(3)$ is the group of rotations of the free atom, $\pi(N)$ is the group of permutations of N identical atoms, and C_i is the group of inversion. The high symmetry determines high degeneracy of the electronic states: all the independent combinations of N atomic functions correspond to different states with the same energy.

By approaching the atoms to each other they begin to interact, the symmetry lowers and the degeneracy is removed (completely or partly). This behavior is quite similar to the JT one, provided the splitting of the electronic states results in

lowering the ground state energy due to either chemical bonding or van der Waals interaction.

Consider an illustrative example. Assume that $N = 13$ and choose the coordinate of their rapprochement Q_L that leads to an icosahedron formation deemed (as above) to be the instant local order in the monoatomic liquid. As in the molecule formation from atoms, we take $Q_L = 0$ at large distances and $Q_L = Q_L^0$ for the icosahedron configuration. For simplicity assume also that each atom has one electron above the closed shell which occupies a nondegenerate ns orbital (an alkaline-like atom).

At the starting point $Q_L = 0$ with the symmetry $G = R(3)\pi(13)C_i$ the electronic state is 13-fold degenerate, and hence it splits under the icosahedral distortion Q_L (the maximum allowed degeneracy in icosahedral symmetry is 5-fold). Since the number of electrons (13) is smaller than the number of states (26), the icosahedral configuration at $Q_L = Q_L^0$ in the ground state has lower energy than at the point of degeneracy $Q_L = 0$ (similar to the two-level case, Fig. 2a). The picture as a whole is similar to the above JT description of bonding in homonuclear diatomics. If all the active atomic states are fully occupied by electrons (as in inert gas atoms), there is still an interaction that results in a van der Waals minimum; as explained above, it can be presented as a kind of PJT effect (Fig. 2b).

This explains the instant local order formation required for the transition to the liquid phase. Similar reasoning is valid for molecular interactions that result in the transition of separate gas molecules to local formations in liquids that represent their instant local ordering.

Thus the necessary condition of SB in gas–liquid phase transition, the spontaneous decrease in energy and symmetry by formation of instant local order in liquids from the gas units, may also be presented as initiated by the JT or PJT effect.

An interesting case of SB is presented by enantiomer formation. In recent papers [15] it was shown that enantiomers can be presented as the low symmetry, PJT distorted configurations of a hypothetical high-symmetry structure, and as such their interaction in the liquid phase via collisions under special conditions may lead to some kind of ‘cooperativity’ and ‘phase transition’ (SB) resulting in single-enantiomer broken symmetry configuration.

5. GENERAL FORMULATIONS

We can now generalize the results of previous sections. According to the condition of spontaneous symmetry breaking or structural phase transition $T_0 = (U_h - U_l)/(S_h - S_l)$ and the obvious assumption that in the lower symmetry (less disordered) configuration *ceteris paribus* the entropy is smaller, the necessary condition of SB is the presence of a mechanism that produces spontaneous reduction of internal energy and symmetry simultaneously. For molecular systems and condensed matter in all its forms this mechanism is provided by the JT vibronic coupling effects, which take place when there is degeneracy or pseudodegeneracy; the JT effects are the only possible source of distortion of high-symmetry

configurations. We thus come to the main conclusion of this paper that “degeneracy or pseudodegeneracy is the necessary precursor of SB in molecular systems and condensed matter, and spontaneous symmetry breaking is always associated with degeneracy or pseudodegeneracy and realized by the JT vibronic coupling effects”.

The picture of consequent SB in condensed matter by cooling is illustrated in Fig. 3. Each SB has its own independent coordinate Q , and only the temperature scale is in common. The temperatures of SB are indicated by orders of magnitude, while their sequence is self-explanatory: atoms $\Rightarrow$ molecules $\Rightarrow$ liquid $\Rightarrow$ crystal(I) $\Rightarrow$ crystal(II) $\Rightarrow$ and so on.

As mentioned in the Section 1, a similar relation between degeneracy and SB is established in particle physics [7]. Moreover, we can further extend the analogy between SB in condensed matter and particle physics to include also pseudodegeneracy. In particle physics a relatively small difference in energy is equivalent to a corresponding difference in the mass of particles. Hence approximate degeneracy (pseudodegeneracy) is equivalent to approximate symmetry. Approximate symmetry breaking definitely takes place in particle physics, for instance, in the SB of strong interactions where the symmetry only becomes exact in the limit of zero

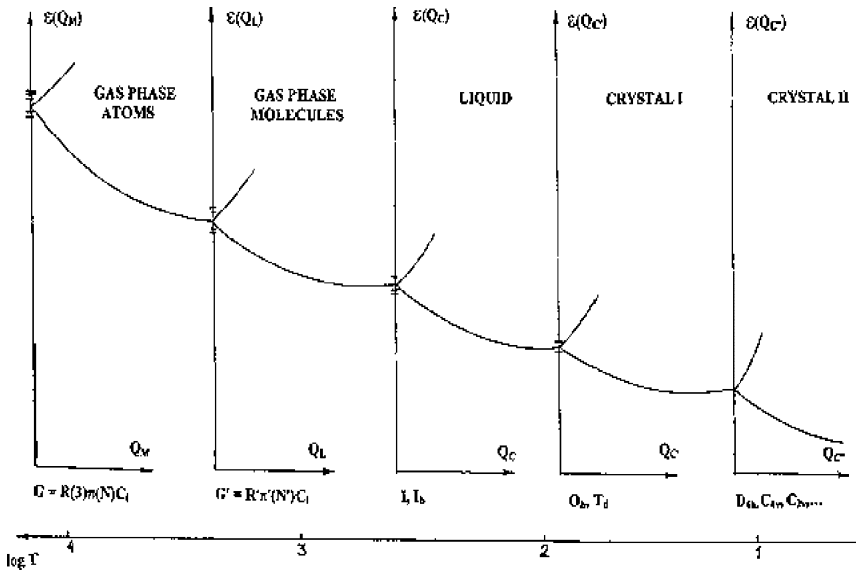


Fig. 3. Conventional scheme of consequent temperature-dependent symmetry breakings triggered by JT or pseudo JT effects. $G = R(3)\pi(N)C_i$ is the symmetry of an atomic gas, where $R(3)$ is the group of rotations of the free atom, $\pi(N)$ is the group of permutation and C_i is inversion; the primed values have the same meaning for the gas of molecules. Crystal I and crystal II denote two crystal phases with decreasing symmetry, respectively. Q_M , Q_L , Q_C , $Q_{C'}$, and $Q_{C''}$ are the separate and independent coordinates of symmetry breaking, while the temperature scale is in common.

quark masses. Here again, as in the bonding in heteronuclear molecules described as a PJT effect (Section 3), the limitation (threshold) (8) for instability and SB is seemingly not applicable, at least this possibility was not explored because at larger energy gaps (mass differences) the initial symmetry is lost.

For elementary particle interactions the mechanism of SB is not described in detail, but from general considerations one can speculate that it should be JT-like in the sense that it spontaneously lowers both the symmetry and energy. We can thus further speculate that “the global picture of formation of matter from the Big Bang by cooling is controlled by a sequence of SBs triggered by JT-like coupling of degenerate or pseudodegenerate states to particle motions (transformations) that lower the symmetry”.

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REFERENCES

- [1] I. B. Bersuker, *Chem. Rev.*, 2001, **101**, 1067.
- [2] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, New York, 1989; I. B. Bersuker, *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry*, Plenum, New York, 1984.
- [3] R. Englman, *The Jahn–Teller Effect in Molecules and Crystals*, Wiley, London, 1972.
- [4] I. B. Bersuker, *Ferroelectrics*, 1989, **95**, 51.
- [5] I. B. Bersuker, *Teor. Eksp. Khim.*, 1991, **27**, 262.
- [6] R. Englman and A. Yabalom, in *Vibronic Interactions: Jahn–Teller Effect in Crystals and Molecules* (eds M. D. Kaplan and G. Zimmerman), NATO Science Series II, Kluwer, Dordrecht, 2001, Vol. 39, p. 5.
- [7] S. Weinberg, *Quantum Theory of Fields*, University Press, Cambridge, 1995, Ch. 11.
- [8] M. D. Kaplan and B. G. Vekhter, *Cooperative Phenomena in Jahn–Teller Crystals*, Plenum Press, New York, 1995.
- [9] I. B. Bersuker, *Ferroelectrics*, 1995, **164**, 75.
- [10] I. B. Bersuker, *Phys. Lett.*, 1966, **20**, 589.
- [11] I. B. Bersuker, *Nouv. J. Chim.*, 1980, **4**, 139; I. B. Bersuker, *Teor. Eksp. Khim.*, 1980, **16**, 291; I. B. Bersuker, *Pure and Appl. Chem.*, 1988, **60**, 1167; I. B. Bersuker, *Fiz. Tverdogo Tela*, Sov. Phys.—Solid State, 1988, **30**, 1738; I. B. Bersuker, *New J. Chem.*, 1993, **17**, 3; I. B. Bersuker, N. N. Gorinchoi and V. Z. Polinger, *Teor. Chim. Acta*, 1984, **66**, 161; I. B. Bersuker, N. B. Balabanov, D. Pekker and J. E. Boggs, *J. Chem. Phys.*, 2002, **117**, 10478.
- [12] I. B. Bersuker, in *Electron–Phonon Dynamics and Jahn–Teller Effects* (eds G. Bevilacqua, L. Martinelli and N. Terzi), World Scientific, Singapore, 1999, p. 63.
- [13] I. B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds. Introduction to the Theory*, Wiley, New York, 1996, pp. 327–334.
- [14] M. E. Eberhart, K. H. Johnson, D. Adler and R. C. O’Handley, *Non-Cryst. Solids*, 1986, **83**, 12.
- [15] G. Bersuker, *J. Chem. Phys.*, 1999, **110** (22), 10907; G. Bersuker and M. Pekker, *J. Chem. Phys.*, 1999, **110** (22), 10923.

Icosahedral Quarks

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Abstract

A general account is given of the use of fictitious particles (called quarks) in atomic and molecular physics, with emphasis on applications to systems possessing icosahedral symmetry. Particular attention is paid to the irreducible representation (IR) G of the icosahedral group I , which can be expressed as the direct product of two 2D IRs of the double icosahedral group I^* . Each of these IRs can be described by an effective spin of $1/2$. This device allows the configurations g^N to be analyzed entirely by means of angular-momentum theory, rather than through the properties of icosahedral Clebsch–Gordan coefficients. Brief descriptions are given of quarks in the icosahedral h shell as well as some features of extensions to didodecahedral (or heptakisoctahedral) symmetry.

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1. INTRODUCTION

The notion of a quark comes originally from high-energy physics, where it was found that a substructure based on the three-dimensional (3D) irreducible representations (IRs) of the special unitary group $SU(3)$ could be combined in various ways to match the properties of fundamental particles such as the neutron, proton, and some mesons [1]. These quarks were at first merely useful mathematical constructs, but their physical reality now seems assured. We have taken the view that we are free to introduce analogous substructures in other fields of physics where there can be no expectation of a direct physical interpretation for them. Our intent is to gain calculational advantages that might come from a new choice of quantum-mechanical basis.

A simple example from atomic physics is provided by the d shell. As a first step, we follow Shudeman [2] and separate the spin-up electrons (N_A in number) from the down-spin electrons (N_B in number). The possible orbital angular momenta L_A allowed by the Pauli's Exclusion Principle for the spin-up electrons are S, P, D, and F if N_A is even (coming from $N_A = 0, 2, 4$, and 2, respectively). We get the same sequence if N_A is odd (for $N_A = 5, 3, 1$, and 3). A similar statement can be made for the spin-down electrons, and a state of the d shell can be formed by coupling L_A to L_B to form a resultant L . Shudeman's factorization can be taken a further step. The sequence S, P, D and F can be formed by coupling two fictitious particles of spins $3/2$ together, and the configuration $(\frac{3}{2})^4$ provides a basis for all the 2^{10} quantum states of the d shell, provided two parity labels (for N_A and N_B) are included. This idea can be readily extended: thus for the f and g shells, the analogous configurations are $(s + f)^4$ and $(d + h)^4$.

We have called these fictitious particles 'quarks' to emphasize their similarities to the quarks of particle theory [3]. Instead of the group $SU(3)$, the relevant group for the l shell is the special orthogonal group $SO(2l + 1)$, and our quarks belong to the simplest spinor representation $(\frac{1}{2} \frac{1}{2} \dots \frac{1}{2})$ of that group. Thus we have $(\frac{1}{2} \frac{1}{2})$ of $SO(5)$ for the d shell, and, under the reduction $SO(5) \rightarrow SO(3)$, we find $(\frac{1}{2} \frac{1}{2}) \rightarrow \frac{3}{2}$. There seems a ready acceptance in European journals for our use of the word quark, since there is little danger in confusing high-energy particle physics with atomic or molecular physics. However, the natural (and often surprising) conservatism and desire for uniformity in American journals has limited our usage there. We were able to go as far as 'quarklike' in an early Physical Review Letter [3], but we had to resort to the more remote language of group theory in a second article in that journal [4], where our use of quark was disallowed by the editor. However, he had the grace not to take up the suggestion of a referee that our quarks might be suitably called 'Shudemanian bogolons.'

2. GAINS

The use of quarks in atomic shell theory provides an alternative basis to the traditional one. The transformations between these bases can be complicated, but there are many special cases where our quarks can account for unusual selection rules and proportionalities between sets of matrix elements that, when calculated by traditional methods, go beyond what would be predicted from the Wigner–Eckart theorem [4,5]. This is particularly true of the atomic f shell. An additional advantage is that fewer phase choices have to be made if the quarks are coupled by the standard methods of angular-momentum theory, for which the phase convention is well established. This is a strong point in favor of quark models when icosahedral systems are considered. A number of different sets of icosahedral Clebsch–Gordan (CG) coefficients have been introduced [6,7], and the implications of the different phases have to be assessed when the CG coefficients are put to use.

3. THE IRREDUCIBLE REPRESENTATION G

The introduction of quarks is often accompanied by the loss of familiar quantum numbers. The Shudeman factorization of Section 1 removes the total spin S as a good quantum number, and the electron number N is also lost when the sequence S, P, D and F is represented as $(\frac{3}{2})^4$. The icosahedral group, in contrast, provides a remarkable example where no comparable loss takes place. All we have to do is notice that the characters of the IR G of I^* (namely 4, -1 , -1 , 1, 0, 4, -1 , -1 , 1) can be reproduced by multiplying, class by class, the characters of the two 2D IRs Γ_6 and Γ_7 of I^* . (We use the class orderings given by Chancey and O'Brien in their book [8].) This strongly hints that G can be constructed from two quarks of spin 1/2. However, it is far from a trivial matter to formally establish that G can be treated as a product of two spins of 1/2. For a detailed analysis, the reader is referred to Backhouse and Gard [9]. These authors point out that $SO(n-1)$ contains as a subgroup the alternating group A_n on n objects. Thus the tetrahedral group is a subgroup of $SO(3)$ and the icosahedral group, being isomorphic to A_5 , is a subgroup of $SO(4)$. As generators of $SO(4)$, we take two different angular momenta ($\mathbf{L}_1$ and $\mathbf{L}_2$) that belong to the respective IRs T_1 and T_2 of I . It is important to recognize that we do not want to take $SO(3)$ (with the components of $\mathbf{L}_1 + \mathbf{L}_2$ for generators) as an intermediary between $SO(4)$ and I , since this would have the effect of coupling the spins of the two quarks and thereby leading to angular momenta 0 and 1, which would correspond to the IRs $A + T_1$, rather than G . The symmetry between T_1 and T_2 stems from the automorphism of I , which interchanges the two classes corresponding to rotations of $\pm 2\pi/5$ and $\pm 4\pi/5$ and, at the same time, interchanges T_1 and T_2 .

To distinguish our two quarks, we can write them as $g^{(\frac{1}{2}0)}$ and $g^{(0\frac{1}{2})}$, where the ranks are specified with respect to $\mathbf{L}_1$ and $\mathbf{L}_2$. However, since we need pairs of them, nothing is lost by combining them in the form $g^{(\frac{1}{2}\frac{1}{2})}$. For a single electron occupying a molecular orbital with symmetry G , we need to include the true electron spin, and this can be done by attaching a third rank of 1/2. The spin-orbital may be constructed from various atomic s, p, or d orbital lying on different sites; but its icosahedral properties are determined simply by specifying $g^{(\frac{1}{2}\frac{1}{2}\frac{1}{2})}$. Since the triple ranks will be invariant for all manipulations, we can simply omit them and use $\mathbf{g}^\dagger$ and $\mathbf{g}$ as creation and annihilation tensors for the eight components of each spin-orbital. We can now write

$$\mathbf{S} = -\sqrt{2}(\mathbf{g}^\dagger \mathbf{g})^{(100)}, \quad \mathbf{L}_1 = -\sqrt{2}(\mathbf{g}^\dagger \mathbf{g})^{(010)}, \quad \mathbf{L}_2 = -\sqrt{2}(\mathbf{g}^\dagger \mathbf{g})^{(001)}, \quad (1)$$

where the resultant ranks (100), (010) and (001) indicate the couplings of the ranks of 1/2 coming from the creation and annihilation operators.

When dealing with the Coulomb interaction between atomic electrons, we use the spherical harmonics Y_{kq} (or $C_q^{(k)}$) in scalar products like $(C_1^{(k)} \cdot C_2^{(k)})$ where the subscripts 1 and 2 refer to the two electrons. For g orbitals, we introduce the tensors

$C^{(kk')} = -(\mathbf{g}^\dagger \mathbf{g})^{(0kk')}$, where k and k' can only be 0 or 1. Our scalar operators must all be of the form

$$e_i = (C_1^{(kk')} C_2^{(tt')})^{(KK')A}, \quad (2)$$

where K and K' can at most be 2. To get an icosahedral scalar A when K and K' are combined, we must have $K = K' = 0$ or 2. (We do not need $K = K' = 1$ because $T_1 \times T_2$ does not contain A .) There are five icosahedral terms in the configuration g^2 , namely ${}^3T_1$, ${}^3T_2$, ${}^1G$, ${}^1H$ and ${}^1A$, and we therefore expect to be able to find five independent operators e_i . They are

$$e_0 = (C_1^{(00)} C_2^{(00)})^{(00)A}, \quad e_1 = (C_1^{(11)} C_2^{(11)})^{(00)A}, \quad e_2 = (C_1^{(11)} C_2^{(11)})^{(22)A}, \quad (3)$$

$$e_4 = (C_1^{(10)} C_2^{(10)})^{(00)A}, \quad e_5 = (C_1^{(01)} C_2^{(01)})^{(00)A}. \quad (4)$$

We can drop e_4 and e_5 from consideration for a similar reason to that for dropping $(C_1^{(1)} \cdot C_2^{(1)})$ in the atomic case, the essential point now being that $G \times G$ does not contain either T_1 or T_2 in its symmetric part.

Having put the Coulomb operators (3) in tensorial form, it is not difficult to use the standard techniques of atomic shell theory to calculate the energies of all the terms of the icosahedral g shell. The details have been given elsewhere [10]. Our results agree with those found earlier by more traditional methods by Plakhutin [11] (provided the entry 9 Table 6 of Ref. [10] is corrected to -9). It is interesting to notice that the terms T_1 and T_2 always occur as degenerate pairs, a result that can be understood by showing that the Coulomb operators (3) are invariant with respect to the automorphism operation [10].

4. QUASISPIN

Further properties of the g shell can be explored by introducing the notion of quasi-spin Q , in analog to its use in atomic shell theory [12]. We define

$$\begin{aligned} Q_+ &= \sqrt{2}(\mathbf{g}^\dagger \mathbf{g}^\dagger)^{(000)}, \\ Q_- &= -\sqrt{2}(\mathbf{g} \mathbf{g})^{(000)}, \\ Q_z &= -\frac{1}{\sqrt{2}}[(\mathbf{g}^\dagger \mathbf{g})^{(000)} + (\mathbf{g} \mathbf{g}^\dagger)^{(000)}]. \end{aligned}$$

The eigenvalue of Q_z is $\frac{1}{2}N - 2$ for a state of g^N . We can now consider that the identical components of $\mathbf{g}^\dagger$ and $\mathbf{g}$ together form a quasi-spin tensor of rank $1/2$, whose array of ranks we can now indicate by writing $G^{(\frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2})}$. The e_i operators can be broken down into parts that have well-defined quasi-spin ranks; however, it turns out that e_2 is a quasi-spin scalar, which can be used to explain some similar matrix elements of e_2 in g^2 and g^4 [10].

We should also mention that other symmetries can be produced by interchanging spin and quasi-spin, an operation that has been referred to as complementarity [12].

It turns out that e_2 reverses sign under this operation, and this accounts for its matrix elements being of opposite signs for the ${}^3G$ and ${}^1G$ terms of g^4 [10].

5. THE ICOSAHERAL h SHELL

The IR H of I possesses a dimension of five, so we cannot expect an h orbital to behave like one of type g and factorize into two non-trivial parts. Indeed, the reduction $SO(4) \rightarrow I$ gives only two options for an h orbital: it can be represented by either $h^{(2,0)}$ or $h^{(0,2)}$. Both could be usefully introduced if we needed to consider electrons in inequivalent h orbitals. However, for a single h shell only one is required, and we can simply represent an h state by a d electron. This allows us to bring in the apparatus of angular-momentum theory again, as well as any Lie groups that have proved useful in studies of the atomic d shell. Thus the states of the icosahedral configuration h^N can be found by first finding those of d^N and then using the branching rules for $SO(4) \rightarrow I$ to find how each L term decomposes into IRs of I . The presence of a null rank in $h^{(2,0)}$ forces the branching rules to become equivalent to those for $SO(3) \rightarrow I$. The correspondence $d \leftrightarrow h$ means that the analysis of Section 1 can be brought into play. In particular, we can reinterpret Shudeman's analysis and replace the $3/2$ quark by its icosahedral representation, namely the IR Γ_8 of I^* . We see at once that the quark configuration $(\frac{3}{2})^4$ for the d shell goes over into $(\Gamma_8)^4$ for the icosahedral h shell. However, such a replacement is only of mathematical interest, since it takes us away from our aim to use the language of angular momentum as much as possible.

Although it seems that introducing a Γ_8 quark will not yield any new insights, Shudeman's factorization by itself yields interesting results. A fact, little noticed by atomic spectroscopists, is that there are as many terms of the type ${}^{2S+1}L$ in the half-filled l shell as in the configurations on either side of it. For example, there are as many spectroscopic terms in d^4 as in d^5 (namely 16), although the number of quantum states is different (210 and 252). To understand why this should be so, we have only to compare the number of states for which $M_S = 0$ in d^4 with the number for which $M_S = \frac{1}{2}$ in d^5 . In the first case we have to couple two spin-up electrons (with $L_A = 1$ and 3) with two spin-down electrons (with $L_B = 1$ and 3). In the second case, we again have two spin-down electrons, but there are now three spin-up electrons. The latter yield $L_A = 1$ and 3 just as before, owing to the symmetry of the spin-up states about the quarter-filled shell. Thus the L values coming from the coupling $(L_A, L_B)L$ are the same in both cases, and are independent of the spin S . These arguments can be carried over to the icosahedral h shell. The result of doing so is nicely illustrated by Table XII of the recent article by Nikolaev and Michel [13], where the 27 icosahedral terms of h^4 are matched, line-by-line, with the 27 terms of h^5 . Moreover, the number of A , T_1 , T_2 , G and H terms is the same in both cases (3, 4, 4, 7 and 9). As we expect, there are always as many T_1 states as T_2 states [14].

Nikolaev and Michel give estimates of the Coulomb energies for several icosahedral configurations of the type h^N , as well as for some mixed configurations [13]. It was Plakhutin [15] who established that, for the h shell, two icosahedral two-electron scalar operators have to be added to the three Coulomb operators taken over from the d shell (and which are automatically scalars with respect to I). The Lie group $SO(5)$ can be used to separate these additional operators by assigning them the IRs (22) and (40) [4]. This group acts in the five-dimensional (5D) space provided by an h orbital, in analogy to Racah's use of $SO(5)$ for the d shell [16].

From the work of Backhouse and Gard [9], we know that, in addition to $SO(5) \supset A_5$, the full orthogonal group $O(5)$ (which includes reflections as well as 5D rotations) contains the symmetric group S_6 as a subgroup. The six permuted objects of S_6 can be taken as the six axes passing through opposite vertices of the icosahedron. Some of the permutations correspond to rotations that send the icosahedron into itself, but others twist it out of shape. The group S_6 is unusual in that it possesses automorphisms of a type that other symmetry groups do not. We have used this property to account for the fact that one of the two ${}^2T_1$ terms of h^3 always coincides with a ${}^2T_2$ term [4]; however, the analysis is quite involved and is not as transparent as one would wish. One problem that recently came to mind is how to determine the contortion of the icosahedron that is related through the automorphism to a given simple 3D rotation. It does not seem susceptible of a simple solution.

6. GENERALIZATIONS

The correspondence $h \leftrightarrow d$ has an analog for the octahedral group, for which Griffith has utilized the connection between the IR t_2 and a p electron [17]. The limitation of the Platonic solids to just five seems to impose restrictions on other geometric images for atomic orbitals. However, the possibility of extensions to non-Euclidean space should not be overlooked. A famous example of a figure comprising 24 regular heptagons meeting in threes at 56 vertices (which we have called a didodecahedron [18]) was provided by Klein over a century ago, and is the subject of a book recently compiled by Levy [19]. The didodecahedral group D contains a 7D IR, which, coincidentally, has been labeled h by King *et al.* and the correspondence $h \leftrightarrow f$ can be established [20]. The group D is not a subgroup of $SO(3)$, but it is a subgroup of G_2 , the exceptional Lie group that Racah used in his analysis of the f shell [21].

Ceulemans *et al.* have included the groups I and D in a sequence of three, which they refer to as pollakisipolyhedral groups [22]. Our D is called by them the heptakisoctahedral group, and they have examined the application of this group to seven-membered rings of carbon atoms. The third member of the sequence exhibits the symmetry of a figure comprising 60 regular undecagons meeting in threes at 220 vertices, and contains I as a subgroup. Kostant has considered possible application of this group to C_{60} [23].

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REFERENCES

- [1] M. Gell-Mann and Y. Ne'eman, *The Eightfold Way*, Benjamin, New York, 1964.
- [2] C. L. B. Shudeman, *J. Franklin Inst.*, 1937, **224**, 501.
- [3] B. R. Judd and G. M. S. Lister, *Phys. Rev. Lett.*, 1991, **67**, 1720.
- [4] E. Lo and B. R. Judd, *Phys. Rev. Lett.*, 1999, **82**, 3224.
- [5] B. R. Judd, *Phys. Rep.*, 1997, **285**, 1.
- [6] R. M. Golding, *Mol. Phys.*, 1973, **26**, 661.
- [7] D. R. Pooler, *J. Phys. A*, 1980, **13**, 1197; D. R. Pooler, *J. Phys. C*, 1980, **13**, 1029.
- [8] C. C. Chancey and M. C. M. O'Brien, *The Jahn–Teller Effect on C₆₀ and Other Icosahedral Complexes*, Princeton University Press, Princeton, NJ, 1997, p. 174.
- [9] N. B. Backhouse and P. Gard, *J. Phys. A*, 1974, **7**, 2101.
- [10] B. R. Judd and E. Lo, *J. Phys. B*, 1999, **32**, 1073.
- [11] B. N. Plakhutin, *Chem. Phys. Lett.*, 1994, **227**, 396.
- [12] B. R. Judd, *Second Quantization and Atomic Spectroscopy*, The Johns Hopkins Press, Baltimore, 1967.
- [13] A. V. Nikolaev and K. H. Michel, *J. Chem. Phys.*, 2002, **117**, 4761.
- [14] B. R. Judd and E. Lo, *J. Chem. Phys.*, 1999, **111**, 5706.
- [15] B. N. Plakhutin, *Theory of Non-Roothaan States in Open-Shell Electronic Systems of High Symmetry*, Thesis (in Russian), Moscow State University, Moscow, 1995. For a more accessible source, see J. M. Oliva, *Phys. Lett. A*, 1997, **234**, 41.
- [16] G. Racah, Group Theory and Spectroscopy, *Ergebnisse der exakten Naturwissenschaften*, Springer-Verlag, Berlin, 1965, **37**, p. 28.
- [17] J. S. Griffith, *The Theory of Transition-Metal Ions*, Cambridge University Press, Cambridge, 1961, see Section 9.5.
- [18] B. R. Judd and E. Lo, *J. Phys. B*, 2000, **33**, 1315.
- [19] S. Levy (ed.), *The Eightfold Way*, *Math. Sci. Res. Inst. Pubs.* 35, Cambridge University Press, Cambridge, 1999.
- [20] R. C. King, F. Toumazet and G. Wybourne, *J. Phys. A*, 1999, **32**, 8527.
- [21] G. Racah, *Phys. Rev.*, 1949, **76**, 1352.
- [22] A. Ceulemans, R. B. King, S. A. Bovin, K. M. Rogers, A. Troisi and W. Fowler, *J. Math. Chem.*, 1999, **26**, 101.
- [23] B. Kostant, *Notices Math. Soc.*, 1995, **42**, 959.

Antilinear Particle–Hole Conjugation Operators in Jahn–Teller Theory

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Abstract

Linear and antiunitary particle–hole conjugation operators have each been proposed, and each for antiparticle theory and for the condensed matter analogues in nuclear, atomic and ligand shell theories. Physics dictates the former, but the choice in the latter context appears to be dictated by usefulness rather than necessity. However, in the latter context, we discuss different remains to be done in elucidating the consequences for ligand field theory; some issues are clarified using the requirement of biparticity for group-theoretical diagrams. These are developed in a more familiar algebraic approach, and yield an advantage to a unitary choice of particle–hole conjugation operator. This further elucidates the power and origin of the selection rules discovered by Ceulemans for Jahn–Teller systems.

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1. INTRODUCTION

Despite their opposite intentions, the shopper's problem in finding a vacancy in a busy car park and the thief's problem in converting a car when the car park is nearly deserted have similarities. By toggling between such scenarios, particle–hole (or charge) conjugation operators C aid the mathematical comparisons of analogous situations in physical theory. However, the various definitions of particle–hole conjugation operator in the literature reveal some diversity over the degree of freedom that exists on the choice of particle–hole conjugation operator, in particular as to whether the particle–hole conjugation operator is a linear or antilinear operator. We explore such matters in this paper. We usually add author initials as suffices to distinguish the various particle–hole conjugation operators discussed in this paper, and also a tilde to help distinguish an antilinear operator.

The original application by Dirac of a particle–hole conjugation operator $\tilde{C}_D$ was to particle (electron) theory. $\tilde{C}_D$ related positive energy (and positive frequency) solutions to negative energy (and negative frequency) solutions. Hence Dirac's $\tilde{C}_D$ was antilinear, transforming $e^{-i\omega t}$ into $e^{i\omega t}$. Dirac rationalized the negative energy solutions by postulating that the vacuum be identified with a filled negative energy sea, and that its (positive energy) holes corresponded to physical antiparticles.

In standard quantum field theory, particles are identified as (positive frequency) solutions ψ of the Dirac equation $(p - m)\psi = 0$, with $p = \gamma^\mu p_\mu$, m is the rest mass and p_μ the four-momentum operator, and antiparticles (the CP conjugates, where P is parity or spatial inversion) as positive energy (and frequency) solutions of the adjoint equation $(p + m)\bar{\psi} = 0$. This requires C_Q to be linear: $e^{-i\omega t}$ must be transformed into itself. Indeed, the Dirac equation and its adjoint are unitarily equivalent, being linked by a unitary transformation (a sign reversal) of the γ matrices. Hence C_Q is unitary.

A non-standard alternative identification $\tilde{C}_H$ has been discussed, in which a (positive energy) antiparticle is identified with the *negative* frequency solution [1]. This avoids the introduction of the Dirac sea, but requires such complications as making the velocity vector antiparallel to the momentum vector. Incidentally, such an antiparallelism is associated with a region of negative slope in the dispersion curve and has been observed directly for R^- rotons in superfluid helium by Tucker and Wyatt [2]. The change in the sign of frequency from particle to antiparticle forces the associated operator $\tilde{C}_H$ to be antilinear, as for $\tilde{C}_D$, and in fact antiunitary (a property which incidentally is not shared by $\tilde{C}_D$). The correct identification of the antiparticle in the mathematical formalism becomes a significant theoretical judgement, not a convention, because it is physically distinct. The predicted physics is very different; for example, Ref. [1] provides us an alternative to CP violation to explain the observed multiplicity of routes of K^0 meson decay.

Four decades ago, Bell [3] introduced a particle–hole conjugation operator C_B into nuclear shell theory. Its operator algebra is essentially isomorphic to that of C_Q (for example, C_B is unitary), the filled Dirac sea now corresponding to systems with half-filled shells. This was later extended to other areas of physics. For example,

a particle–hole conjugation operator was effective in discussing the competition between particles and holes in the Fermi sea of a metal for such transport properties as thermopower [4].

The particle–hole conjugation algebra has also been important in atomic shell theory, where the selection rules appropriate for half-filled shells are well known in ligand field theory. In this context also antiunitary choices have been proposed by Judd [5] and by Stedman [6]. These choices are identical within $SO(3)$, and we refer to both as $\tilde{C}_S$. These authors presented the decision between the linear and antilinear form as a convention, the choice being driven by a pursuit for elegance so as to ensure a complete algebraic analogy of the tensorial properties of $\tilde{C}_S$ (principally its antilinearity and its commutation relations with the quasispin generators $\mathbf{Q}$) with that of the time reversal operator T (as regards its commutation relations with spin), so that particle–hole conjugation is to quasispin as time reversal is to spin. Judd [5] did this by changing $\tilde{C}_S$ so as to make it antilinear in its action on the imaginary unit in Q_y , whereas Stedman [6] included Z following Ref. [4] without changing the remainder of the action, and so explicitly or implicitly by bundling complex conjugation Z and C_B .

These approaches were at best incomplete; a full description should assess the consequences of combining all such operators together into all relevant group algebras. This point has become evident from the seminal though largely ignored work of Ceulemans [7,8,10] and Savage [9], who found novel selection rules associated with particle–hole conjugation, time reversal and their combination. Clearly the content of such selection rules has not been exhausted. However, Ceulemans’ choice of operator conventions is unclear, since the language employed was not that of most shell theorists. A decade later Ceulemans [10] expressed similar results in a more familiar language, but not all gaps were bridged.

At this stage this condensed-matter-theoretic history suggested several things. Whether a linear or antilinear form of particle–hole conjugation operator (generically, C or $\tilde{C}$) is required by physics seemed to be a non-question; the choice as to whether to insert complex conjugation in the definition of particle–hole conjugation operator seemed an innocuous minor player among the phase conventions which abound in Racah algebra [9,11,12]. The most important outstanding question appeared to be the determination of the selection rules following from each choice. The standard theorems of group theory (including the long history of the antilinear time-reversal selection rules) suggest that selection rules may be expected when any of C , $\tilde{C}$, CT or $\tilde{C}T$ have definite commutation (including anticommutation) relations with any Hamiltonians which are of physical interest. Our aim in starting the present work was to explore and categorize all selection rules potentially arising in this manner. The pedigree and history of the Hannibal alternative [1] in quantum field theory is a cautionary tale, raising the possibility that the choice between linear and antilinear particle–hole conjugation operator can be more than a convention. Still, the Hannibal alternative relates to a non-standard assignment of physical particles to the eigenstates of a theory, and it was plausible that the identification of the antiparticle or hole in condensed matter

is a convention rather than a physical decision, when the physical states involved are all well-known shell states [1].

However, in this search we realized that $\tilde{C}_S$ is an unacceptable choice of particle–hole conjugation operator. Because complex conjugation Z acts only on the coefficients of a basis function, the definition of $\tilde{C}_S$ is basis-dependent. For example, Z changes a spherical tensor such as $|1, 1\rangle = Y_1^1 \propto |x\rangle + i|y\rangle$ in a Cartesian basis, but not in a spherical basis. As another example, the definitive anticommutation of $\tilde{C}_S$ with the quasispin generators $\mathbf{Q}$ holds only in a Cartesian basis. Hence, the resulting physics changes with basis choice in a manner, which is inconsistent with quantum theory. Symptomatic of this is a breakdown in biparticity when $\tilde{C}_S$ is used [9]. Biparticity in diagrammatic group theory [12] reflects the manner in which the two quantities whose indices are contracted in any internal tensorial summation must have contravariant behaviour under group operations if they are to form a group invariant. The reason for the over-complacent introduction of Z in Ref. [6] was the precedent afforded by its appearance in a breakdown of T in Dirac electron theory. However, this breakdown itself is also representation-dependent.

Our procedure for securing basis independence follows a group-tensor algebraic approach to shell theory, and examines the algebraic interplay of particle–hole conjugation operators with quasispinors and quasispin tensors. The problem with $\tilde{C}_S$ may be remedied while retaining an antilinear transformation only by replacing Z with another antilinear operation which is physical. Apart from an unimportant phase this can be identified as time reversal T , so that $\tilde{C} \equiv CT$. Hence, the operators to be examined for physical interest are just two in number: C and CT . In a later work we will explore the consequences of the work of Ceulemans [7,8,10] from this perspective.

2. STATES AND jm SYMBOLS

A three-part state labelling scheme is used, following Butler [11] and Stedman [6, 12]: an N -particle eigenstate is written $|A\rangle$ where $A = \alpha\lambda l$. The labels are normally irreducible representation (irrep) labels; λ belongs to the group G representing the symmetry of the system in question (covering both ordinary and spin space, i.e., using double-group irreps), α belongs to any higher group F , and l to any subgroup(s) H , which may be needed to make the labelling unique. In the applications of interest, λ labels the subshell split from others, by a ligand field, for example, with the final symmetry G . We shall assume that l ranges over all time-reversal partners, and that λ is real, if necessary taking λ as a reducible union of λ and $\bar{\lambda}$ to ensure this; hence we do not distinguish α and $\bar{\alpha}$ or λ and $\bar{\lambda}$ below. G can be taken as the product spin/space group, i.e., $G = G \times \text{SU}^S(2)^N$ (and F as $O(3) \times \text{SU}^S(2)^N$) in a coupled basis labelled *via* the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$. A 1-particle state in $O(3) \downarrow O(2)$ is sufficiently labelled by $\lambda l = j, m$ respectively. When the symmetry is octahedral ($G = O$) and spin unimportant, α is J^π of $O(3)$, λ a real or projective irrep of O and l the corresponding component or partner label.

From the character orthogonality theorem [12], for each such state $|\Lambda\rangle$ there exists a unique conjugate state $|\bar{\Lambda}\rangle$ such that the direct products of all corresponding irreps are each the invariant irrep 0. With $\mathbf{G} = O(3) \times \text{SU}^S(2)$ and $\Lambda = \lambda l = jm$ the conjugate state labels are $\bar{\lambda}, \bar{l} = j, -m$. This kind of state conjugation is evident in the action of any antilinear operator taking a ket to a ket, such as time reversal T . We denote its action by an overbar: $T|\Lambda\rangle = |\bar{\Lambda}\rangle$, $TOT^{-1} = \bar{O}$. Note that $|\bar{\Lambda}\rangle$ and $|\bar{\bar{\Lambda}}\rangle$ are distinct; for example, $T|jm\rangle = (-1)^{j-m}|j-m\rangle$. We can identify $|\bar{\bar{\Lambda}}\rangle$ as the state time-reversal conjugate to $|\Lambda\rangle$ up to a phase.

3. TENSOR FORMULATION

In tensor algebra including the Wigner njm symbols [11,13,15] and Racah irreducible states and operators, corresponding free indices in a tensor equation must have the same transformation properties and contractions must form an invariant, so that the contracted indices must have conjugate transformation properties. In the diagram language used in Ref. [12] each index corresponds to a leg terminating on a node (tensor, such as a ket, operator, etc.). Each such termination (each leg on a node, or algebraically each index on a tensor) is assigned a parity, not in the physical sense of symmetry or antisymmetry under physical inversion, but so as to indicate whether that index (associated with irrep λ say) transforms under group operations contravariantly (as for the indices in a $2j$ symbol or a bra, such a terminus being conventionally assigned a parity $+1$) or covariantly (as in a $3j$ symbol or a ket; the terminus being then necessarily assigned a parity -1). Contravariant and covariant indices transform under group operations by the representation matrices $\lambda^*(R)$ (or, thanks to quasiambivalence, equivalently by $[\lambda(R)^*]$) and by $\lambda(R)$, respectively. Complex conjugation (and any antilinear operation such as s conjugation or time reversal), therefore, reverses the parity of any quantity.

In tensor algebra including Racah algebra, the transformation properties of two such indices are cancelled under contraction. Contraction must involve one covariant being summed against its contravariant counterpart, for the summed combination to form a group invariant. In diagrams, each leg connects two node termini which have opposite parity. If all the termini on any node have the same parity (a situation which does not hold for mixed tensors such as the Clebsch–Gordan coefficient, with its one bra and two ket labels, or an operator in a Hilbert space), the parity assignment is nodal and the graph is bipartite, only nodes of opposite parity being linked. It is helpful, therefore, to ignore the fact that $2jm$ symbols can be chosen to be real, which would make their parity indefinite, but to retain the distinction between each quantity and its complex conjugate, and to preserve bipartite construction in the above sense.

Since an operator O acts on a ket to produce a ket, which, therefore, have the same (negative) parity, its matrix element labels are of mixed parity, being -1

and $+1$ for the row (first) and column labels, respectively. For example, the state label Λ in the creation operator $a_\Lambda^\dagger$ has negative parity, as does each ket in: $a_\Lambda^\dagger|0\rangle \equiv |\Lambda\rangle$. Since the label on the corresponding annihilation operator must have positive parity, we write it as a^Λ , using the raising/lowering convention of relativity to indicate parity assignments (a superscript has positive parity, a subscript negative parity). A number operator, for example, is written $n(\Lambda) = a_\Lambda^\dagger a^\Lambda$. As an antilinear operation, Hermitian conjugation must at least toggle contravariant and covariant indices.

The $2jm$ -symbol is a contravariant tensor, corresponding to a positive parity node, since both of its labels couple to covariant labels (kets, of negative parity) to form a group invariant. It can, therefore, be regarded as a contravariant metric tensor $g^{\Lambda\bar{\Lambda}} \equiv (\Lambda\bar{\Lambda})$ which raises indices; for example, $a^{\dagger\Lambda} \equiv g^{\Lambda\bar{\Lambda}} a_\Lambda^\dagger$ where we note that $a_\Lambda^\dagger$ is strictly $(a^\dagger)_\Lambda$ and $a^{\dagger\Lambda}$ is $(a^\dagger)^\Lambda$. The inverse matrix, which for a unitary matrix is its Hermitian conjugate, is the corresponding covariant metric, so that $g_{\Lambda\bar{\Lambda}} = (\bar{\Lambda}\Lambda)^*$. (The asterisk on the $2jm$ symbol corrects Stedman [6].) Biparticity requires the positive-parity $\bar{\Lambda}$ in the operator to be matched to a negative-parity $\bar{\Lambda}$ in the $2jm$ symbol, and the Λ labels to be both negative parity, as denoted by the raising and lowering in equation (1). As in standard tensor analysis $g_{\Lambda\bar{\Lambda}}$ lowers indices; for example, the quantity

$$a_\Lambda \equiv g_{\Lambda\bar{\Lambda}} a^{\bar{\Lambda}} \quad (1)$$

is the covariant form of the annihilation operator, transforming as a standard irreducible tensor operator. Similarly $a^\Lambda = g^{\Lambda\bar{\Lambda}} a_{\bar{\Lambda}}$. Note that $(a_\Lambda)^\dagger$ is not $a_\Lambda^\dagger$, because a_Λ is not the standard annihilation operator a_Λ of second quantization (which satisfies $[a_\Lambda, a_\Lambda^\dagger] = 1$, and which we write as a^Λ), but $(\bar{\Lambda}\Lambda)^* a_\Lambda$. With these cautions we adhere to this tensorial notation throughout this paper. Relations such as the anticommutation relation $[a_\Lambda, a_{\bar{\Lambda}}^\dagger]_+ = g_{\Lambda\bar{\Lambda}}$ for a one-particle state are then plainly tensor equations.

It follows from these relations that in some cases, Hermitian conjugation simply toggles between subscripts and superscripts (with appropriate addition or cancellation of the dagger); for example, $(a_\Lambda^\dagger)^\dagger = a^\Lambda$ and $a^{\dagger\Lambda} = a_\Lambda^\dagger$. However, when the order of the dagger and the state label is reversed in these examples a phase arises in addition: $(a_\Lambda)^\dagger = \{\Lambda\} a^{\dagger\Lambda}$, and $(a^{\dagger\Lambda})^\dagger = \{\Lambda\} a_\Lambda$. Under time reversal, from equation (1): $|\bar{\Lambda}\rangle = g^{\Lambda\bar{\Lambda}} |\Lambda\rangle$; hence $\bar{a}_\Lambda^\dagger = g^{\Lambda\bar{\Lambda}} a_\Lambda^\dagger \equiv a^{\dagger\Lambda}$. Similarly from equation (1): $\bar{a}^\Lambda = a_\Lambda$. For these tensor operators time reversal simply toggles contravariant and covariant labels (without changing the dagger); however, a phase reappears in the remaining relations: $\bar{a}^{\dagger\Lambda} = \{\Lambda\} a_\Lambda^\dagger$ and $\bar{a}_\Lambda = \{\Lambda\} a^\Lambda$. These relations are consistent with $\bar{a}_\Lambda^\dagger = \{\Lambda\} a_\Lambda^\dagger$, $\bar{a}^\Lambda = \{\Lambda\} a^\Lambda$.

For Kramers' (e.g. one-electron) states where the eigenvalue of T^2 , $\{\Lambda\} = -1$, the metric $g_{\Lambda\bar{\Lambda}}$ is antisymmetric, and so relating to symplectic algebras (in relativistic terms to pure torsion rather than to curvature), rather than symmetric as for non-Kramers' systems. The joint action of Hermitian conjugation and time reversal (which is not commutative) is summarized with the above results for these individual operations in Table 1.

Table 1. Behaviour of second-quantized 1-particle tensor operators under Hermitian conjugation, time reversal and their combinations in each order

$(a_\Lambda^\dagger) = a^\Lambda$	$\overline{a_\Lambda^\dagger} = a^{\dagger\Lambda}$	$\overline{(a_\Lambda^\dagger)^\dagger} = a_\Lambda$	$\overline{a_\Lambda^{\dagger\dagger}} = \{\Lambda\}a_\Lambda$
$a^{\Lambda\dagger} = a_\Lambda^\dagger$	$\overline{a^\Lambda} = a_\Lambda$	$\overline{(a^\Lambda)^\dagger} = a^{\dagger\Lambda}$	$\overline{a^{\Lambda\dagger}} = \{\Lambda\}a^{\dagger\Lambda}$
$(a^{\dagger\Lambda})^\dagger = \{\Lambda\}a_\Lambda$	$\overline{a^{\dagger\Lambda}} = \{\Lambda\}a_\Lambda^\dagger$	$\overline{(a^{\dagger\Lambda})^\dagger} = a^\Lambda$	$\overline{a^{\dagger\Lambda\dagger}} = \{\Lambda\}a^\Lambda$
$(a_\Lambda)^\dagger = \{\Lambda\}a^{\dagger\Lambda}$	$\overline{a^\Lambda} = \{\Lambda\}a^\Lambda$	$\overline{(a_\Lambda)^\dagger} = a_\Lambda^\dagger$	$\overline{a_\Lambda^{\dagger\dagger}} = \{\Lambda\}a_\Lambda^\dagger$

For 1-particle operators, $\{\Lambda\} = -1$.

4. QUASISPIN AND QUASI-KRAMERS' SYMMETRIES

In this section we review the quasispin formalism using the above notation. In the following sections we use the biparticity concept to construct a particle–hole conjugation operator from the Cartesian components of quasispin, a problem first attempted in Stedman [6]. Even prior to Bell's introduction of particle–hole conjugation algebra to shell theory in 1959, it was recognized that an angular momentum operator algebra beyond that of spin itself, and in this case of isospin, was of interest in shell theory [14]. Helmers [15] and Kerman [16] later independently noted that an analogue, now called quasispin, was of special interest. Lawson and Macfarlane [17] and Watanabe [18] independently studied its tensorial formulation. Judd [5] made several major steps, such as relating quasispin to Racah's (1942) concept of seniority, introducing an antiunitary particle–hole conjugation operator and exploring in depth the irreducible tensorial nature of the annihilation and creation operators, all within $O(3)$ and higher groups. Wybourne [19] following Sviridov and Smirnov [20] stated the components of quasispin for crystal fields and general point groups. Stedman [6,12] derived the form of quasispin components for point groups, and like Judd [5] chose an antiunitary particle–hole conjugation operator, in this case to enhance the analogy with time reversal selection rules.

4.1. Quasispinors

Let the operators $a_\Lambda^\dagger$ and a_Λ be considered as the two components of a two-component object $\mathbf{A}_\Lambda = \{A_{\Lambda q}|q\}$, which will turn out to be a rank- $\frac{1}{2}$ quasispinor:

$$\mathbf{A}_\Lambda = \begin{pmatrix} A_{\Lambda+} \\ A_{\Lambda-} \end{pmatrix} \equiv \begin{pmatrix} a_\Lambda^\dagger \\ a_\Lambda \end{pmatrix} \quad (2)$$

The component label $q = +\frac{1}{2}, -\frac{1}{2}$, respectively (or for short $+, -$ suffices). Note that these components transform identically under G (since the irrep labels are

identical and covariant), and that the generators of the quasispin group, which couple these operators and are constructed from them, commute with the elements of G .

We now consider Hermitian conjugation of the operators (but not of the quasispin matrices as such), also time reversal and their combination. From equation (2) and Table 1 we derive the results of Table 2.

$\mathbf{A}_\Lambda$ transforms as an irreducible tensor operator under operations of G , and as a rank- $\frac{1}{2}$ spinor in the angular momentum algebra generated by the quasispin operators. We form the quasispin generators as a coupled tensor in quasispin space: $\mathbf{Q}(\lambda) = i[\mathbf{A}_\Lambda \mathbf{A}^\Lambda]^\dagger / \sqrt{2}$, where $[\mathbf{AB}]_m^\dagger \equiv \sum_{qq'} \langle 1m | \frac{1}{2} q \frac{1}{2} q' \rangle A_q B_{q'}^\dagger$. In the Condon and Shortley spherical basis choice (with $m = 1, 0, -1$) for the $\text{SO}(3)$ Clebsch–Gordan coefficients [11–13,21–23] this takes the form [6,21]:

$$(\mathbf{Q}(\lambda)_m) = \frac{i}{\sqrt{2}} \begin{pmatrix} a_\Lambda^\dagger \cdot a^{\dagger\Lambda} \\ (a_\Lambda^\dagger \cdot a^\Lambda + a_\Lambda \cdot a^{\dagger\Lambda})/\sqrt{2} \\ a_\Lambda \cdot a^\Lambda \end{pmatrix} \quad (3)$$

The centred dot denotes another tensorial coupling, namely the formation of a G -invariant contraction: $A_\Lambda \cdot B^\Lambda \equiv \sum_l A_\Lambda B^\Lambda = \sum_l g^{\Lambda\Lambda} A_\Lambda B_{\bar{\Lambda}}$. Note that this tensor algebra does not permit us to replace $a_\Lambda a^\Lambda$ by $a^\Lambda a_\Lambda$, etc.; in fact the commutation relations for 1-particle states (equivalently the antisymmetry of the metric) give $a_\Lambda a^\Lambda = -a^\Lambda a_\Lambda$.

The operators $\{\mathbf{Q}(\lambda)_m\}$ close on the quasispin Lie algebra $\text{SO}(3)_Q$:

$$[Q(\lambda)_{-1}, Q(\lambda)_1] = iQ(\lambda)_0, \quad [Q(\lambda)_{\pm 1}, Q(\lambda)_0] = \pm iQ(\lambda)_{\pm 1} \quad (4)$$

We now convert to a Cartesian basis $\alpha = x, y, z$ using the contra-standard Fano–Racah (1959) transformation [22]

$$\mathbf{Q}(\lambda)_\alpha = \begin{pmatrix} Q(\lambda)_x \\ Q(\lambda)_y \\ Q(\lambda)_z \end{pmatrix} = \mathbf{U} \mathbf{Q}(\lambda)_m, \quad \mathbf{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} i & 0 & -i \\ 1 & 0 & 1 \\ 0 & -i\sqrt{2} & 0 \end{pmatrix} \quad (5)$$

Table 2. Behaviour of quasispinor components under Hermitian conjugation, time reversal and their combinations in each order

$(\mathbf{A}_\Lambda)^\dagger = \mathbf{a} \mathbf{A}^\Lambda$	$\overline{\mathbf{A}}_\Lambda = \mathbf{b} \mathbf{A}^\Lambda$	$\overline{(\mathbf{A}_\Lambda)}^\dagger = \sigma_x \mathbf{A}^\Lambda$	$\overline{\mathbf{A}}_\Lambda^\dagger = \{\Lambda\} \sigma_x \mathbf{A}^\Lambda$
$(\mathbf{A}^\Lambda)^\dagger = \{\Lambda\} \mathbf{a} \mathbf{A}_\Lambda$	$\overline{\mathbf{A}}^\Lambda = \{\Lambda\} \mathbf{b} \mathbf{A}_\Lambda$	$\overline{(\mathbf{A}^\Lambda)}^\dagger = \sigma_x \mathbf{A}_\Lambda$	$\overline{\mathbf{A}}^\Lambda^\dagger = \{\Lambda\} \sigma_x \mathbf{A}_\Lambda$
$\mathbf{a} = \begin{pmatrix} 0 & 1 \\ \{\Lambda\} & 0 \end{pmatrix}$	$\mathbf{b} = \begin{pmatrix} 1 & 0 \\ 0 & \{\Lambda\} \end{pmatrix}$	$\mathbf{b} \mathbf{a} = \sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\mathbf{a} \mathbf{b} = \{\Lambda\} \sigma_x$

In the standard manner we define $A_q^\Lambda \equiv g^{\Lambda\Lambda} A_{\bar{\Lambda}q}$.

for the reasons given in Ref. [12], but correcting an error therein. These become

$$\mathbf{Q}(\lambda)_\alpha = \frac{1}{2} \begin{pmatrix} a_\Lambda \cdot a_\Lambda - a_\Lambda^\dagger \cdot a^{\dagger\Lambda} \\ i(a_\Lambda \cdot a^\Lambda + a_\Lambda^\dagger \cdot a^{\dagger\Lambda}) \\ a_\Lambda^\dagger \cdot a^\Lambda + a_\Lambda \cdot a^{\dagger\Lambda} \end{pmatrix} \quad (6)$$

using the anticommutation relations, $Q(\lambda)_z = n(\lambda) - \frac{1}{2}$, where $n(\lambda) = n(\bar{\lambda}) = a_\Lambda^\dagger \cdot a^\Lambda$.

We derive from the earlier relations the results of Table 3 for Hermitian conjugation of the operators (in the ordinary sense; this Hermitian conjugation action does not conjugate elements of the quasispin matrices), time reversal and their combination. It is necessary where time reversal is involved to assume one-particle spin-orbital states with $\{\Lambda\} = -1$, so as to use anticommutation relations to reorder the operators; this case is taken for the whole table. This shows that for a one-particle state $Q(\lambda)_\alpha$ is Hermitian, while time reversal performs a π rotation about the y -axis of quasispin space.

4.2. Particle–hole conjugation

Bell [3] introduced a particle–hole conjugation operator C_B into nuclear shell theory with the form $C_B a_{jm} C_B^{-1} = (-1)^{j+m} a_{j-m}^\dagger$. Following Wybourne [19] we adapt this for the discussion of particle–hole conjugation within a subshell λ to the form:

$$C(\lambda) a_\Lambda C^\dagger(\lambda) = -a_\Lambda^\dagger, \quad C(\lambda) a_\Lambda^\dagger C^\dagger(\lambda) = a_\Lambda \quad (7)$$

Table 3. Behaviour of quasispin generators in a spherical and also a Cartesian basis under Hermitian conjugation, time reversal and their combination

$\mathbf{Q}(\Lambda)_m^\dagger = \mathbf{c} \mathbf{Q}(\Lambda)_m$	$\overline{\mathbf{Q}(\Lambda)_m} = \mathbf{d} \mathbf{Q}(\Lambda)_m$	$\overline{\mathbf{Q}(\Lambda)_m^\dagger} = \overline{\mathbf{Q}(\Lambda)_m}^\dagger = \mathbf{e} \mathbf{Q}(\Lambda)_m$
$\mathbf{c} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	$\mathbf{d} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\mathbf{e} = \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$
$\mathbf{Q}(\Lambda)_\alpha^\dagger = \mathbf{Q}(\Lambda)_\alpha$	$\overline{\mathbf{Q}(\Lambda)_\alpha} = \mathbf{g} \mathbf{Q}(\Lambda)_\alpha$	$\overline{\mathbf{Q}(\Lambda)_\alpha^\dagger} = \overline{\mathbf{Q}(\Lambda)_\alpha}^\dagger = \mathbf{g} \mathbf{Q}(\Lambda)_\alpha$
	$\mathbf{g} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	

In this case the order is immaterial.

$C(\lambda)$ is unitary and linear, commuting with the metric (so that $C(\lambda)a^\dagger C^\dagger(\lambda) = -a^{\dagger\Lambda}$, etc.) and indeed with all annihilation or creation operators for states outside the subshell λ . The combination operator $C = \prod_{\alpha\lambda} C(\lambda)$ will jointly perform particle–hole conjugation separately within each subshell.

The resulting actions of $C(\lambda)$ on quasispinors and on the generators of quasispin are:

$$\begin{aligned} C(\lambda)\mathbf{A}_\Lambda C^\dagger(\lambda) &= \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \mathbf{A}_\Lambda \\ C(\lambda)\mathbf{Q}(\lambda)_\alpha C^\dagger(\lambda) &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \mathbf{Q}(\lambda)_\alpha \end{aligned} \quad (8)$$

In manifestly preserving transformation character, the above confirm that both quasispin and particle–hole conjugation are scalars in orbital and spin space.

From Keiter *et al.* [4] we can realize $C(\lambda)$ explicitly from quasispin components (correcting equation (14) of Ref. [6]):

$$C(\lambda) \equiv 1 - 4(Q(\lambda)_z)^2 + 2Q(\lambda)_x \quad (9)$$

In addition, a quasispin eigenstate $|Q(\lambda)M_Q\rangle$ has eigenvalues ± 1 with respect to $C(\lambda)^2$. From equation (9), $C(\lambda)$ is Hermitian and (since unitary) self-inverse, and (also using Table 3) $C(\lambda)$ is time-even, commuting with T .

In seeking a simpler algebra than Judd [5], Stedman utilized the presence of an imaginary unit in $Q_y(\lambda)$ and redefined the particle–hole conjugation operator as $\tilde{C}(\lambda) = C(\lambda)Z$ where Z is complex conjugation [6]. All Cartesian components of quasispin then anticommute with $\tilde{C}(\lambda)$, as for parity in ordinary space. However, this assumes that the state creation and annihilation operators all commute with complex conjugation. This assumption does not survive a state basis change such as equation (5). As mentioned in Section 1, Z changes a spherical tensor such as $|11\rangle = Y_1^1 \propto |x\rangle + i|y\rangle$ in a Cartesian basis, but not in a spherical basis, and the anticommutation of equation (2) can hold only in the Cartesian basis in which it was defined; the basis transformation U of equation (5) has some imaginary elements on any phase convention. Since a basis-dependent choice of $\tilde{C}_S$ would imply results which are unphysically dependent on the choice of basis, we have to reject this option. A better way of achieving this phase change and gaining a full anticommutation algebra is to note that in Table 3 and equation (5) $Q_y(\lambda)$ is the oddly phased component under time reversal. Hence, the antilinear operator $\tilde{C}(\lambda) = C(\lambda)T$ has a more robust (basis-independent) anticommutation property with $\mathbf{Q}(\lambda)$.

From the above $\tilde{C}(\lambda)$ is unitary, Hermitian, self-inverse and antilinear (hence antiunitary); it anticommutes with quasispin generators, and commutes with orbital and intrinsic spin. A quasispin eigenstate $|QM_Q\rangle$ has eigenvalues ± 1 with respect to $\tilde{C}(\lambda)^2$. $\tilde{C}(\lambda)$ realizes the goal of Ref. [6] for selection rules of analogous form to those from time reversal for various quantities and arising from the algebra of

quasispin and the particle–hole conjugation. The physical importance of $\tilde{C}(\lambda)$ will become more apparent in a later paper, where we show that it is equivalent to Ceulemans’ [10] operator $O(\phi)$. This leads to such results as the proof that isolated half-filled shell states cannot exhibit first-order Jahn–Teller activity.

4.2.1. Quasispin operators

We write creation and annihilation operators for a state $|\Lambda\rangle$ as $a_A^\dagger$ and a_A , so that $|\Lambda\rangle = a_A^\dagger |0\rangle$. We use the spin-orbital $2jm$ symbols of the relevant spin-orbital group G as the metric components to raise and lower indices: $g^{\Lambda\bar{\Lambda}} = (\Lambda\bar{\Lambda})$ and $g_{\Lambda\bar{\Lambda}} = (\Lambda\bar{\Lambda})^*$. If the group G is the symmetry group of an ion whose levels are split by ligand fields, the relevant irrep λ of G (the main label within Λ) will contain precisely the states in the subshell, the degenerate set of partners. For example, in Ref. [10] $G = O$ and $\lambda = t_2$. In the triple tensor notation $X_{\pi\sigma\tau}^{Kkk}$ of Judd our notation corresponds to $\lambda = \kappa \otimes k$ if G is a product spin-space group; if spin–orbit interaction is included to couple these spaces, λ will be an irrep appearing in the appropriate Kronecker decomposition of $\kappa \otimes k$.

The $2|\lambda|^2 + |\lambda|$ operators $\mathcal{A} = \{a_A^\dagger a_{A'}, a_A^\dagger a_A^\dagger, a_A a_A, \Lambda\Lambda' \in \lambda\}$ (where $\Lambda' = \alpha\lambda l'$ and $l' = 1, \dots, |\lambda|$) close under commutation to give the algebra of the group $\text{SO}(4|\lambda| + 1)$ [5]. One subset which closes on an $\text{SO}(3)$ algebra is that of quasispin. The quasispinor $\mathbf{A}_\Lambda = \{A_{\Lambda q} | q = \frac{1}{2}, -\frac{1}{2}\}$ is defined as $\{A_{\Lambda+}, A_{\Lambda-}\} = \{a_A^\dagger, a_A\}$. Under the coupling of two quasispinors $[\mathbf{A}_\Lambda \mathbf{A}^\Lambda]^j$ we get operators of rank $j = 0$ (a quasispin singlet) and rank $j = 1$ (a quasispin triplet) in total quasispin. In the latter case and in a cartesian basis ($\alpha = x, y, z$) we obtain the quasispin generators $\mathbf{Q}(\lambda) = i[\mathbf{A}_\Lambda \mathbf{A}^\Lambda]^1 / \sqrt{2}$ in the form

$$Q(\lambda)_\alpha = \frac{1}{2} \begin{pmatrix} a_\Lambda \cdot a^\Lambda - a_A^\dagger \cdot a^{\dagger\Lambda} \\ i(a_\Lambda \cdot a^\Lambda + a_A^\dagger \cdot a^{\dagger\Lambda}) \\ a_A^\dagger \cdot a^\Lambda + a_\Lambda \cdot a^{\dagger\Lambda} \end{pmatrix} \quad (10)$$

the centred dot denoting a group-invariant contraction within the subshell: $X_\Lambda \cdot Y^\Lambda = \sum_l X_\Lambda Y^\Lambda$. The quasispin-singlet operator is proportional to $a_A^\dagger \cdot a^\Lambda - a_\Lambda \cdot a^{\dagger\Lambda}$.

The quasispin classification of the ligand-field-split states was detailed in Ref. [19] following Judd’s analysis for the rotation group. This problem turns out to have some subtleties, for example, the difficulty Ceulemans [10] discusses (and resolves) when bestowing a pseudo-angular momentum on his t_2 subshell. From Judd [5] and Wybourne [19] we note the following. The total subshell state space is:

$$\begin{aligned} & \{\Theta_j | j = 1, \dots, (2|\lambda|^2 + |\lambda| + 1)\} \\ &= \left\{ |0\rangle, \{a_A^\dagger |0\rangle\}, \{a_A^\dagger a_{A'}^\dagger |0\rangle\}, \dots, \left(\prod_{l=1}^{|\lambda|} a_A^\dagger \right) |0\rangle \right\} \end{aligned} \quad (11)$$

Since $\{\Theta_j\}$ is closed under the action of the operators $\mathcal{A}$, and since the latter have the $\text{SO}(4|\lambda| + 1)$ algebra, $\{\Theta_j\}$ is a basis for a representation of $\text{SO}(4|\lambda| + 1)$.

The commuting Hermitian operators $H_I \equiv \frac{1}{2}[a_A^\dagger a^A] = a_A^\dagger a^A - \frac{1}{2}$ (which are part of $\mathcal{A}$ and so include some $\text{SO}(4|\lambda| + 1)$ generators) have the simultaneous eigenfunctions $\{\Theta_j\}$. To each Θ_j there corresponds a weight $\mathbf{m}_j$ given by the set of its eigenvalues under the $\{H_I\}$. Each Λ either is or is not present in any Θ_i , hence all weights have the form $\{\pm \frac{1}{2}, \pm \frac{1}{2}, \dots\}$. All possible combinations of sign must exist in the eigenspace of the $\{H_I\}$, so the $\{\Theta_j\}$ representation is irreducible. It is customary to label the irrep (the simplest spin irrep of $\text{SO}(4|\lambda| + 1)$) by the ‘highest’ weight, here that of the filled subshell: $\{\frac{1}{2}, \frac{1}{2}, \dots, \}$.

Now instead of considering the action of $\{H_I\}$ consider the action of the quasispin generators on $\{\Theta_j\}$. In this $\text{SO}(3)$ subalgebra of $\text{SO}(4|\lambda| + 1)$ the $\{\Theta_j\}$ basis is clearly reducible; the quasispin generators do not mix states with odd and even particle number. The conditions under which these subspaces are also irreducible are not immediately obvious. Judd [5] gave a branching scheme from $\text{SO}(4|\lambda| + 1)$ through the quasispin group to the full shell symmetry group, and showed that a unique labelling could be found, making each shell state of definite quasispin and quasispin projection with respect to the quasispin operators of the full shell. However, this is not guaranteed even for the same states when the relevant quasispin operators are those for the subshell. Each Θ_j is an eigenstate of $Q(\lambda)_z$, since the latter is $\sum_I H_I$, and the eigenvalue is the sum of the weight components. This eigenvalue differs in the subshell and full shell, even for the same state; the other and unoccupied shell states each add $-\frac{1}{2}$. This eigenvalue cannot change under intrashell interactions: the quasispin projection for a physical operator is zero since such operators conserve particle number. Wybourne [19] showed that an assignment of quasispin Q through branching schemes was rendered particularly difficult when the representation matrices of the subshell were not unimodular (as in Ceulemans’ example of t_2 states in O [7]), for then they could not be generated in a group chain starting from an orthogonal group. From Cayley’s theorem any finite group with N elements is itself S_N , A_N or isomorphic to a subgroup of S_N where S_N , A_N are the symmetric and alternating groups on N objects. If the G representation matrices for the subshell states $\{\lambda I\}$ are unimodular (have determinant $+1$), then one may embed G via S_N in the unimodular group $\text{SU}(N)$. The condition on $(\mu)S_N$ being unimodular is that the degree of $(\mu/1^2)$ be even; also, the irreps of A_N apart from (2^1) and (2^2) are unimodular [24]. This allows a mapping from $\text{SU}(N)$ to (μ) and so $\lambda(G)$ defining the quasispin character of the latter. If the irrep matrices are not unimodular, it is necessary to subduce using the unitary groups.

In second quantized notation, a single-particle irreducible-tensor operator $V_m^M(aK, d'L, r)$ is written

$$V_m^M(aK, d'L, r) = \sum_{KL} a_K^\dagger a_L v_{kml}^{KML} \quad (12)$$

by the Wigner–Eckart theorem. For more information on the Wigner–Eckart theorem expressed for point groups see Refs. [11,12]. The coefficients v_{kml}^{KML} are proportional to vector coupling coefficients. This constant of proportionality is

known as a reduced matrix element, i.e.,

$$v_{kml}^{KML} = \langle aK || V^{M_r} || a'L \rangle (K\bar{K}) \begin{pmatrix} \bar{K} & M & L \\ \bar{k} & m & l \end{pmatrix}^r \quad (13)$$

Hence the coefficients v_{kml}^{KML} have the symmetry properties as follows, from those of the nj symbols

$$v_{\bar{k}\bar{m}\bar{l}}^{\bar{K}\bar{M}\bar{L}} = \langle a\bar{K} || V^{\bar{M}_r} || a'\bar{L} \rangle (\bar{K}\bar{K}) \begin{pmatrix} K & \bar{M} & \bar{L} \\ k & \bar{m} & \bar{l} \end{pmatrix}^r \quad (14)$$

$$v_{\bar{k}\bar{m}\bar{l}}^{\bar{K}\bar{M}\bar{L}} = \frac{\langle a\bar{K} || V^{\bar{M}_r} || a'\bar{L} \rangle}{\langle aK || V^{M_r} || aL \rangle^*} \{K\} (M\bar{M})^* (v_{kml}^{KML})^* \quad (15)$$

$$v_{lmk}^{LMK} = \frac{\langle a'L || V^{M_r} || aK \rangle}{\langle a\bar{K} || V^{\bar{M}_r} || a'\bar{L} \rangle} (K\bar{L}) (K\bar{K})^* \{\bar{L}MK_r\} v_{\bar{k}\bar{m}\bar{l}}^{\bar{K}\bar{M}\bar{L}} \quad (16)$$

The unit tensor operators are irreducible-tensor operators with reduced matrix elements of unity. They are a valid choice to use as a basis in order to express any arbitrary tensor operator as a linear combination, since they are linearly independent. Attention is restricted to these for the sake of simplicity. Hence the definition of unit tensor single-particle operator $U_m^M(aK, a'L, r)$ is

$$U_m^M(aK, a'L, r) = \sum_{KL} a_K^\dagger a_L (K\bar{K}) \begin{pmatrix} \bar{K} & M & L \\ \bar{k} & m & l \end{pmatrix}^r \quad (17)$$

5. CEULEMANS' SELECTION RULES

5.1. Ceulemans 1984 version

Ceulemans' paper of 1984 generalizes the work of Griffith [25,26] on particle–hole conjugation for the specific case of d^n electrons split by an octahedral symmetry field. He relies on the use of matrices and determinants, in particular Laplace's expansion of the determinant in terms of complementary minors, for the analysis. He bases his selection rule analysis on the properties of a novel particle–hole conjugation operator $O(\phi)$.

Ceulemans considers a d^n electron state, split by an octahedral field into the e and t_2 levels, so that all the n electrons are in the t_2 subshell. In the notation of Sugano *et al.* [27], $\psi(t_2^n S \Gamma M_S M_\Gamma)$ is the multi-electronic wavefunction, with SM_S irrep labels for the total spin and ΓM_Γ irrep labels in the octahedral group for the orbital state. We use a real orbital basis in which all njm factors take their simplest possible forms and suppress S , Γ and M_Γ below. It takes six electrons (three pairs each of opposed spin) to fill this t_2 subshell. Ceulemans' [7] particle–hole conjugation operator $O(\phi)$ has the effect of conjugating the occupancies within this subshell, and of

transforming the d_n state $\psi(t_2^n M_S)$ into the d^{6-n} state $(-1)^{S-M_S} \hat{\psi}(t_2^{6-n} - M_S)$. Note that in $\hat{\psi}$ particles and holes are reversed purely within the t_2 subshell; this differs from the action of a Bell-type particle–hole conjugation CB acting on the whole shell (see Ref. [9]), with respect to which a d^n state would be conjugate to a d^{10-n} state. Note also that $\hat{\psi}$ has the opposite spin projection to ψ , and (though the point is inconspicuous in the chosen basis) its orbital transformation properties are also conjugate to those of ψ .

In contrast the (linear) subshell particle–hole conjugation operator $C(\lambda)$, as defined in Ref. [9] preserves the spin projection, transforming $\psi(t_2^n M_S)$ into $\hat{\psi}(t_2^{6-n} M_S)$. However, the Wigner time reversal operator T [13,16] reverses these projections: $T\psi(t_2^n M_S)T^{-1} = (-1)^{S-M_S} \psi(t_2^n - M_S)$, so that (to within an innocuous phase convention, which we suppress) the combination $\tilde{C}(\lambda) = C(\lambda)T$ is equivalent to $O(\phi)$; both $C(\lambda)T$ and $O(\phi)$ are antiunitary, exchange subshell particles and holes, commute with spatial operations, anticommute with the operators for spin, orbital momentum and quasispin, and have a square with an eigenvalue $+1$ (-1) as the number of electrons in the half-filled ligand shell is even (odd).

5.2. Ceulemans 1994 version

The selection rules were reformatted by Ceulemans [10] to include a discussion of the quasispin character of the states. Ceulemans considered d^n electrons of Cr(III) complexes being split in an environment of octahedral symmetry, forming multiplets labelled e and t_2 (irreps of the octahedral group O). He followed the traditions of the atomic spectroscopists and of Judd [5] in particular. A second quantized ligand-field theoretic approach was used in lieu of Slater determinants, encapsulating fermion statistics and the Pauli’s exclusion principle *via* the anticommutation relations of annihilation and creation generators, rather than in explicit analyses of permutations of rows and columns of determinants. Quasispin, including the triple tensor notation of Judd [5] was introduced, and led to a new derivation of selection rules for half-filled ligand states. In the Judd triple tensor notation $X_{\pi\sigma\tau}^{(K\kappa k)}$ operators [9] are assigned tensorial ranks K , κ , k under Q (quasispin), S (spin), and L (orbital angular momentum), respectively. Second-quantized annihilation and creation operators and their products can then be expanded irreducibly in terms of quasispin.

Ceulemans showed that the time reversal character of a single-particle operator was linked to its quasispin rank. A time-even operator $\mathcal{H}$ contained a quasispin triplet plus a term of the form $\frac{1}{2} \sum_{\xi} \mathcal{H}_{\xi\xi}$ which is totally scalar (in quasispin, spin and orbital angular momentum; ξ labels all spin projections), while a time-odd operator was a quasispin singlet. This relationship underlies the selection rules Ceulemans derived for half-filled shell states, as discussed in Ref. [10].

Between states of well-defined quasispin Q , Q' , the Wigner–Eckart theorem in quasispin space shows that any quasispin tensor has matrix elements proportional to

the $3jm$ symbol

$$\begin{pmatrix} Q & K & Q' \\ -M_Q & 0 & M'_Q \end{pmatrix}$$

the zero arising from particle number conservation. In a half-filled shell ($M_Q = M_{Q'} = 0$) from the Derome–Sharp lemma this $3jm$ symbol vanishes unless $Q + K + Q'$ is even [6,11,12].

If this is combined with the triangle condition, and the results that K is 0, 1 as the interaction is time-odd and time-even, we find that

$$\begin{aligned} K = 0 : \quad \Delta Q &= 0 \\ K = 1 : \quad \Delta Q &= \pm 1 \end{aligned} \tag{18}$$

These conditions imply the following selection rules [10]:

1. Interaction elements between half-filled shell states with different quasispin character will be zero for time-odd one-electron operators.
2. Off-diagonal elements between half-filled shell states with identical quasispin character will be zero for time-even one-electron operators.
3. Diagonal interaction elements will be zero for time-even one-electron operators that are not totally symmetric scalars in spin and orbit space.

The similarity of these rules with the rules of Ref. [7] is striking; if the phrase ‘quasispin character’ is replaced with the word ‘parity’ (with respect to $C(\lambda)$) they are identical. The precise nature of the relationship between the formalisms escaped Ceulemans, however. This will be discussed in Section 6. As before three cases arise:

1. The interaction occurs between half-filled shell states with different quasispin character ($Q \neq Q'$). If the interaction is time-odd in nature then it will have quasispin rank $K = 0$. The interaction matrix element must then vanish.
2. The interaction occurs between half-filled shell states with identical quasispin character ($\Delta Q = 0$). If the interaction is time-even then it has quasispin rank $K = 1$. From these equations such off diagonal interaction matrix elements must vanish.
3. The interaction is time-even ($K = 1$). Hence (from the time-reversal selection rules) within a manifold with $Q = Q'$, $K \in [Q \times Q]_{\{QKQ\}}$ and the requirement that $\{QKQ\} = +1$ the diagonal matrix elements will vanish if the interaction is not a totally symmetric scalar in spin and orbital angular momenta.

5.3. The quasispin character of interaction operators

In the following C_L denotes the generalized form of the particle–hole conjugation operator $C(\lambda)$ which runs over conjugate pairs and is defined as

$$C_L = \prod_{\lambda} C(\lambda) \quad (19)$$

C_L and T have the following effects on states labelled in the quasispin scheme of, for example, Ceulemans [7],

$$C_L |QM_Q SM_S LM_L M_I\rangle = (-1)^{Q-M_Q} |Q - M_Q SM_S LM_L M_I\rangle \quad (20)$$

$$T |QM_Q SM_S LM_L M_I\rangle = (-1)^{S+L-M_S-M_L} (\Gamma\bar{\Gamma}) |QM_Q S - M_S L - M_L \bar{M}_I\rangle$$

where $(\Gamma\bar{\Gamma})$ is the $2jm$ symbol for irrep Γ of group G (in this case the octahedral group, but this will be kept general). Further, if attention is restricted to those shells which are half-filled then $M_Q = 0$. This implies that the effect of T on the half-filled shell gives

$$T |Q0 SM_S LM_L M_I\rangle = (-1)^{S+L-M_S-M_L} (\Gamma\bar{\Gamma}) |Q0 S - M_S L - M_L \bar{M}_I\rangle \quad (21)$$

And C_L gives:

$$C_L |Q0 SM_S LM_L M_I\rangle = (-1)^Q |Q0 SM_S LM_L M_I\rangle \quad (22)$$

Using the result $\tilde{C}_L = C_L T = T C_L$ it can then be seen that

$$\tilde{C}_L |Q0 SM_S LM_L M_I\rangle = (-1)^{Q+S+L-M_S-M_L-M_Q} (\Gamma\bar{\Gamma}) |Q0 S - M_S L - M_L \bar{M}_I\rangle \quad (23)$$

and also

$$T^2 |Q0 SM_S LM_L M_I\rangle = (-1)^{2(S+L)} \{\Gamma\} |Q0 SM_S LM_L M_I\rangle \quad (24)$$

The similarity between $\tilde{C}_L$ and T on half-filled shells should be noted (see the above equations they are identical to within a phase). This example strengthens the identification of $\tilde{C}_L$ as $O(\phi)$, the particle–hole conjugation operator for half-filled shells defined by Ceulemans where $O(\phi)$ is characterized by the properties listed in Ref. [9]. Ceulemans states that $O(\phi)$ shares a number of properties with time reversal (and consequently with $\tilde{C}_L$).

5.4. A new derivation of Ceulemans' selection rules

In a very similar vein to the time reversal selection rule as stated by Stedman (see Ref. [12; page 97]), the Ceulemans' selection rules for half-filled shell states are a set of very simple, broad statements with remarkably wide ranging application and influence.

Paraphrasing the words of Ceulemans: the special configurational symmetry of the half-filled shell also affects the interaction matrix elements. In the case of a one-electron Hermitian operator $\mathcal{H}_m^M$, one has the following [7]:

1. Interaction elements between half-filled shell states of opposite (C_L) parity will be zero if H_m^M is antisymmetric under time reversal.
2. Off-diagonal interaction elements between half-filled shell states of identical (C_L) parity will be zero if H_m^M is symmetric under time reversal.
3. Diagonal interaction elements between half-filled shell states will be zero if H_m^M is symmetric under time reversal and not totally symmetric under the spatial symmetry operations.

The proof of these rules follows directly from the composite nature of the antilinear particle–hole conjugation operator $O(\phi)$ of Ceulemans, which, it is emphasized here again, is equivalent to within a phase to $\tilde{C}_L = C_L T$. It is an interesting point to note that this means that these rules stem from not just a linear choice of particle–hole conjugation operator, nor from just the antilinear choice, but from the effects of both separately and together.

The action of $\tilde{C}_L$ on a half-filled shell state distinguished by the (composite) irrep label K is denoted by

$$\tilde{C}_L |K\rangle \equiv |\widetilde{K}\rangle \quad (25)$$

and similarly for the bra $\langle K|$. In addition, the time reversed kets (and bras) will be denoted by a bar

$$T|K\rangle = |\overline{K}\rangle \quad (26)$$

where it should be noted that both the bar and the tilde are over the entire ket, not just the irrep label(s).

The composite nature of $\tilde{C}_L$ (and the fact that C_L and T commute) allows equation (25) to be written

$$|\widetilde{K}\rangle = TC_L |K\rangle = \pi_K |\overline{K}\rangle \quad (27)$$

where π_K is the eigenvalue of C_L for the half-filled shell and has values of ± 1 . Similarly the parity of C_L for the ket $|L\rangle$ is denoted π_L . Therefore, matrix elements of the operator $\mathcal{H}_m^M$ in the ‘complementary’ space due to the particle–hole conjugation have the following property

$$\langle \widetilde{K} | \mathcal{H}_m^M | \widetilde{L} \rangle = \pi_K \pi_L \overline{\langle K | \mathcal{H}_m^M | L \rangle} \quad (28)$$

The operator $\mathcal{H}_m^M$, being a single particle tensor operator, may be expanded as a linear combination with the unit tensor operators as a basis. It follows from the antiunitary nature of $\tilde{C}_L$ ($\equiv O(\phi)$) that

$$\langle \widetilde{K} | \mathcal{H}_m^M | \widetilde{L} \rangle = \langle K | \tilde{\mathcal{H}}_m^M | L \rangle^* = \langle K | L \rangle^* \langle \mathcal{H}_m^M \rangle - \langle K | \mathcal{H}_m^{M\dagger} | L \rangle^* \quad (29)$$

where the notation $\tilde{\mathcal{H}}_m^M$ has been used to denote the action of $\tilde{C}_L$ on $\mathcal{H}_m^M$ – $\tilde{C}_L \mathcal{H}_m^M \tilde{C}_L^{-1}$, and $\langle \mathcal{H}_m^M \rangle$ represents the expectation value of $\mathcal{H}_m^M$ in the closed shell.

By hypothesis $\mathcal{H}_m^M$ is a Hermitian operator (has real observable eigenvalues) hence

$$\langle \widetilde{K} | \mathcal{H}_m^M | \widetilde{L} \rangle = \langle L | K \rangle \langle \mathcal{H}_m^M \rangle - \langle L | \mathcal{H}_m^M | K \rangle \quad (30)$$

which relates the matrix elements of $\mathcal{H}_m^M$ in the complementary space of particle-hole conjugation to those in the non-conjugate space. From above results, the fact that time reversal is antiunitary, and the assumption that the operator $\mathcal{H}_m^M$ has definite time reversal parity, $\tau_{\mathcal{H}^M}$, it is found that

$$\begin{aligned} \langle \widetilde{K} | \mathcal{H}_m^M | \widetilde{L} \rangle &= \pi_K \pi_L \overline{\langle K | \mathcal{H}_m^M | L \rangle} \\ &= \pi_K \pi_L \langle K | \mathcal{H}_m^M | L \rangle^* \\ &= \pi_K \pi_L \tau_{\mathcal{H}^M} \langle L | \mathcal{H}_m^M | K \rangle \end{aligned} \quad (31)$$

where $\overline{\mathcal{H}_m^M} = T \mathcal{H}_m^M T^{-1} = \tau_{\mathcal{H}^M} \mathcal{H}_m^M$. The selection rules now follow through combination of equations (30) and (31):

$$\pi_K \pi_L \tau_{\mathcal{H}^M} \langle L | \mathcal{H}_m^M | K \rangle = \langle L | K \rangle \langle \mathcal{H}_m^M \rangle - \langle L | \mathcal{H}_m^M | K \rangle \quad (32)$$

This is equivalent to equation (73) of Ceulemans [7], with $p = \pi_K \pi_L$ and $q = \tau_{\mathcal{H}^M}$. There are three cases to consider corresponding to the three selection rules:

1. The interaction occurs between half-filled shell states $|K\rangle$ and $|L\rangle$ which possess different parities with respect to C_L , π_K and π_L , respectively. This implies that necessarily the configurations are different, i.e., $|K\rangle \neq |L\rangle$, and also that the product of parities $\pi_K \pi_L$ has the value -1 . The hypothesis that $\mathcal{H}_m^M$ is antisymmetric under time reversal is represented in equation (32) by setting $\tau_{\mathcal{H}^M} = -1$. It follows that the interaction matrix element $\langle L | \mathcal{H}_m^M | K \rangle$ must vanish if these criteria are met.
2. The interaction occurs between half-filled shell states $|K\rangle$ and $|L\rangle$ with identical C_L parities, i.e., $\pi_K \pi_L = +1$. This does not necessarily imply, however, that the states themselves be identical. Off diagonal interaction elements are considered so that even in the case of an interaction occurring between identical states the matrix elements with value $\langle \mathcal{H}_m^M \rangle$ need not be considered.

Further, if it is hypothesized that $\mathcal{H}_m^M$ be symmetric under time reversal ($\tau_{\mathcal{H}^M} = +1$) then it follows from equation (32) that the off diagonal matrix elements must necessarily vanish.

3. The diagonal matrix elements between half-filled shell states are now considered. If it is assumed that the interaction operator $\mathcal{H}_m^M$ is symmetric under time reversal (also as in case 2), then $\tau_{\mathcal{H}^M} = +1$. The diagonal interaction elements are just the expectation value of $\mathcal{H}_m^M$ in the closed shell, which is zero if $\mathcal{H}_m^M$ is not totally symmetric under spatial operations (Another way of saying this is that $\langle \mathcal{H}_m^M \rangle$ vanishes if $M_r \notin [K \times K]_{\{KM_K r\}}$), but obviously has time reversal parity $+1$. It now follows that if the above criteria are met then the diagonal matrix elements must vanish.

5.5. Implications of Ceulemans’ selection rules

Certainly the most far reaching effect of these three, simply stated, rules follows from statement 2 and 3 [9], since a linear Jahn–Teller interaction corresponds to an operator which is symmetric under time reversal ($\tau_{\mathcal{H}^M} = +1$), but not totally symmetric under spatial symmetry operations. It, therefore, follows that *Linear Jahn–Teller interaction elements between half-filled shell states of the same C_L parity are forbidden*. This is the case for any isolated half-filled shell state. In an earlier paper Ceulemans [8] discussed particle–hole exchange symmetry in organic molecules. In particular he used the group-theoretical implications of the particle–hole conjugation operator to offer a reason why, for instance, the Jahn–Teller theorem is ‘violated’ by the $|^1E'\rangle$ wavefunctions for planar Trimethylene-methane as reported by Borden in 1976 [28]. In fact Borden was of the opinion that this lack of Jahn–Teller activity was an indication that the $|^1E'\rangle$ wavefunctions were not the correct ones. Ceulemans was able to refute this hypothesis with an argument based on the fact that the molecular wavefunctions in equation were of e^2 symmetry (half-filled e ligands) and thus fall into the general category covered by the selection rules. Further experimental verification of the absence of (expected) Jahn–Teller activity in transition metal ion complexes is discussed at length by Ceulemans [10]. For example, mention is made of some very accurate experimental observations which suggest the complete absence of the linear (first-order) Jahn–Teller effect in the excited $^2E_g(t_{2g}^3)$ state of Cr(III) complexes. It is also commented upon that ‘no detailed explanation of these remarkable observations appears to be available in the literature’. We now offer a generalized development of Ceulemans’ selection rules including any explanation for such phenomena.

6. THE CONNECTION BETWEEN THE 1984 [7] AND 1994 [10] SELECTION RULES

Section 5 highlights a remarkable feat by Arnout Ceulemans. He was able to, over the time interval of 10 years, derive essentially the same selection rules twice by two dramatically different methods. The only thing more remarkable of this achievement was the fact that since the methods used in each case were so different, Ceulemans was unable to reconcile the relationship between the two formalisms. The connection is in fact, beautiful in its simplicity [9]. The 1984 derivation relied upon the eigenvalues of a linear particle–hole conjugation operator. An operator that was both Hermitian and unitary, i.e., was equal to its own inverse. This operator was identified (to within a phase) as being C_L . The effects of this operator on the annihilation and creation operators of second quantization and on arbitrary shell terms of good quasispin eigenvalues QM_Q are given in equations (8) and (20). Also since for a shell state transforming as the irrep $\lambda(G)$ (of group G) of dimension

λ the value of the quasispin projection eigenvalue is

$$M_Q = \frac{1}{2}(\lambda - N) \quad (33)$$

then for a half-filled shell $N = \lambda$ and $M_Q = 0$. So for those terms for which Q, M_Q are applicable eigenvalues for a half-filled shell, $|Q0\rangle$, C_L has eigenvalue $\pi_Q = (-1)^Q$, i.e.,

$$C_L|Q0\rangle = \pi_Q|Q0\rangle = (-1)^Q|Q0\rangle \quad (34)$$

Hence in his 1984 paper [7], when Ceulemans referred to the parity of a half-filled shell state with respect to a linear particle-hole conjugation operator he was actually referring to the ‘quasispin character’ of the state, see equation (34). For a half-filled shell state Q is always integral, hence $(-1)^Q = \pi_Q = \pm 1$. This is just the result derived by Ceulemans in 1984 [7] with no knowledge whatsoever of the concept of quasispin. The governing equation from which Ceulemans’ 84 selection rules stem, expressed in terms of half-filled shell states, may be labelled with the quasispin scheme proposed by Ceulemans in 1994 [10];

$$\pi_Q \tau_{\mathcal{H}^K} \pi_Q \langle Q'0 | \mathcal{H}_k^K | Q0 \rangle = \langle Q'0 | Q0 \rangle \langle \mathcal{H}_k^K \rangle - \langle Q'0 | \mathcal{H}_k^K | Q0 \rangle \quad (35)$$

Furthermore, the two equations, in which Ceulemans [10] expressed the relationship between the quasispin rank of a single-particle interaction operator and its time-reversal signature, may be summarized

$$\tau_{\mathcal{H}^K} = -(-1)^K, \quad K = 0, 1 \quad (36)$$

With the relationship expressed in this form, and with the knowledge that the C_L parity, π_X , of a state or operator with quasispin rank X and quasispin projection $x = 0$ (for example, for a half-filled shell state or a single-particle interaction) is

$$\pi_X = (-1)^X \quad (37)$$

then, the relationship between the time-reversal parity, the C_L parity and the quasispin character of a state or operator becomes

$$\tau_{\mathcal{H}^K} = -(-1)^K = -\pi_K \quad (38)$$

In particular equation (35) may now be expressed as

$$-\pi_Q \pi_K \pi_Q \langle Q'0 | \mathcal{H}_0^K | Q0 \rangle = \langle Q'0 | Q0 \rangle \langle \mathcal{H}_0^K \rangle - \langle Q'0 | \mathcal{H}_0^K | Q0 \rangle \quad (39)$$

or, in another variation, as

$$-(-1)^{Q+K+Q'} \langle Q'0 | \mathcal{H}_0^K | Q0 \rangle = \langle Q'0 | Q0 \rangle \langle \mathcal{H}_0^K \rangle - \langle Q'0 | \mathcal{H}_0^K | Q0 \rangle \quad (40)$$

Thus three important points have been recovered from a re-expression of Ceulemans 1984 paper:

1. The general rule for the non-vanishing of interaction matrix elements is equivalent to Wybourne’s [31] ‘crucial’ condition on the matrix elements of an

interaction between half-filled shells, given here as

$$Q + K + Q' \text{ is even}$$

2. Ceulemans' rules (both versions 1984 and 1992) may be reinterpreted as a general statement about C_L parities: must have

$$\pi_Q \pi_K \pi_{Q'} = +1$$

for the interaction matrix element not to vanish.

3. *There are two types of half-filled shells*; this relates to the symmetries noted by Judd and Runciman [30].

As for the latter point, the analysis of Ref. [7] includes the following. Define the projection operator $C_L = O(\phi)T$, where T is the time reversal operator. For half-filled shells:

$$O(\phi)T = |\mathbf{T}|^{-1}TO(\phi) \quad (41)$$

where $|\mathbf{T}|$ is the determinant of the matrix representation of T , the $2jm$ matrix. For a spin orbital (fixed $m_l, m_s = \pm \frac{1}{2}$) and a suitable normalization choice [12] the matrix $\mathbf{T}$ has the unimodular form

$$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

Since $O(\phi)T \equiv \tilde{C}_L T \equiv C_L T^2 = C_L \{K\}$ it is obtained that for a half-filled shell

$$C_L T^2 = (-1)^Q (-1)^{2(S+L)} \{ \Gamma \} \quad (42)$$

A similar result is obtained for $TO(\phi) \equiv TC_L T = \tilde{C}_L T^2 = \tilde{C}_L \{K\}$, in that it is possible to show that to within a phase $O(\phi)T$, which is equivalent to C_L , is its own inverse and hence generates a group of dimension two. This group, according to Ceulemans, must contain two irreps both of singular dimension, i.e., the totally symmetric A_1 and the totally antisymmetric A_2 irreps ($\mathbf{1}$ and $\tilde{\mathbf{1}}$ in Butler's notation) [12]. Using this fact, symmetry adapted basis functions are constructed using the projection operator

$$\mathcal{A}^\pm = 1 \pm |\mathbf{T}|^{1/2} O(\phi)T \quad (43)$$

where $|\mathbf{T}|^{1/2}$ is the square root of the determinant of the matrix representation of T – time reversal – and as previously mentioned is related to the product of $2j$ phases. This means that to within a phase

$$\mathcal{A}^\pm = 1 \pm C_L \quad (44)$$

Since it is known that $C_L = C_L^\dagger = C_L^{-1}$, following Ceulemans' argument it can be said that C_L is the generator for an Abelian group of order two, which has two irreps $\mathbf{1}$ and $\tilde{\mathbf{1}}$. According to Ceulemans [7,8,10] this gives a group theoretical justification

for the two types of half-filled shell (mentioned in, for example, Refs. [14,16]). The other way of looking at these two types of half-filled shells is that C_L has eigenvalue ± 1 on the half-filled shell [9].

7. CONCLUSION

There is a rich algebraic structure to the irreducible tensor operators and the operators of time reversal and Hermitian conjugation which has not been fully analyzed before in the context of quasispin algebra; we give some results and consequences of this for the first time; we discuss some different remains to be done in elucidating the consequences for ligand field theory. Some issues are clarified using the requirement of biparticity for group-theoretical diagrams. These are developed in a more familiar algebraic approach, and yield an advantage to a unitary choice of particle–hole conjugation operator. This further elucidates the power and origin of the selection rules discovered by Ceulemans for Jahn–Teller systems.

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REFERENCES

- [1] L. Hannibal, *Found. Phys. Lett.*, 1995, **8**, 309–326.
- [2] M. A. H. Tucker and A. F. G. Wyatt, *Science*, 1999, **283**, 1150–1152.
- [3] J. S. Bell, *Nucl. Phys.*, 1959, **17**, 117–124.
- [4] G. E. Stedman and A. B. Kaiser, *J. Phys. C. Solid State Phys.*, 1987, **20**, 3943–3951.
- [5] B. Judd, *Second Quantization and Atomic Spectroscopy*, The John Hopkins Press, Baltimore, 1967.
- [6] G. E. Stedman, *J. Phys. A: Math. Gen.*, 1987, **20**, 2629–2643.
- [7] A. Ceulemans, *Molecular symmetry and the theory of transition metal ions*, *Mededelingen van de Koninklijke Academie voor Wetenschappen, Letteren en Schone Kunsten van België, Klasse der Wetenschappen*, 1984, **46**, 81–115.
- [8] A. Ceulemans, *Chem. Phys.*, 1982, **66**, 169–175.
- [9] E. D. Savage, PhD Thesis. *Higher Symmetries in Jahn–Teller systems*, University of Canterbury, 1999.
- [10] A. Ceulemans, *The doublet states in Chromium(III) complexes: a shell theoretic view*, Topics in Current Chemistry, Springer, Berlin, 1994, Vol. 171, pp. 27–67.
- [11] P. H. Butler, *Point Group Symmetry Applications: Methods and Tables*, Plenum Press, New York, 1981.

- [12] G. E. Stedman, *Diagram Techniques in Group Theory*, Cambridge University Press, Cambridge, 1990.
- [13] E. P. Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra*, Academic Press, New York, 1959.
- [14] B. H. Flowers, *Proc. R. Soc. Lond. A: Math*, 1952, **212**, 248.
- [15] K. Helmers, *Nucl. Phys.*, 1961, **23**, 594–611.
- [16] A. K. Kerman, *Annals of Phys.*, 1961, **12**, 300–329.
- [17] L. D. Lawson and M. H. McFarlane, *Nucl. Phys.*, 1965, **66**, 80–96.
- [18] H. Watanabe, *Prog. Theor. Phys.*, 1964, **32**, 106–125.
- [19] B. G. Wybourne, *Int. J. Quantum Chem.*, 1973, **7**, 1117–1137.
- [20] D. T. Sviridov and Y. F. Smirnov, *Soviet Phys.*, 1968, **13**, 565–567, Translated from *Doklady Akademii Nauk SSSR*, 1968, **180**(4), 843–846.
- [21] G. E. Stedman, *Adv. Phys.*, 1985, **34**, 513–587.
- [22] U. Fano and G. Racah, *Irreducible Tensorial Sets*, Academic Press, New York, 1959.
- [23] M. Rotenberg, R. Bivins, N. Metropolis and J. K. Wooton, *The 3-j and 6-j symbols*, The Technology Press, Cambridge, MA, 1959.
- [24] R. C. King, *J. Math. Phys.*, 1974, **15**, 258–267.
- [25] J. S. Griffith, *The Theory of Transitional Metal Ions*, Cambridge University Press, New York, 1961.
- [26] J. S. Griffith, *The Irreducible Tensor Method for Molecular Symmetry Groups*, Prentice-Hall, Englewood Cliffs, NJ, 1962.
- [27] S. Sugano, Y. Tanabe and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals*, Academic Press, New York, 1970.
- [28] W. T. Borden, *J. Am. Chem. Soc.*, 1976, 2695–2700.
- [29] B. G. Wybourne, in *Symmetry and Structural Properties of Condensed Matter* (ed. W. Florek), World Scientific, Singapore, 1991, pp. 155–186.
- [30] B. R. Judd and W. A. Runciman, *Proc. R. Soc. Lond. A: Math*, 1976, **352**, 91–108.

Renner–Teller Interaction Matrices and Green’s Function Formalism

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Abstract

The general structure of the interaction matrices for the Renner–Teller $E \otimes \varepsilon$ vibronic system at any order in the phonon variables and with orbital electronic functions of different symmetry is here determined by means of a simple approach based on the Slater–Koster expressions of two-center integrals and connected to the symmetry group approach. Starting from the case of orbital doublet with p -like functions, through suited canonical transformations in electronic and phonon variables, it is shown that the Renner–Teller problem can be mapped exactly into a set of independent double chains of orthonormal states with interactions between a small number of neighbor states (depending on the order of the interaction considered). The key point of the transformations introduced exploits the axial symmetry of the problem, so the procedure is generally valid also for other symmetries of the orbital functions. Then the Green’s function formalism combined with the recursion–renormalization procedure can be efficiently applied to determine with high accuracy the vibronic eigenstates for Renner–Teller systems with interaction matrices expressed in whatever general form.

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1. INTRODUCTION

Almost all the papers and textbooks describing the Jahn–Teller effect quote the statement [1,2]: “a polyatomic molecule in a degenerate electronic orbital state is

unstable unless the equilibrium positions of atoms lie on a straight line". This exception represents the Renner–Teller effect [3], which describes the coupling of the electronic orbital motion with the nuclear motion in degenerate states of a linear molecule, including molecules that can become linear as a result of vibrations. The symmetry of the linear molecules leads to adiabatic potential energy sheets even functions of the bending coordinates, while the linear electron–phonon coupling (peculiar to the Jahn–Teller system) is absent.

The concept of Renner–Teller coupling has become essential for understanding the complex optical spectra of many triatomic molecules (BH_2 , NH_2 , HCO , NCO , NO_2 , SO_2 , etc.). For reviews of the Renner–Teller effect, its theory and applications, see, for instance, Refs. [4–10].

The $E \otimes \varepsilon$ Renner–Teller vibronic system describes an orbital doublet (E) interacting with a two-dimensional vibrational mode of ε symmetry. In Section 2 we determine the general formal structure of the electron–phonon interaction matrices with orbital electronic functions of different symmetry (p -like, d -like, f -like, etc.), exploiting their intuitive relation with the Slater–Koster matrices of the two-center integrals. A direct connection with the form obtained through the molecule symmetry is discussed in Section 3.

Then we focus on the case of an orbital doublet with p -like functions. This model has been extensively studied in the literature and vibronic states have been evaluated within the framework of the perturbation theory [3,11–14], or diagonalization of symmetry adapted basis functions [15] up to a reasonably manageable phonon number. In Section 4 we propose a very reliable procedure, suitable also when the quadratic coupling is strong enough, or quartic terms are required. The main point is the axial molecular symmetry, which preserves the total angular momentum J along the axis of the molecule. So we can perform appropriate canonical transformations on the Renner–Teller Hamiltonian and map it into a set of independent double chains of orthonormal states for each (integer) value of J . It is easily understood that the procedure can be immediately extended also to d -like, f -like, etc. orbital functions. The recursion procedure or the renormalization method provide directly the vibronic levels. Section 5 contains the conclusions.

2. RENNER–TELLER ELECTRON–PHONON INTERACTION MATRICES

In this section we show how the general form of Renner–Teller interaction matrices can be obtained at any order in the phonon variables and with electron orbital functions of different symmetry (p -like, d -like, f -like, etc.). For this purpose, we use an intuitive approach [18] based on the Slater–Koster [19] technique and its generalization [20] to express crystal field or two-center integrals in terms of independent parameters in the tight-binding band theory [21]; then we apply standard series developments in terms of normal coordinates.

Consider a doublet of electronic orbitals (f_α, f_β) localized around some reference atom taken at origin. We assume that the environment potential felt by an electron in the reference atom is the sum of atomic-like spherically symmetric potentials $V_a(\mathbf{r} - \mathbf{R})$ centred at the other atomic positions $\mathbf{R}$, and we take as z -axis the interatomic axis of the linear molecule in the equilibrium configuration. We consider thus the matrix

$$M_{\alpha\beta} = \int f_\alpha^* V_a(\mathbf{r} - \mathbf{R}) f_\beta \, d\mathbf{r} \quad (1)$$

Here $\mathbf{R} = (q_x, q_y, q_0)$; α, β label the partner functions of the electron orbitals that can be chosen p -like (x, y), or d -like, ($xy, x^2 - y^2$), or f -like ($x^3 - 3xy^2, -y^3 + 3x^2y$) and so on. For simplicity, the distance q_0 of the atom under consideration from the origin is taken as unit, and the nuclear displacements q_x and q_y , perpendicular to the z -axis of the linear molecule, are assumed to be small quantities.

Let us start considering p -like electronic orbitals f_x, f_y taken in real form. The matrix elements (1) can be expressed in terms of independent parameters, following the techniques initiated by Slater and Koster [19]. We have

$$\begin{aligned} \int f_x^* V_a(\mathbf{r} - \mathbf{R}) f_x \, d\mathbf{r} &= l_x^2 [(pp\sigma, R) - (pp\pi, R)] + (pp\pi, R) \\ \int f_x^* V_a(\mathbf{r} - \mathbf{R}) f_y \, d\mathbf{r} &= l_x l_y [(pp\sigma, R) - (pp\pi, R)] \\ \int f_y^* V_a(\mathbf{r} - \mathbf{R}) f_y \, d\mathbf{r} &= l_y^2 [(pp\sigma, R) - (pp\pi, R)] + (pp\pi, R) \end{aligned}$$

where $(pp\sigma, R)$ and $(pp\pi, R)$ are the two independent integrals corresponding to orbitals oriented parallel or perpendicular to the inter-atomic vector $\mathbf{R}$, with director cosines l_x, l_y . Matrix (1) then becomes

$$M_p(\mathbf{R}) = [(pp\sigma, R) - (pp\pi, R)] \begin{pmatrix} l_x^2 & l_x l_y \\ l_x l_y & l_y^2 \end{pmatrix} + (pp\pi, R) \mathbf{I} \quad (2)$$

where $\mathbf{I}$ is the 2×2 unit matrix. The trace of the first matrix in the right-hand side of equation (2) is $l_x^2 + l_y^2$; to obtain a zero trace matrix we add and subtract $(1/2) \times (l_x^2 + l_y^2)$ (multiplied by the unit matrix) then:

$$M_p(\mathbf{R}) = A_p(R) \begin{pmatrix} l_x^2 - l_y^2 & 2l_x l_y \\ 2l_x l_y & -l_x^2 + l_y^2 \end{pmatrix} + B_p(R) \mathbf{I} \quad (3)$$

where

$$A_p(R) = \frac{1}{2} [(pp\sigma, R) - (pp\pi, R)], \quad B_p(R) = \frac{1}{2} [(pp\sigma, R) + (pp\pi, R)]$$

For small values of q_x, q_y we can consider the following series developments:

$$|R(q_x, q_y, 1)| = \sqrt{1 + q_x^2 + q_y^2} = 1 + \frac{1}{2}q^2 - \frac{1}{8}q^4 + \frac{1}{16}q^6 + \dots$$

$$l_x l_y = \frac{q_x q_y}{1 + q_x^2 + q_y^2} = q_x q_y (1 - q^2 + q^4 - q^6 + \dots)$$

$$A_p(R) = g_0 + g_2 q^2 + g_4 q^4 + \dots, \quad B_p(R) = f_0 + f_2 q^2 + f_4 q^4 + \dots$$

where $q^2 = q_x^2 + q_y^2$ and $g_0, g_2, \dots, f_0, f_2, \dots$ are quantities that depend on the particular molecule under consideration. Thus, matrix (3) takes the form

$$M_p(q_x, q_y) = (g_0 + g_2 q^2 + g_4 q^4 + \dots) \begin{pmatrix} q_x^2 - q_y^2 & 2q_x q_y \\ 2q_x q_y & -q_x^2 + q_y^2 \end{pmatrix} + f_0 + f_2 q^2 + \dots \quad (4)$$

Introducing the rotational angle φ such that $\tan \varphi = q_y / q_x$, matrix (4) becomes [22]

$$M_p(q, \varphi) = (g_0 + g_2 q^2 + \dots) \begin{pmatrix} q^2 \cos(2\varphi) & q^2 \sin(2\varphi) \\ q^2 \sin(2\varphi) & -q^2 \cos(2\varphi) \end{pmatrix} + f_0 + f_2 q^2 + \dots \quad (5)$$

Let us now consider an orbital doublet of d -like functions (always in real form) $f_{xy}, f_{x^2-y^2}$. We have

$$\begin{aligned} \int f_{xy}^* V_a(\mathbf{r} - \mathbf{R}) f_{xy} d\mathbf{r} &= l_x^2 l_y^2 [3(dd\sigma, R) - 4(dd\pi, R) + (dd\delta, R)] + (l_x^2 + l_y^2)(dd\pi, R) \\ \int f_{xy}^* V_a(\mathbf{r} - \mathbf{R}) f_{x^2-y^2} d\mathbf{r} &= \frac{1}{2} l_x l_y (l_x^2 - l_y^2) [3(dd\sigma, R) - 4(dd\pi, R) + (dd\delta, R)] \\ \int f_{x^2-y^2}^* V_a(\mathbf{r} - \mathbf{R}) f_{x^2-y^2} d\mathbf{r} &= \frac{1}{4} (l_x^2 - l_y^2)^2 [3(dd\sigma, R) - 4(dd\pi, R) \\ &\quad + (dd\delta, R)] + (l_x^2 + l_y^2)(dd\pi, R) \end{aligned}$$

After some manipulations similar to the previous case, the matrix becomes

$$M_d(\mathbf{R}) = A_d(R) \begin{pmatrix} (l_x^2 - l_y^2)^2 - 4l_x^2 l_y^2 & -4l_x l_y (l_x^2 - l_y^2) \\ -4l_x l_y (l_x^2 - l_y^2) & -(l_x^2 - l_y^2)^2 + 4l_x^2 l_y^2 \end{pmatrix} + B_d(R) \mathbf{I} \quad (6)$$

where

$$\begin{aligned} A_d(R) &= -\frac{1}{8} [3(dd\sigma, R) - 4(dd\pi, R) + (dd\delta, R)], \\ B_d(R) &= \frac{1}{8} [3(dd\sigma, R) + 4(dd\pi, R) + (dd\delta, R)] \end{aligned}$$

For small values of q_x, q_y through the same previous series developments we obtain:

$$M_d(q_x, q_y) = f_0 + f_2 q^2 + \dots + (g_0 + g_2 q^2 + \dots) \\ \times \begin{pmatrix} (q_x^2 - q_y^2)^2 - 4q_x^2 q_y^2 & -4q_x q_y (q_x^2 - q_y^2) \\ -4q_x q_y (q_x^2 - q_y^2) & -(q_x^2 - q_y^2)^2 + 4q_x^2 q_y^2 \end{pmatrix}$$

Then, in terms of the rotational angle φ , the interaction matrix takes the simple form:

$$M_d(q, \varphi) = (g_0 + g_2 q^2 + \dots) \begin{pmatrix} q^4 \cos(4\varphi) & -q^4 \sin(4\varphi) \\ q^4 \sin(4\varphi) & -q^4 \cos(4\varphi) \end{pmatrix} + f_0 + f_2 q^2 + \dots \quad (7)$$

For an orbital doublet of f -like functions we proceed in the same way, using the two-center integrals recently obtained by Doni [20]. Following the patterns previously traced, we arrive at:

$$M_f(\mathbf{R}) = A_f \begin{pmatrix} l_x^6 - l_y^6 + 15l_x^2 l_y^4 - 15l_x^4 l_y^2 & +6l_x l_y^5 - 20l_x^3 l_y^3 + 6l_x^5 l_y \\ 6l_x l_y^5 - 20l_x^3 l_y^3 + 6l_x^5 l_y & -(l_x^6 - l_y^6 + 15l_x^2 l_y^4 - 15l_x^4 l_y^2 - 15l_x^4 l_y^2) \end{pmatrix} + B_f \mathbf{I}$$

where

$$A_f(R) = \frac{1}{32} [10(\langle ff | \sigma, R \rangle - 15(\langle ff | \pi, R \rangle + 6(\langle ff | \delta, R \rangle - (\langle ff | \phi, R \rangle))]$$

$$B_f(R) = \frac{1}{32} [10(\langle ff | \sigma, R \rangle - 45(\langle ff | \pi, R \rangle + 6(\langle ff | \delta, R \rangle + (\langle ff | \phi, R \rangle))]$$

For small atom displacements, and in terms of the rotational angle φ , the Renner–Teller interaction matrix takes again a very simple and elegant form:

$$M_f(q, \varphi) = (g_0 + g_2 q^2 + \dots) \begin{pmatrix} q^6 \cos(6\varphi) & q^6 \sin(6\varphi) \\ q^6 \sin(6\varphi) & -q^6 \cos(6\varphi) \end{pmatrix} + f_0 + f_2 q^2 + \dots \quad (8)$$

Alternatively, the same interaction matrices form can be obtained exploiting the $C_{\infty v}$ (or $D_{\infty h}$) symmetry of the molecule, as described in Section 3. Of course, the main motivation of the present section is not the general structure of the interaction matrices, but rather the detailed information about the electron–phonon coupling parameters; this information is important in view of future *a priori* elaboration of the coupling constants, instead of their estimation on the basis of semi-empirical approaches.

3. RENNER–TELLER MATRICES BY SYMMETRY ONLY REQUIREMENTS

The symmetry group of a linear molecule of different atoms is $C_{\infty v}$. It is well-known that its irreducible representations are all two-dimensional except the two unidimensional ones that contain scalars and pseudo-scalars. The basis functions for each two-dimensional representations E_k are $\phi_{\pm k} = e^{\pm ik\varphi}$. The product of E_k and $E_{k'}$ is

$$E_k \times E_{k'} = E_{k+k'} + E_{|k-k'|};$$

and the symmetric part of an irreducible representation with itself is

$$[E_k \times E_k] = E_0 + E_{2k}$$

where E_0 is the totally symmetric irreducible representation.

The vibration coordinates of interest are displacements in the plane orthogonal to the symmetry axis so they transform to the irreducible representation E_1 . Later on, it will be useful to keep in mind these decompositions

$$[E_1]^2 = E_0 + E_2$$

$$[E_1]^3 = 2E_1 + E_3$$

$$[E_1]^4 = 2E_0 + 3E_2 + E_4$$

$$[E_1]^5 = 5E_1 + 4E_3 + E_5$$

$$[E_1]^6 = 5E_0 + 9E_2 + 5E_4 + E_6$$

as well as

$$[E_2 \times E_2] = E_0 + E_4, \quad [E_3 \times E_3] = E_0 + E_6$$

As usual the numerical factors denote how many irreducible representations of a given kind are present. It is well known from general theory on vibronic coupling (see, for instance, the Bersuker and Polinger book [8]) that only coordinates transforming as the symmetric part of the electronic irreducible representation Γ can be coupled. For p -like functions $\Gamma = E_1$, for d -like functions $\Gamma = E_2$ and so on. Thus for p -like functions the only vibrational combinations that can be coupled are of type E_2 and are coming from $[E_1]^2, [E_1]^4, \dots$, namely

$$q^2(e^{i2\varphi}, e^{-i2\varphi}), \quad q^4(e^{i4\varphi}, e^{-i4\varphi}), \dots \quad (9a)$$

while for d -like functions the vibrational combination are of type E_4 and are coming from $[E_1]^4, [E_1]^6, \dots$

$$q^4(e^{i4\varphi}, e^{-i4\varphi}), \quad q^6(e^{i6\varphi}, e^{-i6\varphi}), \dots \quad (9b)$$

The same procedure for f -like functions leads to

$$q^6(e^{i6\varphi}, e^{-i6\varphi}), \dots \quad (9c)$$

To obtain the form of the coupling matrices, consider the Taylor expansion of the potential¹

$$\Delta U = \sum_i \frac{\partial U}{\partial q_i} q_i + \frac{1}{2!} \sum_{i,j} \frac{\partial^2 U}{\partial q_i \partial q_j} q_i q_j + \frac{1}{3!} \sum_{i,j,l} \frac{\partial^3 U}{\partial q_i \partial q_j \partial q_l} q_i q_j q_l + \dots$$

for an out-of-axis small nuclear displacement and think about the relevant matrix elements $\langle \phi_{\pm k} | \Delta U | \phi_{\pm k} \rangle$ where $k = 1, 2, 3, \dots$, respectively, for p -like, d -like and f -like and so on. Here the matrix elements are taken, as in standard vibronic theory (see Ref. [8]), over the electronic coordinates only. It is easy to see that the operators $\{U_n \equiv \partial^n U / \partial q_{i_1} \dots \partial q_{i_n}\}$, acting on the electronic subspace, transform (reducibly) as $[E_1]^n$. Obviously linear combinations of them transforming irreducibly can be extracted according to the previous decompositions, as well as from the nuclear coordinates products $q_{i_1} \dots q_{i_n}$. For instance, we can rewrite the quadratic term as

$$\begin{aligned} \frac{1}{2!} \sum_{i,j} \frac{\partial^2 U}{\partial q_i \partial q_j} q_i q_j &= [U_2]_{E_0} (q_x^2 + q_y^2) + [U_2]_{E_2}^c (q_x^2 - q_y^2) + [U_2]_{E_2}^s (2q_x q_y) \\ &= [U_2]_{E_0} q^2 + [U_2]_{E_2}^+ q^2 e^{-2i\varphi} + [U_2]_{E_2}^- q^2 e^{2i\varphi} \end{aligned}$$

So matrix elements of $[U_2]_{E_2}^{\pm}$ can be worked quite easy observing that $[U_2]_{E_2}^{\pm}$ transform as $e^{\pm 2i\varphi}$. In fact using the well-known Wigner–Eckart theorem

$$\langle \phi_k | [U_2]_{E_2}^{\pm} | \phi_{k'} \rangle = W(E_k, E_2, E_{k'}) \langle \phi_k; \phi_{\pm 2} | \phi_{k'} \rangle$$

where $W(E_k, E_2, E_{k'})$ is the usual constant depending only on the irreducible representations but not on their functions, and the Clebsh–Gordan coefficient $\langle \phi_k; \phi_{\pm 2} | \phi_{k'} \rangle$ which is simply proportional to

$$\int_0^{2\pi} d\varphi e^{-ik\varphi} e^{\pm i2\varphi} e^{ik'\varphi} = \delta(-k \pm 2 + k')$$

Without going any further into technical details we report the final result for p -like functions

$$\begin{aligned} \left\langle \phi_{\pm 1} \left| \sum_{i,j} \frac{\partial^2 U}{\partial q_i \partial q_j} \right| \phi_{\pm 1} \right\rangle q_i q_j \\ = W(E_1, E_0, E_1) q^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + W(E_1, E_2, E_1) q^2 \begin{pmatrix} 0 & e^{-2i\varphi} \\ e^{2i\varphi} & 0 \end{pmatrix} \quad (10) \end{aligned}$$

A similar expression, with increasing powers of q , can be obtained for the higher-order derivatives as soon as their decomposition contains E_0 or E_2 and should be added to the total interaction. The form obtained in equation (10) obviously

¹As usual here we only assume that U belongs to the totally symmetric irreducible representation.

can be restated as in equation (5) using the p -like functions real form $\phi_x = (\phi_{+1} + \phi_{-1})/\sqrt{2}$ and $\phi_y = -i(\phi_{+1} - \phi_{-1})/\sqrt{2}$. If U is explicitly assumed as in Section 2, a simple inspection shows that $f_2 = W(E_1, E_0, E_1)$ and $g_0 = W(E_1, E_2, E_1)$. This approach can be applied to whatever electronic functions, d -like, f -like and so on, leading to results in perfect agreement with those obtained using the Slater–Koster approach outlined in Section 2. However, the formal procedure based only on symmetry considerations leads to more entangled information about the microscopic expressions of the coupling constants.

4. MODEL P -LIKE HAMILTONIAN AND CALCULATION PROCEDURE

We wish to introduce here a very reliable calculation procedure to determine the eigenstates of a general Renner–Teller problem. It is convenient to start writing the matrix representation of the Hamiltonian of a Renner–Teller system on two degenerate p -like electronic states f_x, f_y and with the interaction part in the form given in Section 2, neglecting at the moment the quartic or higher order terms:

$$H_{\text{RT},p} = \frac{1}{2} \hbar \omega (p_x^2 + p_y^2 + q_x^2 + q_y^2) \mathbf{I} + \frac{1}{2} g \hbar \omega \begin{pmatrix} q_x^2 - q_y^2 & 2q_x q_y \\ 2q_x q_y & -q_x^2 + q_y^2 \end{pmatrix} \quad (11)$$

where $p_x = -i\partial/\partial q_x$ and $p_y = -i\partial/\partial q_y$ denote the conjugated moment of the dimensionless normal symmetrized coordinates q_x and q_y , and g is the dimensionless quadratic coupling parameter, related to g_0 (equation (4)) by $\frac{1}{2} g \hbar \omega = g_0$. From now on, the quantum of energy $\hbar \omega$ is taken as the unit of energy.

The adiabatic potential energy surfaces (APES) can be easily calculated in a standard way and the explicit form of the two APES is

$$W_{\pm} = \frac{1}{2} (1 \pm g) q^2 \quad (12)$$

where $q^2 = q_x^2 + q_y^2$. These surfaces have an extremum at the point of degeneracy, with no instability for $g < 1$ and with instability for $g > 1$.

The continuous rotational symmetry shown by the APES is related to the constant of motion of the total angular momentum operator J_z

$$J_z = L_z + \sigma_y = (q_x p_y - q_y p_x) + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (13)$$

Circularly polarized linear combinations $f_{\pm} = (f_x \pm i f_y)/\sqrt{2}$, suggested by the APES continuous rotational symmetry, allow σ_y to be put in diagonal form.

Then introducing a similar transformation on the vibrational creation and annihilation operators $b_{\pm} = (a_x \mp i a_y)/\sqrt{2}$ we obtain a full diagonalization of L_z :

$$L_z = b_+^{\dagger} b_+ - b_-^{\dagger} b_-$$

After these transformations, the Renner–Teller Hamiltonian adopts the following simple and very convenient aspect

$$H_{\text{RT}} = (b_+^\dagger b_+ + b_-^\dagger b_- + 1) + \frac{1}{2}g \begin{pmatrix} 0 & (b_+ + b_-^\dagger)^2 \\ (b_+^\dagger + b_-)^2 & 0 \end{pmatrix} \quad (14)$$

Noticing that

$$b_- + b_+^\dagger = (a_x + a_x^\dagger + ia_y + ia_y^\dagger)/\sqrt{2} = q_x + iq_y \equiv q_+ = q e^{i\varphi}$$

we recover an expression of H_{RT} in agreement with equation (10).

We consider now the complete basis set of vibronic functions $|f_\pm; m, n\rangle$ obtained as the direct product of the electronic functions $|f_+\rangle$ and $|f_-\rangle$ by the phonons wave functions $|m, n\rangle$, where the integer numbers m and n (positive or zero) label the occupation numbers of the boson operators $b_+^\dagger b_+$ and $b_-^\dagger b_-$, respectively. The Renner–Teller Hamiltonian (14) when applied to any vibronic function $|f_\pm; m, n\rangle$ couples it with three states (at most); in fact it holds that:

$$\begin{aligned} H_{\text{RT}}|f_+; m, n\rangle &= (m + n + 1)|f_+; m, n\rangle + \frac{1}{2}g\sqrt{m(m-1)}|f_-; m-2, n\rangle \\ &+ \frac{1}{2}g\sqrt{(n+1)(n+2)}|f_-; m, n+2\rangle \\ &+ g\sqrt{m(n+1)}|f_-; m-1, n+1\rangle \end{aligned} \quad (15a)$$

$$\begin{aligned} H_{\text{RT}}|f_-; m, n\rangle &= (m + n + 1)|f_-; m, n\rangle + \frac{1}{2}g\sqrt{n(n-1)}|f_+; m, n-2\rangle \\ &+ \frac{1}{2}g\sqrt{(m+1)(m+2)}|f_+; m, n+2\rangle \\ &+ g\sqrt{n(m+1)}|f_+; m+1, n-1\rangle \end{aligned} \quad (15b)$$

Furthermore, for the angular momentum operator J_z , we have

$$J_z|f_\pm; m, n\rangle = (m - n \pm 1)|f_\pm; m, n\rangle \quad (16)$$

The above results indicate that the Renner–Teller Hamiltonian (14) can be mapped exactly into a set of independent double chains of interacting states, as shown in Fig. 1.

When the orbital functions are chosen as d -like or f -like, the axial symmetry of the molecule again leads to factorize the Renner–Teller Hamiltonian in a double chain. In effect the total angular momentum J_z remains a constant of motion and can be put in a diagonal form by means of the same type of canonical transformation, so we have

$$J_z|f_\pm; m, n\rangle = (m - n \pm 2)|f_\pm; m, n\rangle \quad (17)$$

for d -like orbital functions. For f -like functions the eigenvalues of J_z are $j = m - n \pm 3$. In other words, at fixed j only the states having $m - n = j \pm 2(m - n = j \pm 3)$ can interact among them.

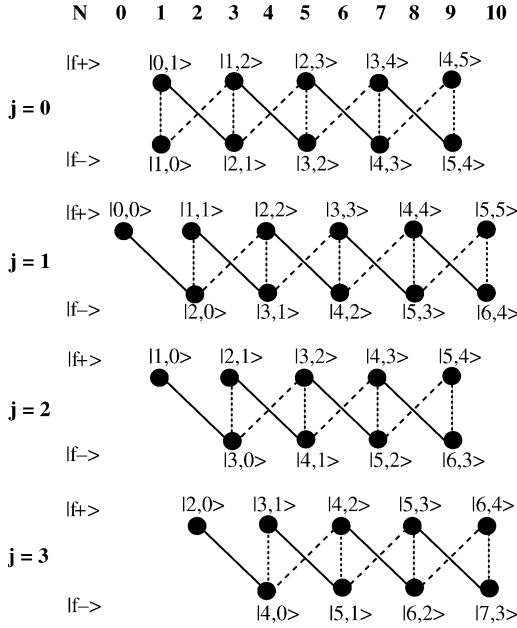


Fig. 1. Double interacting chains of orthonormal states, with definite values of j , representing the Renner–Teller system for orbital p -like functions. N represents the total number of phonons.

At this point all the vibronic eigenstates can be easily evaluated numerically by means of the recursion method or alternatively the renormalization method.

These are iterative procedures that allow the calculation of the Green's function matrix elements without explicit diagonalization of the Hamiltonian [18]. In the present case the Hamiltonian is factorized into double chains, and the renormalization method can be conveniently and efficiently applied, since its implementation simply requires the handling and the inversion of small matrices of rank two. For more details and elaboration of the renormalization procedures, see, for example, Ref. [23].

As an example for comparison with the results obtained in the literature with different procedures, we have calculated the vibronic levels of Renner–Teller systems with p -like orbital functions. Notice also that the chain with $j = 0$ has analytic solution [3,15] $2(n+1)\sqrt{I \pm \bar{g}}$, referred to levels A_1, A_2 , while the chains with j and $-j$ ($j \neq 0$) are degenerate. The vibronic levels are computed through the renormalization procedure, as a function of the quadratic coupling constant, with and without a diagonal quartic term. The stability of the results have been checked with a range of energies and strengths of the coupling considered, and a very large number of phonons (of the order of hundred or more) have been easily introduced to reach stable eigenvalues also near $g = 1$.

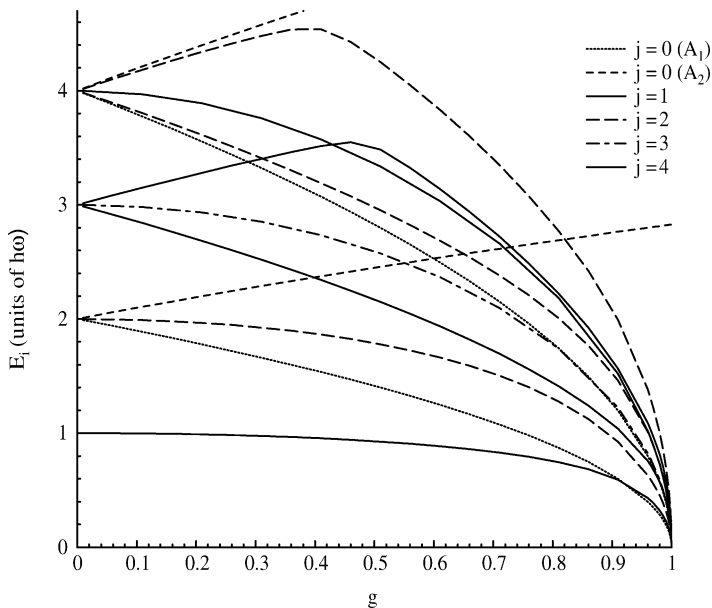


Fig. 2. Computed energy levels versus the quadratic coupling constant g , $0 < g < 1$ in the case of orbital p -like functions.

In Fig. 2 the computed vibronic energy levels are shown for $0 < g < 1$ and no quartic term. The overall results agree with those of Sakamoto [15], but for $g \approx 1$ we have some features that deserve closer discussion. As expected, when g is approaching one, most vibronic levels become soft and tend to vanish, as a consequence of the flattening of the lowest APES. Moreover, at about $g > 0.92$ the ground vibronic state ($j = 1$) crosses the $j = 0$ state, then it becomes non-degenerate, so indicating a change in the molecular configuration. In the limit $g \rightarrow 1$ the tunneling energy goes to zero, but it is always negative, in agreement with the analytic calculations [24] carried out decoupling the motion in the lower and upper APES.

It is worthwhile to remember that negative tunneling has been observed in different Jahn–Teller systems [16,25], and in particular in the $E \otimes \varepsilon$ Jahn–Teller system, where the ground vibronic state becomes not degenerate for small linear and large quadratic coupling constants. This change of symmetry has been also correlated to a change of the Berry phase [26] from π to zero. Notice that the negative tunneling energy of the Renner–Teller system for g near to one is possible because of the zero Berry phase of this system.

In Fig. 3, the computed vibronic energy levels are shown for $0 < g < 2$ including quartic terms in the Renner–Teller Hamiltonian of the type $f q^4$. Looking at Figs 2 and 3, we can see that for small g values (near $g = 0$) the behavior of the vibronic energy levels without and with quartic terms is similar. However, with increasing g , relevant

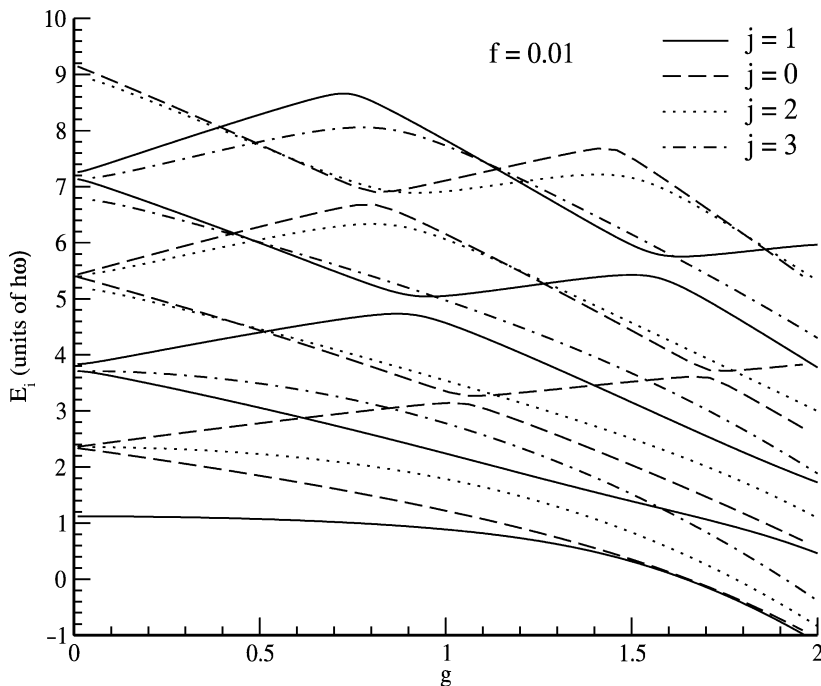


Fig. 3. Computed energy levels versus the quadratic coupling constant g ($0 < g < 2$) and with the quartic coupling constant $f = 0.01$. Orbital p -like functions are considered and only the first few levels for the j indicated are shown.

differences emerge due to the contribution of the quartic term, even if weak. In particular we notice the lack of the collapse of the energy levels at $g = 1$ and the disappearing of the crossing among the ground vibronic state and the first excited state.

5. CONCLUSIONS

The general form of the Renner–Teller electron–phonon interaction matrices has been obtained for different symmetries of the electronic orbital doublet exploiting the $C_{\infty v}$ symmetry of the molecule, and the coupling constant has been explicitly related to the Slater–Koster matrices of the two-center integrals. Moreover, the axial symmetry of the Renner–Teller systems, not violated even if orbital functions of different symmetry are considered, suggests proper canonical transformations that allow the mapping of the Renner–Teller Hamiltonian into a set of semi-infinite double chains. In this situation the recursion or the renormalization methods provide very efficient tools to determine with high precision the eigenstates of the problem for any orbital function symmetry and for whatever range of the coupling constants.

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This paper is intended as a homage to Professor Isaac B. Bersuker on the occasion of his 75th birthday. We feel very fortunate for having scientific and personal contacts with him.

REFERENCES

- [1] H. A. Jahn and E. Teller, *Proc. R. Soc. Lond., Ser. A*, 1937, **161**, 220.
- [2] Forward of E. Teller, in Proceedings of the XIV International Symposium on Electron–Phonon Dynamics and Jahn–Teller Effect (eds G. Bevilacqua, L. Martinelli and N. Terzi), World Scientific, Singapore, 1999.
- [3] R. Renner, *Z. Phys.*, 1934, **92**, 172.
- [4] H. C. Longuet-Higgins, *Adv. Spectrosc.*, 1961, **2**, 429.
- [5] G. Herzberg, *Electronic Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1966.
- [6] R. Englman, *The Jahn–Teller Effect in Molecules and Crystals*, Wiley, New York, 1972.
- [7] H. Köppel, W. Domcke and L. S. Cederbaum, *Adv. Chem. Phys.*, 1984, **57**, 59; H. Köppel, W. Domcke and L. S. Cederbaum, *J. Chem. Phys.*, 1984, **74**, 2945.
- [8] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, Berlin, 1989, and references quoted therein.
- [9] M. Perić, B. Engels and S. D. Peyerimhoff, in *Quantum Mechanical Electronic Calculations with Chemical Accuracy* (ed. S. R. Langhoff), Kluwer, Dordrecht, 1995, p. 261.
- [10] I. B. Bersuker, *Chem. Rev.*, 2001, **101**, 1067.
- [11] W. Moffit and A. D. Liehr, *Phys. Rev.*, 1957, **106**, 1195.
- [12] J. A. Pople, *Mol. Phys.*, 1960, **3**, 16.
- [13] M. Perić and S. D. Peyerimhoff, *Mol. Phys.*, 1983, **43**, 379.
- [14] M. Perić, S. D. Peyerimhoff and R. J. Buenker, *Chem. Phys. Lett.*, 1984, **105**, 44.
- [15] N. Sakamoto, *J. Phys. C: Solid State*, 1982, **15**, 6379.
- [16] H. Koizumi and I. B. Bersuker, *Phys. Rev. Lett.*, 1999, **83**, 3009; H. Koizumi, I. B. Bersuker, J. E. Boggs and V. Z. Polinger, *J. Chem. Phys.*, 2000, **112**, 8470.
- [17] G. Bevilacqua, L. Martinelli and G. Pastori Parravicini, *Phys. Rev. B*, 2001, **63**, 132403.
- [18] G. Grosso and G. Pastori Parravicini, *Solid State Physics*, Academic Press, London, 2000, p. 282.
- [19] J. C. Slater and G. F. Koster, *Phys. Rev.*, 1954, **94**, 1498.
- [20] E. Doni, Electrons and Photons in Solids, in *Collana Quaderni della Classe di Scienze della Scuola Normale Superiore* (eds G. Grosso, G. La Rocca and M. Tosi), Scuola Normale Superiore, Pisa, 2001, pp. 95–104.
- [21] F. Bassani and G. Pastori Parravicini, *Electronic States and Optical Transitions in Solids*, Pergamon Press, Oxford, 1975.
- [22] The structure of the interaction matrices has been provided also by R. Englman, private communication, R. Englman, A. Yahalom, *Adv. Chem. Phys.* 2002, **124**, 197.
- [23] R. Farchioni, G. Grosso and P. Vignolo, in *Organic Electronic Materials: Conjugated Polymers and Low Molecular Weight Organic Solids* (eds R. Farchioni and G. Grosso), Springer Series in Materials Science, Springer, Berlin, 2001, Vol. 41.
- [24] G. Bevilacqua, PhD Thesis. University of Pisa, 1999.
- [25] M. C. P. Moate, M. C. M. O’Brien, J. L. Dunn, C. A. Bates, Y. M. Liu and V. Z. Polinger, *Phys. Rev. Lett.*, 1996, **77**, 4362.
- [26] F. S. Ham, *Phys. Rev. Lett.*, 1987, **58**, 725. see also, F. S. Ham, *J. Phys.: Condens. Matter*, 1990, **2**, 1163.

Tunneling in Jahn–Teller Systems and Multidimensional WKB Approximation

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Abstract

We develop a general WKB approach to multidimensional tunneling in Jahn–Teller (JT) systems. To solve the path branching problem, we introduce the so-called *junction rule* for nodes in a multidimensional web of tunneling paths connecting equivalent wells. For any complex JT system, it provides enough equations to reduce the multidimensional tunneling to one-dimensional penetration through just one potential barrier. The junction rule is shown to include the symmetry properties of the ground-state wave function, same as the operator of symmetry projection. The tunneling splitting energy gap is shown to be proportional to probability flux through the bottle-neck point of the potential barrier, where it is highest. The order of energy levels in the ground-state tunneling multiplet is determined by the factor $\cos \varphi_B$, where φ_B is the corresponding Berry phase. Several examples of practical interest are considered in detail.

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1. INTRODUCTION

Originally, the Jahn–Teller (JT) theorem was formulated as a prediction of a symmetry break for any non-linear polyatomic molecule with an orbital degeneracy in its ground state. However, as we understand it now, the real meaning of the JT theorem is a non-zero slope of the adiabatic potential energy surface (APES) at the point of electron degeneracy. This does not necessarily result in a lowering of

symmetry. In all JT systems, on the lowest APES, there are several wells. The points of the bottom of the wells correspond to low-symmetry distorted nuclear configurations that are symmetry equivalent to one another. Correspondingly, there are several low-symmetry localized ground states, their number being equal to w , the number of wells. If potential barriers separating the wells are not infinitely large, the ground state of the system is determined by tunneling through the barriers from one well into another.

Due to the tunneling, the w -fold degeneracy of the ground state is partly or completely lifted. This is the so-called tunneling splitting of vibronic energy levels. The ground state electronvibrational (vibronic) wave function is a high-symmetry superposition of the low-symmetry states in the wells. Without a low-symmetry perturbation, due to tunneling, the average values of low-symmetry vibrational coordinates are all zero. In other words, due to tunneling, the nuclear frame of the JT system is not distorted, and its ground vibronic state remains degenerate. A lowering of symmetry may happen under a symmetry breaking perturbation if the latter is strong enough to destroy tunneling. Then nuclear motion becomes locked in one of the low-symmetry wells. Thus, tunneling restores the original high symmetry of the system. Therefore, the tunneling splitting in the lowest vibronic multiplet is one of the most important characteristics of a JT system.

A general explanation and quantitative evaluation of tunneling splitting in JT systems were given in Refs. [1–3] (for a detailed review of the problem, also, see Ref. [4]). In the most general approach developed by Bersuker [1,2,4], the tunneling splitting is obtained in a simple perturbation treatment of the w -fold degenerate ground state. The matrix elements of the corresponding secular equation are calculated with w ground states of harmonic approximation at the bottom of the potential wells of the APES. The splitting is proportional to overlap integrals between localized states in nearest-neighboring wells. The oscillator states are chosen in such a way as they include low-symmetry anisotropy of the wells. In this respect they are good in describing small oscillations of nuclei at the bottom of the wells. At the same time, the major contribution in the overlap results from tails of the ground states under potential barriers where the oscillator functions are not accurate enough. From this point of view, the harmonic approximation may be rather crude in evaluating the tunneling splitting energy gaps.

For many years, the perturbation treatment of Bersuker was sufficiently accurate. The situation was changed in 1996, when the phenomenon of a ground-state crossover was found in the icosahedral $H \otimes h$ case [5]. Its five-dimensional space of nuclear vibrations was shown to provide enough room for an alternative tunneling path with a reversed order of energy levels in the ground-state tunneling multiplet. However, to better understand conditions when this alternative dominates, we need a detailed examination of the possible tunneling paths on the lowest APES. To evaluate accurately the critical value of JT coupling constant for which the crossover takes place, we need a more accurate calculation of the tunneling splitting energy gaps. Both issues were solved recently in Ref. [6].

In most cases, such as chemical reactions, the dominant contribution in tunneling comes from penetration through just one potential barrier and tunneling along other classical paths can be neglected. In this respect the JT tunneling is essentially different. In each well, the classical path splits into several symmetry equivalent branches. However, the contribution to tunneling from none of these branches can be neglected. In the $E \otimes e$ case, an approximate separation of tunneling along the warped trough enables the problem to be reduced to a one-dimensional analysis [7]. Unfortunately, this is the only JT case with no branching. Next in the list is the cubic $T \otimes t_2$ case with four trigonal wells on the lowest APES. The four minimum points form a tetrahedron in the 3D space of the JT-active t_2 mode [4]. For a ground state localized in one of the four wells, there are three possible directions of tunneling into the other three wells through the corresponding potential barriers. Therefore, in each well the tunneling path splits into three branches. We come to a tetrahedron-like web of tunneling paths with four nodes. Evidently, the one-dimensional approximation cannot be used in a close vicinity of such a node. Branching of tunneling paths is a general property of most JT systems. In this respect, all other JT cases are similar to the cubic $T \otimes t_2$ case. In both, the cubic $T \otimes t_2$ [7,8] and the icosahedral $H \otimes h$ [6] cases, based upon the analogy with the simpler $E \otimes e$ case and using symmetry arguments, the branching was disregarded and the corresponding tunneling splitting energy gap was assumed to be proportional to a one-barrier tunneling integral. The path branching problem was held back to a later time.

The most appropriate formalism for the WKB approximation is the Feynman path integral formulation of quantum mechanics [9]. In this approach, the corresponding Green functions are evaluated by summing over all possible paths across the potential barriers between minimum points. The WKB approximation follows as the saddle-point asymptotic expansion applied to the corresponding path integral. A detailed solution to the multidimensional tunneling problem based on the Feynman formalism was developed in Refs. [10,11] where the so-called path decomposition expansion was introduced. Also, it is relevant to mention a more accurate tunneling calculation in a non-separable potential field in Ref. [12] and the perturbation theory approach for almost separable potentials developed in Ref. [13].

Unfortunately, the usual adiabatic separation of nuclear motion does not reduce the problem to one of the simple cases considered in Refs. [10,11] and the JT tunneling has an important distinction. The Born–Oppenheimer wave function is a product of an electron and a nuclear wave function. The former gains a phase factor, $\exp(i\varphi_B)$ with the so-called Berry phase φ_B , along a loop encircling the point of electron degeneracy [14,15]. To satisfy the condition of uniqueness of the product wave function, on the same loop the corresponding nuclear function must gain a factor of $\exp(-i\varphi_B)$. Without the Berry phase, a naive application of the path decomposition expansion developed in Refs. [10,11] results in a wrong order of tunneling energy levels and, correspondingly, wrong sign of the tunneling splitting energy gap. Evidently, the path decomposition expansion in its direct form presented in Refs. [10,11] does not apply to the phenomenon of crossover in the ground-state tunneling multiplet. Meanwhile, other examples of JT systems and

corresponding explanation of the similar type of crossover have since been given in Refs. [16–18]. In particular, for tunneling in the simpler $E \otimes e$ case with warping, Koizumi and Bersuker [16] introduced the idea of competing contribution of alternative paths with a reversed order of energy levels. With the alternative paths included, the issue of path branching becomes important in the $E \otimes e$ case as well. The corresponding tunneling splitting energy gap was evaluated in the WKB approximation [16] and, again, the path branching problem was put off until better days.

In this paper, we solve the problem of the branching of tunneling paths in JT systems and show the important implication of the Berry phase. In this respect we fill a gap in the general WKB approach to multidimensional tunneling. Compared to the path decomposition expansion developed in Refs. [10,11], we present a simpler way to evaluate tunneling splitting energy gaps in JT systems. First, in Section 2, we use the fact that in a JT system contributions to tunneling through different barriers are symmetry equivalent. We formulate some general properties of tunneling states in a JT system that follow from its high symmetry. In Section 3, using a simple example of two non-degenerate electronic states coupled to one mode, we demonstrate the importance of the phase factor due to the Born–Oppenheimer nature of the ground state. Also, in this section we show that the tunneling splitting energy gap is proportional to the probability flux through the bottle-neck point at which the potential barrier is highest. In Section 4, we consider the problem of branching and introduce the so-called *junction rule* that enables solution to this problem in a vicinity of branching regions of the classical paths. In Section 5, we show the way the *junction rule* operates in three dimensions in a cubic JT system with $T \otimes t_2$ coupling. We use this example to show that the tunneling splitting energy gap is proportional to $\cos \varphi_B$, where φ_B is the Berry phase. In Section 6, in view of the general approach developed in the previous sections, we revisit the crossover problem for the icosahedral quintet, the $H \otimes h$ case, and provide the results reported in Ref. [6] with a solid background. Finally, in Section 7, we formulate some general conclusions. In the same section, we suggest a simple shortcut to obtain correct WKB expressions for tunneling splitting energy gaps for any JT case.

2. SYMMETRY PROPERTIES OF TUNNELING STATES IN JAHN-TELLER SYSTEMS

Some general properties of the tunneling multiplet in a JT system result from symmetry arguments only. In the first part of this section, up to equation (3), we follow the ideas introduced in the theory of JT effect by Dagis and Levinson [19], Martinenas and Dagis [20], and by Ceulemans [21]. Let $\mathbf{G}$ be the reference symmetry group of a polyatomic system with no vibronic coupling. The Hamiltonian of JT coupling, H_{JT} , is a scalar of this group. In other words, H_{JT} transforms into itself under operations of the reference symmetry group $\mathbf{G}$. According to the JT theorem, due to the presence of linear vibronic coupling terms

in H_{JT} , the high-symmetry point is not a minimum of the APES. Instead, several low-symmetry wells are present on the lowest sheet of the APES. Let $\mathbf{L}$ be the corresponding low symmetry group of the system at the bottom of the wells. It is referred to as the stabilizer of the critical point [21]. For example, for a cubic system, the reference symmetry group can be O_h . For an electron T_{1u} term, due to its linear coupling to trigonal modes, there are four trigonal wells on the lowest sheet of the APES. The local group at the bottom of a trigonal well is D_{3d} . Therefore, in this example the reference symmetry group, $\mathbf{G} = O_h$, is lowered to $\mathbf{L} = D_{3d}$.

Consider those symmetry operations of the reference symmetry group $\mathbf{G}$ that transform the i th minimum point into itself. For the corresponding distorted nuclear configuration, they act as the identity element and form invariant subgroups $\mathbf{L}_i$ of $\mathbf{G}$, where $i = 1, 2, \dots, w$, is the number of the well. For simplicity, in what follows we neglect spin degeneracy and consider orbital degeneracy only. The ground-state wave function $\Psi_i(r, Q)$ localized in the i th well transforms as one of the (orbital) singlet representations, Γ_L , of the group $\mathbf{L}_i$. Otherwise, if Γ_L is not a singlet representation, then, according to the JT theorem, Q_i is not a minimum of the APES.

For simplicity, neglect the overlap of the wave functions localized in different wells. Then, for an arbitrary element G of the reference group $\mathbf{G}$, we have $\langle \Psi_i | G | \Psi_i \rangle \neq 0$, if G transforms the well i into itself and $\langle \Psi_i | G | \Psi_i \rangle = 0$, if G transforms the well i into any other well. The latter two equations can be combined to $\langle \Psi_i | G | \Psi_i \rangle = \chi_L(G) \delta(i, Gi)$, where $\chi_L(G)$ is the character of the non-degenerate irreducible representation Γ_L of the local group $\mathbf{L}_i$ and $\delta(i, Gi)$ is Kronecker's delta. Here we used the fact that all the local symmetry groups $\mathbf{L}_i$ of different wells are isomorphous with one another. Therefore, $\chi_L(G)$ is the same for different i . Then the number of times, $n(\Gamma)$, a given irreducible representation Γ of $\mathbf{G}$ occurs in the reducible representation of the w ground-state functions Ψ_i is given by [4]:

$$n(\Gamma) = \frac{1}{l} \sum_{\mathbf{L}} \chi_L(G) \chi_{\Gamma}^*(G) \quad (1)$$

For all subgroups of all point groups, the sum (1) has been evaluated already. The corresponding correlation tables can be found in different group-theoretical books (e.g. see Refs. [22,23]). For example, in the cubic $T \otimes t_2$ case, the wells have trigonal symmetry. If, as in the above example, the reference group is O_h , then at the bottom of a trigonal well the local symmetry is D_{3d} . Thus, if the electronic triplet is T_{1u} of O_h , then lowering the symmetry to D_{3d} splits T_{1u} into $A_{2u} + E_u$ of the trigonal group D_{3d} . According to the JT theorem, the electronic singlet A_{2u} must be the ground term. Therefore, in this case $\Gamma_L = A_{2u}$ of D_{3d} . The reducible representation realized by the four ground states localized in trigonal wells is fourfold degenerate. Tunneling lifts this accidental degeneracy. According to the equation (1), in order to find tunneling components of the fourfold degenerate multiplet, we need to find which irreducible representations of the group O_h include A_{2u} of D_{3d} . From the correlation tables in

Ref. [23], one can see that these are A_{2u} and T_{1u} of O_h . Each includes A_{2u} of D_{3d} just once. The 4-fold tunneling multiplet splits into $A_{2u} + T_{1u}$ of O_h .

To find the symmetry-adapted combinations $\Psi_{\Gamma\gamma}$ that represent the tunneling multiplet, we can apply symmetry projection:

$$\Psi_{\Gamma\gamma} = \frac{[\Gamma]}{g} \sum_{k=1}^g \Gamma_{\gamma\bar{\gamma}}^*(G_k) G_k \Psi_1 \quad (2)$$

where Ψ_1 is one of the ground-state localized wave functions, the index $k = 1, 2, \dots, g$ labels different elements of the reference group $\mathbf{G}$, $\Gamma_{\gamma\bar{\gamma}}(G)$ is $\gamma\bar{\gamma}$ th matrix element of irreducible representation Γ of the symmetry element G , and $[\Gamma]$ is dimension of Γ . In what follows in this paper we assume that the ground state in a well is normalized, $\langle \Psi_1 | \Psi_1 \rangle = 1$. Also, we use the ground-state energy in a well, $E_0 = \langle \Psi_1 | H | \Psi_1 \rangle = H_{11}$, as the reference level for energy. Therefore, everywhere in this paper we assume $E_0 = \langle \Psi_1 | H | \Psi_1 \rangle = H_{11} = 0$. Neglecting overlap integrals $\langle \Psi_i | \Psi_j \rangle$ compared to $\langle \Psi_1 | \Psi_1 \rangle = 1$, in the first-order perturbation theory, the corresponding energy can be expressed as:

$$E_{\Gamma} = \frac{\langle \Psi_{\Gamma\gamma} | H | \Psi_{\Gamma\gamma} \rangle}{\langle \Psi_{\Gamma\gamma} | \Psi_{\Gamma\gamma} \rangle} = \frac{1}{w} \sum_{i,j} \Gamma_{\gamma\bar{\gamma}}(G_j) \Gamma_{\gamma\bar{\gamma}}^*(G_i) \langle \Psi_1 | G_j^{-1} H G_i | \Psi_1 \rangle \quad (3)$$

where w is the number of equivalent wells.

The summation over i and j in equation (4) can be performed in two steps. First, we can run the sum over the elements of the local group $\mathbf{L}$. Then we can sum over the non-trivial elements, the ones that transform the wells into one another. They form the factor-group, $\mathbf{F} = \mathbf{G}/\mathbf{L}$, its order being w . The reference group is a product, $\mathbf{G} = \mathbf{F} \times \mathbf{L}$. Its elements can be presented as corresponding products of the elements of $\mathbf{F}$ and $\mathbf{L}$: $G = F_i L_j$, with $i = 1, 2, 3, \dots, w$, and $j = 1, 2, 3, \dots, g/w$. Evidently, elements of the local group do not change the corresponding matrix elements and overlap integrals in equation (3). They result in appearance of the common factor l , the number of elements in $\mathbf{L}$, in the numerator and denominator in equation (3) that can be reduced. The only non-trivial contribution in equation (3) comes from the elements F_i of the factor group $\mathbf{F}$.

The off-diagonal matrix elements, $H_{ij} = \langle \Psi_1 | F_i^{-1} H F_j | \Psi_1 \rangle = \langle \Psi_i | H | \Psi_j \rangle$, in the numerator can be visualized as ‘chemical bonds’ of a given ‘atom’ with all other ones in a set of w identical ‘atoms’ in a polyatomic ‘molecule’ with the symmetry $\mathbf{F}$. One can distinguish the following two cases. The ‘molecule’ can have just one transitive set of interatomic distances or more than one set. In the former case, all interatomic distances are equal to one another and, correspondingly, the off-diagonal matrix elements, H_{ij} , $i \neq j$, all are equal to one another, all $H_{ij} = H_{12}$. For example, if the reference group is T_d , then at the bottom of a trigonal well the local symmetry is C_{3v} . Then the factor group is $T_d/C_{3v} = D_2$. The simplest molecule with all the symmetry elements of the group D_2 has four identical atoms and is a regular tetrahedron. Its interatomic distances equal one another. Therefore, the four off-diagonal matrix elements are all equal to one another, $H_{23} = H_{34} = H_{13} = H_{12}$.

Alternatively, the ‘molecule’ may have several transitive sets of interatomic distances. Correspondingly, in this case there are several different off-diagonal matrix elements, H_{1r} , with $r = 1, 2, \dots, N_s$, where N_s is the number of different sets in the ‘molecule’ with the symmetry $\mathbf{F}$. For example, in the icosahedral case $H \otimes h$ with 10 trigonal wells, the reference symmetry group is I_h . The local symmetry in a trigonal well is D_{3d} . The corresponding factor group is $I_h/D_{3d} = D_5$. The simplest molecule with all symmetry elements of D_5 is a regular pentagon. It has two different interatomic distances, one separates nearest neighbors, the other one is between a vertex and its second neighbor. In this case there are two different off-diagonal matrix elements, H_{1a} and H_{1b} .

With these relationships for off-diagonal matrix elements, equation (3) can be written in the following general form:

$$E_\Gamma = \sum_r m_r(\Gamma) H_{1r} \quad (4)$$

The sum in equation (4) runs over different transitive sets in the ‘molecule’ with the symmetry $\mathbf{F}$, and $m_r(\Gamma)$ are the corresponding weight factors. It follows from equation (4) that the tunneling splitting energy gaps are all proportional to the corresponding tunneling rate factors,¹

$$\Gamma_r = |H_{1r}| \quad (5)$$

The rate factors Γ_r interrelate just two wells, the well 1 and the well r . For just one barrier separating the two wells, the classical path under the barrier does not split into branches. The classical path in the restricted area is approximately separable (see Section 5 later). Therefore, in JT systems, after the weight factors $m_r(\Gamma)$ are established, the multidimensional tunneling problem reduces to a one-dimensional consideration.

In the above example of the icosahedral $H \otimes h$ case with 10 trigonal wells, the accidental 10-fold degeneracy of the ground multiplet, $A + H + G$, is lifted by tunneling, and the corresponding energies for the terms A , G , and H are [5]

$$E_A = 6H_{1a} + 3H_{1b}, \quad E_G = H_{1a} - 2H_{1b}, \quad E_H = -2H_{1a} + H_{1b} \quad (6)$$

Therefore, in this case the weight factors are $m_a(A) = 6$, $m_b(A) = 3$, $m_a(G) = 1$, $m_b(G) = -2$, $m_a(H) = -2$, and $m_b(H) = 1$. A general expression for the weight factors $m_r(\Gamma)$ and their numerical values can be obtained for all JT cases. However, its derivation is beyond the purpose of the present work, and we omit it here.

Except for first-order perturbation theory, we did not use any approximation in obtaining equations (4) and (5). These results are based upon the assumption that the vibronic coupling part of the Hamiltonian, H_{JT} , has the same high symmetry as

¹Although the traditional notation Γ for tunnelling rate factors is somewhat confusing (it coincides with Γ for irreducible representations), we keep it here. It originates from spectroscopy where Γ is the half-width of the corresponding spectral line associated with a local energy level in a well when the corresponding localized state dissipates into a continuous spectrum.

the zero-coupling Hamiltonian. The only approximation behind equations (4) and (5) is the reasonable assumption that the overlap integrals S_{ij} are small compared to 1. It applies to strong coupling and, as follows from numerical evaluation of tunnelling splitting energy gaps, it extends up to intermediate values of vibronic coupling parameters (see Section 5 later). Therefore, the results expressed by equations (4) and (5) are asymptotically accurate.

Additionally, all the results of the present section apply to a pseudo-JT effect [4, 24] with no change. For example, in cubic perovskites, internal hindered rotation of an off-center ion about the on-center high-symmetry point is described in terms of the well-known Devonshire model [25]. It assumes the existence of several off-center wells on the lowest APES. If in the high-symmetry (on-center) point, the ground state is an orbital singlet, the low-symmetry (off-center) wells on the lowest APES are due to the pseudo-JT admixture of an excited electronic term of the corresponding symmetry [4,26]. The tunneling multiplet satisfies the symmetry conditions of the present section, and the corresponding energy gaps are described by equation (4).

3. TUNNELING SPLITTING IN A TWO-LEVEL SYSTEM WITH PSEUDO-JAHN–TELLER COUPLING

First, we consider a system with inversion symmetry and a pseudo-JT coupling for its two opposite-parity non-degenerate electronic states separated by an energy gap $2\Delta\hbar\omega$ (Δ is the corresponding dimensionless parameter of the gap) and mixed by a non-degenerate odd mode. For certainty, we assume that positive Δ corresponds to lower energy of the even state. The simplest example of such a system is a linear triatomic molecule AB_2 with the atom A at the midpoint between the other two atoms [24]. An off-center displacement Q of the central atom A along the B–B axis, accompanied with the opposite displacement of the two atoms B, has odd parity and mixes the two electronic states. The JT Hamiltonian of the system with linear vibronic coupling can be written as:

$$H_{JT} = \hbar\omega \left\{ \frac{1}{2} Q^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \Delta \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + kQ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right\} \quad (7)$$

where Q is the dimensionless coordinate of the odd mode active in this vibronic coupling, ω is its frequency, and k is the dimensionless constant of linear coupling. The two eigenvectors of equation (7) are

$$\begin{aligned} \psi_+(\Omega) &= \frac{1}{\sqrt{2}} \begin{pmatrix} \cos(\theta/2) \\ \sin(\theta/2) \end{pmatrix}, & \psi_-(\Omega) &= \frac{1}{\sqrt{2}} \begin{pmatrix} -\sin(\theta/2) \\ \cos(\theta/2) \end{pmatrix}, \\ \tan(\theta) &= \frac{kQ}{\Delta} \end{aligned} \quad (8)$$

In this case, the corresponding APES is a two-valued function of Q expressed by the two eigenvalues of the 2×2 matrix Hamiltonian (7),

$$U_{\pm}(Q) = \hbar\omega \left\{ \frac{1}{2}Q^2 \pm \sqrt{\Delta^2 + k^2 Q^2} \right\} \quad (9)$$

Both have an extremum at $Q = 0$. For the upper curve, $U_+(Q)$, this point is a minimum at any value of k . The curvature of the lower curve, $U_-(Q)$, depends on the relative value of the parameters k and Δ . At weak coupling, when $k^2 < \Delta$, the curvature of $U_-(Q)$ at $Q = 0$ is positive, and this point is a minimum. In the opposite case of strong coupling, when $k^2 > \Delta$, the curvature is negative at $Q = 0$, and this point is a maximum of $U_-(Q)$. If $k^2 \rightarrow \Delta$, the two minimum points approach one another and, at $k^2 = \Delta$, they coalesce into one minimum at $Q = 0$. The symmetric double-well potential curve expressed by $U_-(Q)$ in equation (9) is shown in Fig. 1. Most important, the shape of $U_-(Q)$ is determined by one parameter, k^2/Δ . The factor $\hbar\omega$ in equation (9) is just a scaling coefficient.

Let Ψ_1 be the vibronic ground state localized in the left well of the double-well potential, and Ψ_2 be the right-side ground state. The reference symmetry group of the undistorted molecule AB_2 is $D_{\infty h}$. An off-center displacement of the central atom A along the axis B–B reduces this symmetry to $C_{\infty v}$. This means that the local symmetry group L in the wells is $C_{\infty v}$. The ground-state wave functions Ψ_1 and Ψ_2 transform as the totally symmetric representation Σ^+ of the group $C_{\infty v}$. According to equation (1), the twofold degenerate reducible representation of $D_{\infty h}$ realized by Ψ_1 and Ψ_2 splits into representations $\Sigma_g^+ + \Sigma_u^+$ of $D_{\infty h}$. Then, according to equation (2), the symmetry-adapted combinations are:

$$\Psi_g = \frac{1}{\sqrt{2}}(\Psi_1 + \Psi_2), \quad \Psi_u = \frac{1}{\sqrt{2}}(\Psi_1 - \Psi_2) \quad (10)$$

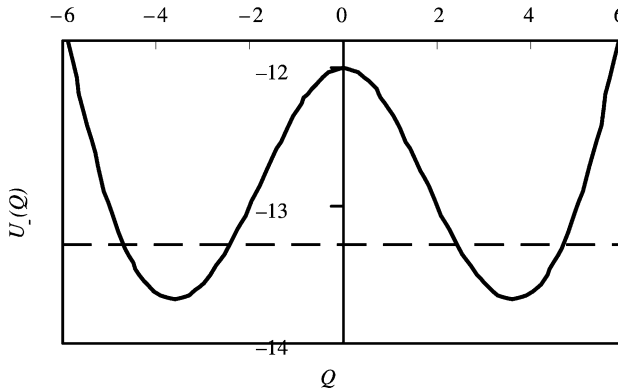


Fig. 1. Symmetric double-well potential $U_-(Q)$ for a pseudo-JT molecule with two non-degenerate electronic terms coupled to one low-symmetry mode [equation (9)]. The curve corresponds to strong coupling case with $k = 4$ and a relatively large energy gap, $\Delta = 12$ (both in units of $\hbar\omega$). The dashed line represents the twofold degenerate ground-state energy level subject to a tunneling splitting.

Neglecting the overlap integral S_{12} as compared to $\langle \Psi_1 | \Psi_1 \rangle = \langle \Psi_2 | \Psi_2 \rangle = 1$, and assuming that $H_{11} = E_0 = 0$, the corresponding first-order energy is

$$E_g = \frac{\langle \Psi_g | H | \Psi_g \rangle}{\langle \Psi_g | \Psi_g \rangle} = H_{12}, \quad E_u = \frac{\langle \Psi_u | H | \Psi_u \rangle}{\langle \Psi_u | \Psi_u \rangle} = -H_{12} \quad (11)$$

Correspondingly, the tunneling splitting energy gap:

$$\delta = E_u - E_g = -2H_{12} \quad (12)$$

As pointed above, for strong coupling, the result (12) is asymptotically accurate. In obtaining equation (11), the only approximation involved is perturbation theory. It assumes smallness of the overlap integral S_{12} . The stronger the vibronic coupling, the smaller is S_{12} and, correspondingly, the better is equation (12) in describing the gap.

Up to this point, the non-adiabatic mixing of the two electronic states is included. For an accurate evaluation of the matrix element H_{12} and the overlap integral S_{12} , we need accurate expressions for the ground-state wave functions in the wells, Ψ_1 and Ψ_2 . Strictly speaking, in this case the corresponding Schrödinger equation is a coupled system of differential equations, and the problem remains very complex. In order to simplify it, we can apply the adiabatic approximation. Slow motion of nuclei can be separated from the fast motion of electrons if the value of 2Δ (the energy gap separating the two electronic terms in terms of $\hbar\omega$) is big enough, $2\Delta \gg 1$. Obviously, among different possibilities, the case of strong vibronic coupling, $k^2 > \Delta$, combined with a large energy gap, $2\Delta \gg 1$, providing adiabatic separability of the lowest electronic state, presents a special interest. Easy to see that the above system of inequalities is consistent with the condition of existence of one or more localized states in the wells.

In the adiabatic approximation, the ground-state wave functions in the wells, Ψ_1 and Ψ_2 , can be written as Born–Oppenheimer products, $\Psi_1(r, Q) = \psi_-(r, Q)\Phi_1(Q)$, $\Psi_2(r, Q) = \psi_-(r, Q)\Phi_2(Q)$, where $\psi_-(r, Q)$ is the lower-sheet eigenfunction of the JT Hamiltonian (7), and $\Phi_1(Q)$ and $\Phi_2(Q)$ are the ground-state wave functions of nuclear motion in the left and right wells, respectively. The double-well potential (10) is a scalar of inversion, $Q \rightarrow -Q$. Operator of inversion, I , transforms the vibrational wave function in the left well into the right-well function, $\Phi_1(-Q) = \Phi_2(Q)$, so $\Psi_2 = I\Psi_1$. Therefore, instead of the two functions we can discuss just one, $\Phi_2(Q) = \Phi_0(Q)$ and $\Phi_1(Q) = \Phi_0(-Q)$.

In finding the tunneling splitting energy gap, we follow the remarkable approach of Landau and Lifshits [27]. Let E_0 be the ground-state energy in one well. This means that in the right half of the vibrational space, $Q > 0$, E_0 is the lowest eigenvalue of the vibronic Hamiltonian,

$$H = -\frac{1}{2} \frac{d^2}{dQ^2} + H_{JT}$$

with H_{JT} determined in equation (8). At the same time, E_g is the lowest eigenvalue of

H in all the region, $-\infty < Q < \infty$. The corresponding Schrödinger equations are

$$\frac{d^2 \Psi_2}{dQ^2} + 2(E_0 - H_{JT})\Psi_2 = 0, \quad \frac{d^2 \Psi_g}{dQ^2} + 2(E_g - H_{JT})\Psi_g = 0 \quad (13)$$

Multiply the first of the above equations from the left by Ψ_g^+ and the second one by Ψ_2^+ , integrate over the electron coordinates (we mean the corresponding matrix multiplication), and over the vibrational coordinate from $Q = 0$ to $Q = \infty$. Then subtract the two equations from one another. This gives

$$2(E_0 - E_g)\langle \Psi_g | \Psi_2 \rangle = \langle \Psi_2 | \Psi_g'' \rangle - \langle \Psi_g | \Psi_2'' \rangle \quad (14)$$

Neglecting the overlap integral $\langle \Psi_1 | \Psi_2 \rangle$ compared to $\langle \Psi_2 | \Psi_2 \rangle = 1$, we can simplify the left side of the above equation. It becomes $(E_0 - E_g)\sqrt{2}$. Using the equation $\Psi_2 = I\Psi_1$ and integrating by parts in the right side, we transform it into

$$\langle \Psi_g | \Psi_2'' \rangle - \langle \Psi_2 | \Psi_g'' \rangle = \frac{1}{\sqrt{2}} \langle \psi_-(0) | I | \psi_-(0) \rangle [\Phi_2(0)\Phi_1'(0) - \Phi_1(0)\Phi_2'(0)],$$

where I is the operator of inversion, and we neglect the terms with $\Phi_1(\infty)$ and $\Phi_2(\infty)$. Due to the inversion symmetry of the wells, $\Phi_1(0) = \Phi_2(0) = \Phi_0(0)$ and $\Phi_2'(0) = -\Phi_1'(0) = \Phi_0'(0)$. Assuming $E_0 = 0$ and combining altogether,

$$E_g = -\langle \psi_-(0) | I | \psi_-(0) \rangle \Phi_0(0)\Phi_0'(0) \quad (15)$$

Similarly, for E_u we find

$$E_u = \langle \psi_-(0) | I | \psi_-(0) \rangle \Phi_0(0)\Phi_0'(0) \quad (16)$$

Finally, subtracting equations (16) and (17), we find the tunneling splitting energy gap,

$$\delta = E_u - E_g = 2\langle \psi_-(0) | I | \psi_-(0) \rangle \Phi_0(0)\Phi_0'(0) \quad (17)$$

This expression resembles the classical result of Landau and Lifshits [27]. The new element here, specific for the JT case, is the factor $\langle \psi_-(0) | I | \psi_-(0) \rangle = \langle \psi_-(0_-) | \psi_-(0_+) \rangle = |\Delta|/\Delta = \text{sign}(\Delta)$, the electron overlap integral. It is due to the Born–Oppenheimer nature of the ground state. It includes the phase gained by the electronic wave function when the particle moves from the well 1 into the well 2. The result (17) has a clear physical meaning. The factor $\Phi_0(0)\Phi_0'(0)$ is proportional to the probability flux at the bottle-neck point for tunneling, $Q = 0$, where the barrier is the highest. The derivative, $\Phi_0'(0)$, is the slope of the right-well state at $Q = 0$ and is positive. Hence, for positive Δ , the energy gap δ in equation (17) is positive. The ground vibronic state has even parity, same as the ground electron state. If Δ is negative, the overlap integral, $\langle \psi_-(0) | I | \psi_-(0) \rangle = \langle \psi_-(0_-) | \psi_-(0_+) \rangle = \text{sign}(\Delta)$, changes to opposite, and the tunneling energy gap δ in equation (17) becomes negative. The vibronic energy levels flip. Thus, the order of vibronic energy levels in the ground-state tunneling multiplet reproduces the order of the original electronic terms. Comparing equation (17) with

equation (12), we can conclude that

$$H_{12} = -\langle \psi_-(0) | I | \psi_-(0) \rangle \Phi_0(0) \Phi_0'(0) \quad (18)$$

where $\langle \psi_-(0) | I | \psi_-(0) \rangle = \langle \psi_-(0_-) | \psi_-(0_+) \rangle$ is the electron overlap integral, $Q = 0$ corresponds to the top point of the potential barrier, and $\Phi_0(Q)$ is the ground-state vibrational wave function to the right from the point $Q = 0$. Equation (18) can be obtained directly by presenting the matrix element H_{12} as a sum of two equal contributions, from the left side, $-\infty < Q < 0$, and the right side, $0 < Q < \infty$, and integrating the kinetic energy term by parts [27]. Equation (18) is quite general and applies to all JT cases.

4. THE JUNCTION RULE FOR PROBABILITY FLUX

So far, we did not apply the WKB approximation yet. The assumptions on which the above results are based, the strong vibronic coupling, $k^2 > \Delta$, and large energy gap in the electron spectrum, $\Delta \gg 1$, are typical for all tunneling problems in JT systems. If, as in the early papers of Bersuker [1,2], we substitute the oscillator ground-state wave functions in equation (17), then we come to the approximate results that can be obtained directly from the matrix element (12) with the oscillator functions.

The WKB approximation was applied to the symmetric double-well potential so many times that it makes it difficult to provide a comprehensive list of references. In the context of the present paper, the most important references are the famous text of Landau and Lifshits [27], where tunneling in a symmetric double-well is given as a sample problem, and the paper of Auerbach and Kivelson [11] where the symmetric double-well potential is considered as one of the model cases.

Although the shortest way to the tunneling gap δ is the solution of Landau and Lifshits [27], here we consider the problem from a different perspective. Like in the theory of electric circuits, instead of a detailed consideration of each particle, one can apply some simple rules that provide enough equations to solve the problem. One is the *junction rule*. It is based upon the probability conservation law for a stationary state, $\Psi(Q, t)$. At any point Q in the domain of $\Psi(Q, t)$, the probability density, $|\Psi(Q, t)|^2$ remains constant, $d|\Psi(Q, t)|^2/dt = 0$. Consider the part of a vibronic state that is located in a potential well. In this region, the probability density, $|\Psi(Q, t)|^2$, looks like an octopus with its tentacles extended into the restricted areas under the barriers.² If we construct a closed surface S around the body of the ‘octopus’, then, due to conservation of probability density, the total flux of probability through the surface S must be equal to zero,

$$\oint_S \mathbf{j} \cdot d\mathbf{A} = 0 \quad (19)$$

² This parallel belongs to M. C. M. O’Brien [28].

where $\mathbf{j}$ is density of the probability flux, and $d\mathbf{A}$ is an infinitesimal element of area of the surface S . The advantage of the JT case is that under the barriers, the ‘tentacles’ are thin and symmetry equivalent. Therefore, we can consider thin flux tubes around the ‘tentacles’ of equal cross-sectional area Σ and, in a good approximation, neglect the probability flux through the rest of the surface S . Then equation (19) can be presented in the following simplified form:

$$j_1 \Sigma + j_2 \Sigma + j_3 \Sigma + \cdots + j_n \Sigma = 0$$

where n is the number of equivalent barriers around a particular potential well under consideration. After reducing the equation by the common factor Σ , it transforms into the following *junction rule*: For any node of tunneling paths, the total flux of probability entering the junction must be equal to the total flux of probability leaving the junction,

$$j_1 + j_2 + \cdots + j_n = 0 \quad (20)$$

Here we conventionally assume that the flux entering the junction is positive, whereas the terms that describe the leaving part are taken negative. The advantage of the junction rule is that it allows to avoid the detailed consideration of system’s dynamics inside the junction (inside the body of the ‘octopus’) and provides the results of tunneling through the tentacles.

To show how the junction rule works, consider the above example of tunneling in the double-well potential. In this case we have two nodes connected by just one tunneling path. Let the starting position of the system be in the left well with the ground-state wave function $\Psi_1 = C_1 \psi_1(r) \Phi_1(Q)$. Here both $\psi_1(r)$ and $\Phi_1(Q)$ are assumed to be normalized, and C_1 is the amplitude in the left well, so that $|C_1|^2$ is the probability to find the system in this well. The corresponding tail of the WKB ground-state wave function under the barrier should decrease with Q exponentially,

$$\Phi_1(Q) = \sqrt{\frac{\omega}{2\pi|P|}} \exp\left(-\int_b^Q |P(q)| dq\right), \quad b < Q < c \quad (21)$$

Here $P(Q) = \sqrt{2[E_0 - U_-(Q)]}$ is the linear momentum conjugated with Q , $U_-(Q)$ is the lower-sheet potential energy expressed by equation (9), a and b are the left and right turning points in the first well respectively, and c is the left turning point in the right well. The coefficient $\sqrt{[\omega/(2\pi|P|)]}$ in equation (21) is chosen to normalize the corresponding wave function in the left well. The factor ω in the root in equation (21) is the frequency of small oscillations at the bottom of the well,

$$\omega = \frac{2\pi}{T}, \quad T = 2 \int_a^b \frac{dq}{P(q)} \quad (22)$$

Then the probability flux in the restricted region, at $Q = 0$, is

$$\begin{aligned} j_1 &= -C_1^2 \Phi_1(0) \Phi_1'(0) = C_1^2 \frac{\omega}{2\pi} \exp\left(-2 \int_b^0 |P(q)| dq\right) \\ &= C_1^2 \frac{\omega}{2\pi} \exp\left(-\int_b^c |P(q)| dq\right) \end{aligned} \quad (23)$$

Here we used the inversion symmetry of the barrier, so that

$$\int_b^0 |P(q)| dq = \int_0^c |P(q)| dq = \frac{1}{2} \int_b^c |P(q)| dq \quad (24)$$

The right side in equation (23) has a clear physical meaning. The probability flux j_1 is proportional to C_1^2 , the probability of finding the system in the left well. Also the probability flux is proportional to $\omega/(2\pi)$, the frequency with which the ‘particle’ hits the barrier wall, and to the exponential tunneling factor, which is the probability of tunneling through the barrier at each hit.

Quite similarly, if the starting position of the system is in the right well with the ground-state wave function $\Psi_2 = C_2 \psi_2(r) \Phi_2(Q)$, then the corresponding tail of the WKB ground-state wave function under the barrier should increase with Q ,

$$\Phi_2(Q) = \sqrt{\frac{\omega}{2\pi|P|}} \exp\left(-\int_Q^c |P(q)| dq\right), \quad b < Q < c$$

Then, as in equation (23), at $Q = 0$ inside the barrier,

$$\begin{aligned} j_2 &= -C_2^2 \Phi_2(0) \Phi_2'(0) = -C_2^2 \frac{\omega}{2\pi} \exp\left(-2 \int_0^c |P(q)| dq\right) \\ &= -C_2^2 \frac{\omega}{2\pi} \exp\left(-\int_b^c |P(q)| dq\right) \end{aligned} \quad (25)$$

Substituting equations (23) and (25) into the corresponding junction-rule equation, $j_1 + j_2 = 0$, and reducing the equation by common factors, we come to $C_1^2 - C_2^2 = 0$. On the other hand, except the factors C_1 and C_2 , both WKB functions in the wells are normalized. Therefore, the total probability to find the system in both wells is $C_1^2 + C_2^2 = 1$. This system of two equations has two real solutions:

$$C_1 = \frac{1}{\sqrt{2}}, \quad C_2 = \frac{1}{\sqrt{2}} \quad \text{and} \quad C_1 = \frac{1}{\sqrt{2}}, \quad C_2 = -\frac{1}{\sqrt{2}} \quad (26)$$

which coincide with the factors in the two wave functions (10) obtained from symmetry arguments. We come to the following conclusion. The junction rule includes the transformation properties of the vibronic wave functions required by the corresponding high symmetry of the system. If the symmetry-adapted functions (3) are used, the junction rule (20) does not provide new equations.

Finally, substituting $\langle \psi_-(0_-) | \psi_-(0_+) \rangle = \text{sign}(\Delta)$ and $\Phi_2(0) \Phi_2'(0) = \Phi_0(0) \times \Phi_2'(0)$ from equation (25) into equation (18), we find the WKB expression for

the tunneling splitting energy gap in the two-level pseudo-JT case considered in Section 3,

$$\delta = E_u - E_g = 2 \operatorname{sign}(\Delta) \frac{\omega}{2\pi} \exp\left(-\int_b^c \sqrt{2[U_-(q) - E_0]} dq\right) \quad (27)$$

with $U_-(Q)$ from equation (10) and ω from equation (22). Correspondingly, the tunneling rate,

$$\Gamma = |H_{12}| = \frac{\omega}{2\pi} \exp\left(-\int_b^c \sqrt{2[U_-(q) - E_0]} dq\right) \quad (28)$$

is the product of the frequency $\omega/(2\pi)$ the system hits the barrier wall and the exponential tunneling factor, which is the probability of tunneling through the barrier at each hit.

5. JAHN–TELLER TUNNELING IN THREE DIMENSIONS: THE $T \otimes t_2$ CASE

For the double-well potential considered above, the tunneling is one-dimensional. In the $E \otimes e$ case, the APES is in two dimensions, Q_0 and Q_ε . However, the tunneling can be reduced to one dimension along the classical path [7]. This is because the APES is approximately separable and, most important, the tunneling path does not split in the wells. In this respect, the cubic $T \otimes t_2$ case is essentially different. From every well, there are three symmetry equivalent directions of tunneling into the neighboring wells. The classical path has three branches in three dimensions of the JT active modes, Q_ξ , Q_η , and Q_ζ , and, therefore, the cubic $T \otimes t_2$ case is essentially three-dimensional. However, the branching problem can be solved with the help of the junction rule of Section 4 or, equivalently, by using the high local symmetry of the wells and of the system as a whole.

For certainty, assume that, as in the earlier example of Section 2, the JT term is the orbital triplet T_{1u} of O_h . The matrix JT Hamiltonian of the orbital triplet term linearly coupled to a threefold degenerate t_{2g} mode can be written as:

$$H_{JT} = \hbar\omega \left\{ \frac{1}{2}(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + k \begin{pmatrix} 0 & -Q_\zeta & -Q_\eta \\ -Q_\zeta & 0 & -Q_\xi \\ -Q_\eta & -Q_\xi & 0 \end{pmatrix} \right\} \quad (29)$$

where k is the corresponding dimensionless coupling constant, the matrices in equation (29) are electron operators in the electron basis ψ_x , ψ_y , and ψ_z of the T_{1u} term, and the indexes $\xi \sim yz$, $\eta \sim xz$, and $\zeta \sim xy$ label components of the irreducible representation T_{2g} . The APES is a three-valued function. Following the procedure suggested in Ref. [24], we can express coordinates of the extremum points of the APES in terms of direction cosines, x , y , and z , of the ground-state adiabatic electron

eigenvector of the matrix Hamiltonian (29), $\psi_0 = x\psi_x + y\psi_y + z\psi_z$ [24],

$$Q_\xi = 2kyz, \quad Q_\eta = 2kxz, \quad Q_\zeta = 2kxy \quad (30)$$

with the normalizing condition $x^2 + y^2 + z^2 = 1$. The latter allows to represent any electron eigenvector of the matrix (29) by a point on the unit sphere (Fig. 2). Symmetry operations in the real space are represented by the corresponding operations in the electronic space $\{x, y, z\}$. Substituting equation (30) in equation (29), we can find the corresponding isostationary function [21]:

$$\langle \psi_0 | H_{JT} | \psi_0 \rangle = -3E_{JT}f(x, y, z)$$

where $f(x, y, z) = x^2y^2 + x^2z^2 + y^2z^2$ and $E_{JT} = (2/3)k^2$. Obviously, the isostationary function $\langle \psi_0 | H_{JT} | \psi_0 \rangle$ is a scalar of the reference group, $\mathbf{G} = O_h$, and the equipotential cross-sections of the real APES are mapped onto the surface of the unit sphere $x^2 + y^2 + z^2 = 1$, shown in Fig. 2. One important feature of the isostationary surface is that every point in the Q space has its antipodal double in the electronic space $\{x, y, z\}$. In Fig. 2, the antipodal positions of the wells 1, 2, 3, and 4 are labeled as $1'$, $2'$, $3'$, and $4'$. The latter can be obtained by applying the inversion operator I to the corresponding wells 1, 2, 3, and 4. Existence of the antipodal doubles reflects even parity of JT active coordinates and is a general property of all JT Hamiltonians. From this point of view, any 2π -revolution in the Q space is an improper rotation. It manifests the fact that the JT Hamiltonian (29) includes the pseudo-spin-1 matrices, and the corresponding wave functions are spinors.

The lowest sheet has four symmetry-equivalent trigonal wells separated by six orthorhombic saddle points. In the electronic space, the trigonal wells are at

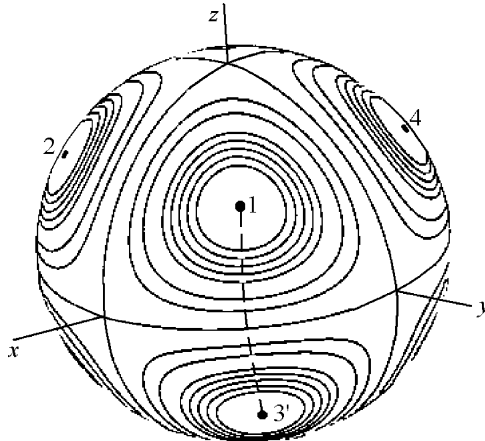


Fig. 2. Unit sphere in the electronic space $\{x, y, z\}$ of the matrix Hamiltonian (29). Solid lines are equipotential cross-sections of the isostationary function and bold dots are trigonal minimum points. The wells are labeled 1, 2, 3, and 4. The corresponding antipodal doubles are labeled $1'$, $2'$, $3'$, and $4'$. The broken line connecting 1 with $3'$ is the line of steepest descent.

$(1, 1, 1)/\sqrt{3}$, $(1, -1, 1)/\sqrt{3}$, $(-1, -1, 1)/\sqrt{3}$, and $(-1, 1, 1)/\sqrt{3}$. In the $\{Q_\xi, Q_\eta, Q_\zeta\}$ space, the corresponding coordinates are (Q_0, Q_0, Q_0) , $(-Q_0, -Q_0, Q_0)$, $(-Q_0, Q_0, -Q_0)$, and $(Q_0, -Q_0, -Q_0)$, with $Q_0 = (2/3)k$. Topology of the lowest sheet of the APES can be represented by the four-vertex Petersen graph shown in Fig. 3 in which the vertices are wells and the edges are the corresponding tunneling paths.

The junction rule (20) applied to each of the four vertexes results in the following four equations for the amplitudes of the ground-state wave functions in the wells:

$$C_2^2 + C_3^2 + C_4^2 - 3C_1^2 = 0$$

$$C_1^2 + C_3^2 + C_4^2 - 3C_2^2 = 0$$

$$C_2^2 + C_1^2 + C_4^2 - 3C_3^2 = 0$$

$$C_1^2 + C_2^2 + C_3^2 - 3C_4^2 = 0$$

Simultaneous solution of this system of equations, together with the normalizing condition, $C_1^2 + C_2^2 + C_3^2 + C_4^2 = 1$, results in the four linearly independent and, therefore, orthogonal solutions:

$$(a) \quad C_1 = \frac{1}{2}, \quad C_2 = \frac{1}{2}, \quad C_3 = \frac{1}{2}, \quad C_4 = \frac{1}{2};$$

$$(b) \quad C_1 = \frac{1}{2}, \quad C_2 = -\frac{1}{2}, \quad C_3 = \frac{1}{2}, \quad C_4 = -\frac{1}{2};$$

$$(c) \quad C_1 = -\frac{1}{2}, \quad C_2 = -\frac{1}{2}, \quad C_3 = \frac{1}{2}, \quad C_4 = \frac{1}{2};$$

$$(d) \quad C_1 = \frac{1}{2}, \quad C_2 = -\frac{1}{2}, \quad C_3 = -\frac{1}{2}, \quad C_4 = \frac{1}{2}$$

Analyzing transformation properties of the combinations, $C_1\Psi_1 + C_2\Psi_2 + C_3\Psi_3 + C_4\Psi_4$, where Ψ_i , ($i = 1, 2, 3, 4$) are ground-state wave functions in the wells, we find that the solution (a) is a vibronic singlet state, Ψ_A , and the one labeled (b) transforms as the row $\xi \sim yz$ of O_h . The same result follows from equation (3).

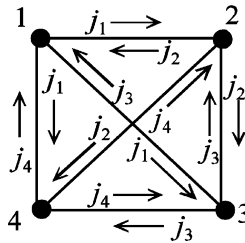


Fig. 3. The four-vertex Petersen graph representing the tunneling paths between the trigonal wells in the $T \otimes t_2$ case. The arrows show the direction of probability flux from the corresponding wells.

If, as in the example of Section 2, the JT term is T_{1u} , the fourfold degenerate tunneling multiplet splits into $A_{2u} + T_{1u}$ of O_h . According to equation (2), the symmetry-adapted wave functions are

$$\Psi_A = \frac{1}{2}(\Psi_1 + \Psi_2 + \Psi_3 + \Psi_4), \quad \Psi_{T_{1x}} = \frac{1}{2}(\Psi_1 + \Psi_2 - \Psi_3 - \Psi_4) \quad (31)$$

The other two components of the vibronic triplet term, transforming as y and z , can be obtained by applying symmetry operations of the group O_h to the x component in equation (31). Thus, as in the example of Section 4, the junction rule gives the same result as the symmetry projection techniques. The corresponding eigenvalues are

$$E_A = \frac{\langle \Psi_A | H | \Psi_A \rangle}{\langle \Psi_A | \Psi_A \rangle} \approx 3H_{12}, \quad E_T = \frac{\langle \Psi_{T_x} | H | \Psi_{T_x} \rangle}{\langle \Psi_{T_x} | \Psi_{T_x} \rangle} \approx -H_{12} \quad (32)$$

where, as in Section 3, we use symmetry equivalence of the wells, so that all diagonal elements, $H_{ii} = H_{11}$, and all the off-diagonal elements, $H_{ij} = H_{12}$. Correspondingly, the tunneling gap is [2,4]

$$\delta = E_A - E_T = 4\Gamma, \quad \Gamma \approx H_{12} \quad (33)$$

From equation (33) it follows that, thanks to the high symmetry of the JT system, there is no need to solve the tunneling problem over all the infinite space of the three modes, Q_ξ , Q_η , and Q_ζ . Evidently, the tunneling rate Γ is the same for the six potential barriers in this case, and we need to find Γ for just one barrier separating any couple of neighboring wells.

An accurate application of the WKB approximation, as suggested by the saddle-point asymptotic expansion in the corresponding path integral, includes finding the classical path in the restricted region under the barriers [10–13]. Instead of solving the corresponding Lagrange equations, we can apply an intuitive understanding of the motion on the isostationary potential surface shown in Fig. 2. Although the system has three degrees of freedom, at strong coupling, as a reasonable approximation, the angular motion along the line of steepest descent can be considered separately from the motion in the perpendicular direction. This is an example of the so-called approximately separable potential [11,13]. Actually, in addition to the adiabatic separation of the lowest sheet of the APES, consideration of the curvilinear motion along the line of steepest descent implies the following two approximations.

(a) Tunneling splitting energy gap, δ is expected to be small compared to $\hbar\omega$, or, using dimensionless magnitudes, $\delta \ll 1$. The small value of δ proportional to $\exp(-\text{const} \times k^2)$, corresponds to tunneling along the line of steepest descent. For the perpendicular motion, the characteristic energy gap is $\hbar\omega$. We can assume that the perpendicular motion is much faster compared to the angular motion. Therefore, at strong coupling, $k^2 \gg 1$, another adiabatic separation of motions applies. Fast radial motion can be averaged out [8,29].

(b) Obviously, the classical path should be close to the line of steepest descent shown by the solid line in Fig. 2, because for this line, the action integral is close to

a minimum. The small deviation of the line of steepest descend from the classical path is due to the centrifugal term not included in U_- . It is inversely proportional to the corresponding rotational inertia of the system. In this case (and quite generally in all JT systems), the radius of curvature of the classical path is proportional to linear coupling constant k . Therefore, the centrifugal term is inversely proportional to k^2 , and at strong coupling, can be neglected.

Consider the well 1 with coordinates (Q_0, Q_0, Q_0) and the well 3 at $(-Q_0, -Q_0, Q_0)$. The saddle point separating the two wells is at $(0, 0, k)$. The three points are in the plane $Q_\xi = Q_\eta$, and, evidently, the classical path between the two minimum points should belong to the plane $Q_\xi = Q_\eta$ as well. The easy way to select this plane is to use the cylindrical coordinates, $Q_\xi = Q \cos \varphi$, $Q_\eta = Q \sin \varphi$, $Q_\zeta = Q_\zeta$, and then set $\varphi = 45^\circ$. In this plane, the JT Hamiltonian (29) simplifies

$$H_{\text{JT}} = \hbar\omega \left\{ \frac{1}{2}(Q^2 + Q_\zeta^2) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + k \begin{pmatrix} -Q_\zeta & -Q & 0 \\ -Q & 0 & 0 \\ 0 & 0 & Q_\zeta \end{pmatrix} \right\} \quad (34)$$

where, instead of the original electron basis set, ψ_x , ψ_y , and ψ_z of the T_{1u} term, we use symmetry-adapted electron states, $|+\rangle = (\psi_x + \psi_y)/\sqrt{2}$, $|-\rangle = (\psi_x - \psi_y)/\sqrt{2}$, and $|\zeta\rangle$. It follows from equation (34) that in the selected plane, one of the three states, namely, $|-\rangle = (|\xi\rangle - |\eta\rangle)/\sqrt{2}$, does not participate in the vibronic coupling and can be separated. Thus, the three-state JT problem (29) is reduced to the two-state problem with the effective Hamiltonian

$$H_{\text{JT}} = \hbar\omega \left\{ \frac{1}{2}(Q^2 + Q_\zeta^2 - kQ_\zeta) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{k}{2} \begin{pmatrix} Q_\zeta & 2Q \\ 2Q & -Q_\zeta \end{pmatrix} \right\} \quad (35)$$

similar to equation (8) with $(-1/2)kQ_\zeta$ replacing Δ . Eigenvectors of equation (33) are (compare to equation (9)):

$$\psi_+(\varphi) = \frac{1}{\sqrt{2}} \begin{pmatrix} \cos(\Omega/2) \\ \sin(\Omega/2) \end{pmatrix}, \quad \psi_-(\varphi) = \frac{1}{\sqrt{2}} \begin{pmatrix} -\sin(\Omega/2) \\ \cos(\Omega/2) \end{pmatrix} \quad (36)$$

with $\tan(\Omega) = 2Q/Q_\zeta$. The lowest sheet of the APES, corresponding to ψ_- in equation (36), has the form:

$$U_-(Q, z) = \frac{1}{2}(Q^2 + Q_\zeta^2 - kQ_\zeta) - \frac{1}{2}k\sqrt{4Q^2 + Q_\zeta^2} \quad (37)$$

Equipotential cross-sections of the potential surface (37) are shown in Fig. 4. Obviously, this is the case of a non-separable potential. However, as in the $E \otimes e$ case, radius of curvature of the classical path is proportional to k . The stronger the vibronic coupling, the less the path is curved. The centrifugal term is inversely proportional to k^2 and, at strong coupling, can be neglected. Therefore, at strong coupling, the potential (35) is approximately separable. The classical path is close to the line of steepest descend. Approximately, the latter can be found from equation

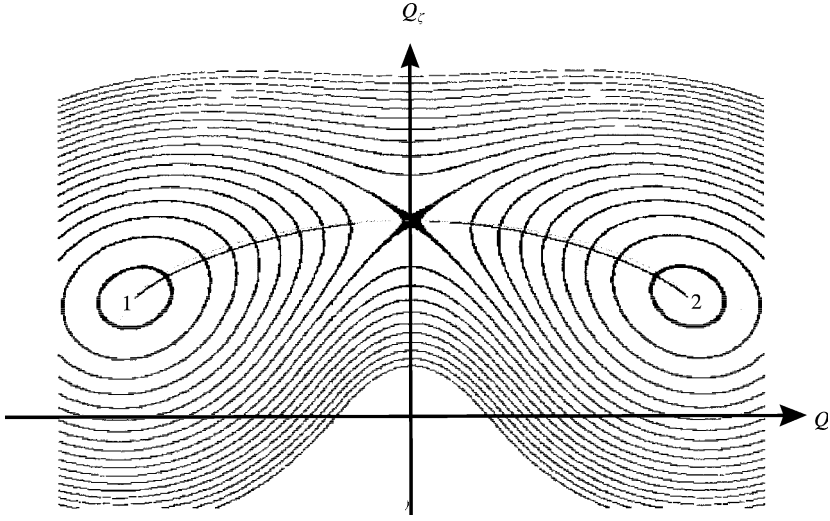


Fig. 4. Equipotential cross-sections of the lowest sheet of the APES described by equation (35). The solid line connecting the wells is the line of steepest descent approximately expressed by equation (36).

(30) by introducing spherical coordinates in the electronic space, $x = \cos \varphi \cos \theta$, $y = \sin \varphi \cos \theta$, $z = \sin \theta$, and setting $\varphi = 45^\circ$ (see Fig. 2). In the Q space, this gives [9,30]:

$$Q = k \sin 2\theta, \quad Q_z = k \cos^2 \theta \quad (38)$$

where $-\pi/2 < \theta < \pi/2$. The cross-section of the potential surface (35) along the curve (36) is shown in Fig. 5. It has the double-well shape resembling the potential curve in Fig. 1 above. The values of $\theta = \pm(1/2)\cos^{-1}(1/3)$ correspond to the

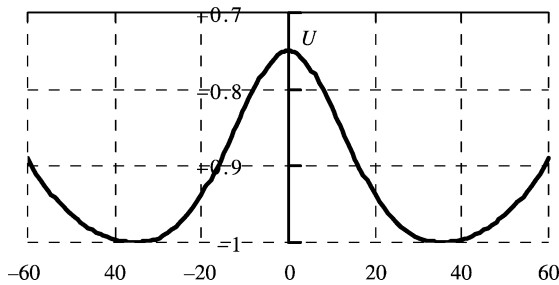


Fig. 5. Section of the lowest sheet of the APES (31) (in units of $E_{IT}/\hbar\omega$) along the curve (32) used in the WKB calculation plotted as a function of the angle θ (in degrees)

minimum points (Q_0, Q_0, Q_0) and $(-Q_0, -Q_0, Q_0)$ of the well 1 and the well 2, respectively, with $Q_0 = (2/3)k$, whereas $\theta = 0$ gives the saddle point $(0, 0, k)$.

Based upon the similarity of the JT problem described by the Hamiltonian (33) and the pseudo-JT effect with the Hamiltonian (8), we can avoid repetition of the detailed calculation of Section 3. Direct application of equation (18) gives

$$H_{12} = H_{13} = -\langle \psi_-(0) | I | \psi_-(0) \rangle \Phi_0(0) \Phi'_0(0) \quad (39)$$

where ψ_- is determined in equation (36), I is the operator of inversion in the Q space, $\Phi_0(q)$ is the nuclear wave function localized in the right well of Fig. 4, and q is the pathlength along the curve (38), $(dq)^2 = k^2(1 + 3 \cos^2 2\theta)(d\theta)^2$. The factor $\langle \psi_-(0) | I | \psi_-(0) \rangle = \langle \psi_-(0_-) | \psi_-(0_+) \rangle = \cos \varphi_B$ represents the phase change of the adiabatic electron function compared to its antipodal value. Therefore,

$$H_{12} = -\cos(\varphi_B) \Phi_0(0) \Phi'_0(0) \quad (40)$$

In most JT cases, including the $T \otimes t_2$ case in this section, $\varphi_B = \pi$ and the overlap integral $\langle \psi_-(0) | I | \psi_-(0) \rangle = \cos \varphi_B = -1$. Alternatively, if the Berry phase $\varphi_B = 0$, then $\langle \psi_-(0) | I | \psi_-(0) \rangle = \cos \varphi_B = 1$. Substituting $\langle \psi_-(0) | I | \psi_-(0) \rangle = -1$ in equation (39), we find:

$$\Gamma = H_{12} = \Phi_0(0) \Phi'_0(0) \quad (41)$$

Thus, again, as in the pseudo-JT effect considered in Section 3 and, also, in the $E \otimes e$ case [7], the tunneling rate Γ is proportional to the probability flux through the bottleneck point of the potential barrier. Similar to equation (21), the right-side ($\theta > 0$) ground-state WKB wave function under the barrier is

$$\Phi_0(q) = \sqrt{\frac{\omega}{2\pi|p|}} \exp\left(\int_b^q \sqrt{2[U_-(q) - E_0]} dq\right) \quad (42)$$

Here, as in the above, q is the pathlength along the curve (38), $p = \sqrt{\{2[E_0 - U_-(q)]\}}$ is the linear momentum conjugated to q , $U_-(q)$ is the lower-sheet potential energy expressed by equation (35), a , b , c , and d are the turning points in the double-well potential of Fig. 4 ordered from left to right, and ω is the one-well frequency determined in equation (22). Finally, substituting equation (41) in equation (40), we find [7,8]:

$$\Gamma = \frac{\omega}{2\pi} \exp\left(-\int_b^c \sqrt{2[U_-(q) - E_0]} dq\right) \quad (43)$$

This result verifies the correctness of the expression for Γ given in Ref. [7], where it was just a guess based upon the analogy with the one-dimensional $E \otimes e$ case. It has the same clear-cut physical meaning. Γ represents the probability of decay of the metastable state in the well. It is proportional to the number of ‘particle’ collisions with the barrier wall per second, $\omega/2\pi$, and to the exponential factor, that is the probability of tunneling through the barrier at each of these collisions.

The tunneling splitting energy gap, $\delta = 4\Gamma$, with Γ expressed by equation (43) was calculated numerically in Ref. [8]. The most accurate calculation of δ was

Table 1. A comparison of tunneling splitting in a cubic $T \otimes t_2$ system with linear vibronic coupling calculated by different methods

k	$-\log \delta$ by matrix diagonalization	$-\log \delta$ by steepest descent	$-\log \delta$ by minimum path
4.4	11.5523	11.8397	
4.7	13.3875	13.7567	
5.0	15.3551	15.8083	15.3272
5.4	18.1829	18.7525	18.1829
5.7	20.4559	21.1168	20.4579
6.0	22.859	23.6141	22.8635
6.4	26.267	27.1508	26.2678

According to Ref. [28].

performed by a numerical diagonalization of the corresponding exact Hamiltonian in the basis of a large number of oscillator wave functions [30,31]. The approximate calculation of δ presented in this paper can be improved by using the true classical path under the barrier, the one that minimizes the action integral in the exponent of equation (39). This was done by O'Brien [28] numerically by applying a Runge–Kutta routine. All the results are summarized in Table 1 [28].

As we can see, the WKB approach is remarkably accurate in describing the tunneling splitting energy gap. Compared to the exact results of a numerical diagonalization of a large Hamiltonian matrix, the error in the WKB value of $-\log \delta$ is about 0.2% at $k = 5$ and decreases rapidly to 0.03% at $k = 6.4$. Replacement of the classical path by the line of steepest descent slightly overestimates the potential barrier and, correspondingly, reduces the tunneling splitting energy gap. In this case, the value of $-\log \delta$ is off by about 3% at $k = 5$ and the error decreases to about 0.5% at $k = 6.4$.

6. THE CROSSOVER PROBLEM IN THE ICOSAHEDRAL $H \otimes h$ CASE

In this section we consider JT tunneling in a fullerene ion, such as C_{60}^+ , whose reference symmetry group is I_h . Its ground state is an orbital quintet H_u . According to the JT theorem, the H_u term can be coupled to low-symmetry modes transforming as the irreducible representations G_g and H_g of I_h . Here we focus our consideration at the case of a dominant coupling to the quintet modes, the so-called $H \otimes h$ problem. The work on general topology of the corresponding APES was done by Ceulemans and Fowler [32]. As distinguished from the simple-reducible case of cubic groups, in the icosahedral molecule C_{60}^+ two different kinds of linear vibronic coupling to H_g modes are possible. Due to the arbitrary choice of the phase factors, there is an uncertainty in the corresponding Clebsch–Gordan coefficients. We follow the choice of phase factors recommended in Ref. [33] and used in Ref. [32]. It was found

that, depending on the relative strength of linear vibronic coupling to two different kinds of vibrational modes, the lowest APES can have two different kinds of minimum points, of D_{3d} and D_{5d} symmetry. We limit our consideration with the most interesting case with crossover in the ground-state tunneling multiplet [5], the case of dominant coupling to just one type of modes, the one that results in appearance of trigonal minimum points only. The JT Hamiltonian in this case is the matrix 5×5 determined in the basis set of zero-coupling electron wave functions of the H_u term:

$$H_{JT} = H_0 + H_{\text{int}}, \quad H_0 = \frac{\hbar\omega}{2}(Q_\theta^2 + Q_\varepsilon^2 + Q_\xi^2 + Q_\eta^2 + Q_\zeta^2) \quad (44)$$

$$H_{\text{int}} = \hbar\omega k \begin{pmatrix} 3Q_\theta & -3Q_\varepsilon & -Q_\xi & -Q_\eta & 2Q_\zeta \\ -3Q_\varepsilon & -3Q_\theta & \sqrt{3}Q_\xi & -\sqrt{3}Q_\eta & 0 \\ -Q_\xi & \sqrt{3}Q_\xi & -Q_\theta + \sqrt{3}Q_\varepsilon & -2\sqrt{2}Q_\zeta & -2\sqrt{2}Q_\eta \\ -Q_\eta & -\sqrt{3}Q_\eta & -2\sqrt{2}Q_\zeta & -Q_\theta - \sqrt{3}Q_\varepsilon & -2\sqrt{2}Q_\xi \\ 2Q_\zeta & 0 & -2\sqrt{2}Q_\eta & -2\sqrt{2}Q_\xi & 2Q_\theta \end{pmatrix} \quad (45)$$

Here, as in the examples considered above, k is the dimensionless coupling constant and Q_i are the corresponding dimensionless vibrational coordinates. The lowest sheet of the APES in this case has 10 trigonal minimum points (their local symmetry group being D_{3d}) separated by several ridges of equipotential points. A simple way to visualize the topology of the APES is to map real rotations in three-dimensional space onto the five-dimensional space of the H_g modes. This can be done in terms of regular spherical coordinates for the direction cosines x , y , and z in the real three-dimensional space by including transformation properties of the five components $\theta \sim z^2\sqrt{3} + (x^2 - y^2)\sqrt{5}$, $\varepsilon \sim (x^2 - y^2)\sqrt{3} - z^2\sqrt{5}$, $\xi \sim yz$, $\eta \sim xz$, and $\zeta \sim xy$. Then, as in Section 5, the isostationary function is mapped onto the unit sphere, $x^2 + y^2 + z^2 = 1$. To visualize its icosahedral symmetry properties, in Fig. 6 we introduce plane faces of the corresponding icosahedron. Instead of showing all the unit sphere, as we did in Fig. 2 for the cubic case, in Fig. 6 only vertexes of the icosahedron belong to the unit sphere. In this mapping, the trigonal minimum points are exactly at the center of the triangular faces of the icosahedron (Fig. 6).

An important characteristics of this case is the presence of two different interconversion paths from one trigonal well into another [32]. At every point of one path, the system holds a residual symmetry C_2 . This path is shown in Fig. 6 by the broken line. The other path, shown in Fig. 6 by dotted line, has no symmetry left. At each point its symmetry is C_1 .

The residual symmetry of the C_2 path suggests the following simple parametrization. Consider the two wells labeled i and j in Fig. 6 (we keep the same labeling as in Ref. [5]). In the real three-dimensional space the path is in the $(1\ 0\ 0)$ plane, which means $z = 0$. This gives that $\xi = 0$, $\eta = 0$, and we have just

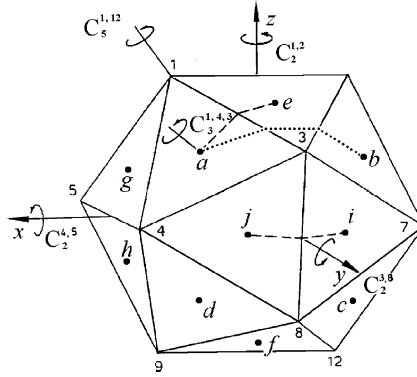


Fig. 6. Trigonal minimum points shown by bold dots, are at the center of triangular faces of the icosahedron. The two possible paths for tunneling interconversion between trigonal wells are shown by broken line (symmetry C_2) and by dotted line (symmetry C_1). Other paths, symmetry equivalent to the ones shown above, can be obtained from the shown ones by applying symmetry operations.

three non-zero direction cosines, θ , ε , and ζ . Combined with the normalization condition, $\theta^2 + \varepsilon^2 + \zeta^2 = 1$, this gives a simplified isostationary function. It depends on two independent parameters only. In spherical coordinates we have: $\theta = \cos \gamma \cos \delta$, $\zeta = \sin \gamma \cos \delta$, $\varepsilon = \sin \delta$. This corresponds to hyperspherical coordinates of Louck [34] with the radial coordinate equal to 1 and the angular coordinate $\beta = 0$. In these coordinates, two of the five electron states, namely, $|\xi\rangle$ and $|\eta\rangle$, decouple from the other ones, and the five-states problem simplifies to a three-states one. The lowest sheet of the APES has a double-well shape, as seen in Fig. 5 earlier. The wells i and j are at $\delta = 0$ and $\gamma = \pm \tan^{-1}(1/\sqrt{2})$. The saddle point belongs to the $\mathbf{T}$ ridge. In terms of Ceulemans and Fowler [32], this is one of the points of the μ orbit that has the parameter $\varphi = 0$. It is at $\delta = 0$ and $\gamma = 0$. Evidently, all these points belong to the plane where $\delta = 0$, so that $\theta = \cos \gamma$, $\zeta = \sin \gamma$, and $\varepsilon = 0$. This gives the following approximated parametric form for the line of steepest descend:

$$\begin{aligned} Q_\theta &= -k(3\cos^2 \gamma + 2\sin^2 \gamma), \\ Q_\varepsilon &= 0, \quad Q_\xi = 0, \quad Q_\eta = 0, \\ Q_\zeta &= -2k \sin 2\gamma \end{aligned} \quad (46)$$

An accurate result for the line of steepest descend can be obtained from condition that the path is parallel to the gradient of the lowest APES. This brings to a differential equation that was solved numerically in Ref. [6].

According to equation (6), the tunneling splitting energy gaps are

$$E_A - E_H = 8H_{ab} + 2H_{ae}, \quad E_G - E_H = 3H_{ab} - 3H_{ae} \quad (47)$$

Here the indexes a , b , and e , correspond to the labeling of the wells used in Ref. [5]

and shown in Fig. 6. There is no need to repeat the detailed calculation of the tunneling rate. Instead, we can apply equation (40),

$$H_{ab} = -\cos(\varphi_{1B})\Phi_b(0)\Phi'_b(0), \quad H_{ae} = -\cos(\varphi_{2B})\Phi_e(0)\Phi'_e(0) \quad (48)$$

where φ_{1B} and φ_{2B} are the Berry phase around the C_1 path and the C_2 path, respectively. The easy way to find out if the Berry phase is 0 or π , is to evaluate the overlap integral of the frozen Born–Oppenheimer electron states localized in the neighboring wells. A simple matrix multiplication of the corresponding column matrices gives $\langle\psi_a|\psi_b\rangle = -1/3$ and $\langle\psi_a|\psi_e\rangle = 1/3$. This means that there is a phase change of π around the C_1 loop, whereas there is no phase change around the loop C_2 . More accurately, the overlap integrals of the floating states, $\langle\psi_a|\psi_b\rangle$ and $\langle\psi_a|\psi_e\rangle$, were calculated numerically along the two loops [6]. The result found in Ref. [6] is the same, $\varphi_{1B} = \pi$ and $\varphi_{2B} = 0$. Substituting these values into equation (48), we find

$$H_{ab} = \Phi_b(0)\Phi'_b(0), \quad H_{ae} = -\Phi_e(0)\Phi'_e(0) \quad (49)$$

and

$$E_A - E_H = 2(4\Gamma_1 - \Gamma_2) \quad (50)$$

where $\Gamma_1 = \Phi_b(0)\Phi'_b(0)$ and $\Gamma_2 = \Phi_e(0)\Phi'_e(0)$. Thus, the tunneling splitting energy gap depends on the competing contribution of the two tunneling paths, the longer C_1 path from a to b with a lower barrier and the shorter C_2 path from a to e with a higher barrier. The fact that these two paths contribute differently, follows from the analysis of the Berry phase around the loop C_2 compared to the Berry phase for the loop C_1 . As it follows from equations (48)–(50), the order of energy levels in the ground-state tunneling multiplet is determined by the Berry phase, $\varphi_{1B} = \pi$ and $\varphi_{2B} = 0$.

As in the cubic $T \otimes t_2$ case considered in Section 5, there is no need to repeat the detailed calculation of the tunneling rate. Instead, we can directly apply equation (28),

$$\Gamma_2 = \frac{\omega_2}{2\pi} \exp(-S_2), \quad S_2 = \int_i^j \sqrt{2[U_0(q) - E_0]} dq \quad (51)$$

where U_0 is the ground-state eigenvalue of the matrix Hamiltonian (44) and (45), the integration in equation (51) is along the curve (46), I_2 is the corresponding action integral under the barrier, and ω_2 is the frequency of small oscillations of the system at the bottom of a trigonal well in the direction along the tunneling path C_2 . Similarly, for Γ_1 we have:

$$\Gamma_1 = \frac{\omega_1}{2\pi} \exp(-S_1), \quad S_1 = \int_a^b \sqrt{2[U_0(q) - E_0]} dq \quad (52)$$

The only difference in this case is absence of any residual symmetry along the C_1 path. This does not allow a simple parametrization for the tunneling curve. Therefore, all the work was done numerically [6]. The frequencies ω_1 and ω_2 associated with the tunneling paths C_1 and C_2 , respectively, were evaluated numerically as well [6].

The corresponding values turned out to be equal to normal frequencies in the wells [5]: $\omega_1 = \omega\sqrt{5/14}$ and $\omega_2 = \omega\sqrt{5/6}$, where ω is the original frequency of the JT active H_g mode without vibronic coupling. For the action integrals S_1 and S_2 , we find the following numerical approximations:

$$S_1 \approx 0.1346k^2 - 1.084, \quad S_2 \approx 0.0719k^2 - 0.946 \quad (53)$$

Combining equations (50)–(53), we can evaluate the ratio

$$\frac{4\Gamma_1}{\Gamma_2} \approx 2.619 \exp(-0.0627k^2 + 0.138)$$

At intermediate values of k , $k \lesssim 4.2$, this ratio is greater than one, and the positive contribution of the C_1 tunneling in the energy gap (50) dominates. Starting at about $k = 4.2$, the C_1 barrier becomes too big, and the dominating contribution comes from the C_2 tunneling. Because of the opposite Berry phase for these two types of tunneling interconversion, the corresponding contributions have opposite sign, which explains the crossover in the ground-state tunneling multiplet reported in Ref. [5].

7. CONCLUDING REMARKS AND DISCUSSION

Usually, tunneling in many dimensions can be reduced to consideration of a one-dimensional path. This is due to approximate separability of the classical path in the restricted region under the barrier. In most cases, such as chemical reactions, dominant contribution in tunneling comes from penetration through just one potential barrier. Tunneling along other classical paths can be neglected. In this respect, the JT tunneling is essentially different. In each well, the classical path splits into several symmetry equivalent branches. The tunneling contribution from none of these branches can be neglected. This issue can be resolved with the help of the *junction rule* introduced in Section 4. In several examples considered in this paper, the junction rule combined with the corresponding symmetry arguments, was shown to generate symmetry-adapted wave functions, similar to those obtained from the well-known group-theoretical projection operator technique. Then the corresponding tunneling splitting energy gap can be expressed in terms of the tunneling integral, H_{12} , between localized ground-state wave functions in just two neighboring wells. Due to their symmetry equivalence, it does not matter which wells are used in the calculation of H_{12} . Note that the junction rule follows directly from fundamental principles of quantum mechanics. Therefore, compared to symmetry projection, it is more general and, with a minor modification, applies to low-symmetry tunneling problems as well, when group-theoretical methods cannot be used.

APES in all JT problems is smooth. The radius of curvature of the classical path in the restricted region under potential barriers is proportional to the corresponding constant of vibronic coupling, k . Therefore, in any JT case the APES is approximately separable. Compared to tunneling along the classical path, motion in

the perpendicular directions is much faster. Therefore, adiabatic separation of the tunneling motions along the corresponding classical path applies. Motion in the perpendicular directions can be averaged out. Tunneling along the classical path can be considered separately in an average field of perpendicular vibrations [29]. The stronger the vibronic coupling, the better is this approximation.

The tunneling integral, H_{12} , is shown to be proportional to density of probability flux, $j = -\Phi_0(0)\Phi'_0(0)$, at the bottle-neck point, $Q = 0$,

$$H_{12} = -\langle\psi_-(0)|I|\psi_-(0)\rangle\Phi_0\Phi'_0$$

Here $Q = 0$ is the top point of the potential barrier separating the well 1 from the well 2, $\psi_-(Q)$ is the ground-state electron wave function of adiabatic approximation, I is the operator of inversion in the Q space, and $\Phi_0(Q)$ is the ground-state vibrational wave function in the well, the one to the right along the classical path in the restricted region under the barrier, so the derivative $\Phi'_0(0)$ is positive. The matrix element $\langle\psi_-(0)|I|\psi_-(0)\rangle$ represents overlap of the adiabatic electron wave function, $\psi_-(Q)$, with its antipodal value $I\psi_-(Q)$ at the bottle-neck point of the barrier. This overlap integral is the phase factor, $\langle\psi_-(0)|I|\psi_-(0)\rangle = \cos \varphi_B$ gained by the adiabatic wave function $\psi_-(Q)$ around a loop encircling the point of electron degeneracy. If the corresponding Berry phase, $\varphi_B = \pi$, then $\cos \varphi_B = -1$, and the order of energy levels in the tunneling multiplet is flipped as compared to a non-JT case with a similar potential energy surface.

The obvious advantage of the approximate separation of the classical path is the reduction of the multidimensional tunneling to one dimension. For a numerical evaluation of the tunneling splitting energy gap, we need $\Phi_0(0)$, the tail value of the ground-state vibrational wave function at the top point of the potential barrier. Best description of $\Phi_0(Q)$ in the restricted region is provided by the WKB approximation. It gives H_{12} in terms of the corresponding action integral along the classical path, $H_{12} = -\Gamma \cos \varphi_B$, with the tunneling rate

$$\Gamma = \frac{\omega}{2\pi} \exp\left(-\int_b^c \sqrt{2[U_-(q) - E_0]} dq\right) \quad (54)$$

Here $U_-(q)$ is the ground-state value of the APES and q is the pathlength parameter along the classical path. The latter result has a simple physical meaning. The tunneling rate is proportional to the frequency $\omega/(2\pi)$ at which the ‘particle’ is hitting the barrier wall, and to the exponential factor that is probability of tunneling penetration through the barrier at each hit.

Finding the classical path involves a minimization of the action integral. In its turn, this brings to solving a Cauchy problem for a system of the corresponding Lagrange equations with the end points of the path fixed at the bottom of the two wells. The minimization can be avoided if the exact classical path is approximately replaced by the line of steepest descent. For a given APES, this is a much simpler numerical problem related to its geometry. Numerical evaluation of this approximation presented by O’Brien [28] (see Table 1 in Section 5 earlier) reveals a slight overestimate of the potential barrier along the line of steepest descent.

Obviously, this is to be expected because the line of steepest descend does not provide the minimum value of the action integral. The difference is due to the centrifugal energy term. It originates from the corresponding kinetic energy absent in the APES. An additional contribution in the centrifugal energy comes from diabatic contribution described by the so-called Born–Huang correction to adiabatic approximation. In classically allowed regions the centrifugal force points away from the center of the curve and pulls the ‘particle’ up the outer wall of the potential well. In classically restricted regions under the barrier this force has opposite direction. It pulls the ‘particle’ toward the center of the curve [35]. This explains the surprisingly different shape of the classical path in the $T \otimes t_2$ case, compared to the line of steepest descend, found by O’Brien [28]. The classical path crosses the Q_z axis of Fig. 5 (see Section 5 earlier) somewhat closer to the origin than the saddle point. Evidently, the centrifugal term is inversely proportional to k^2 and, at strong coupling, its contribution rapidly decreases with k . Therefore, the error in the value of $-\ln \delta$ decreases to about 0.5% at $k = 6.4$ (see Table 1 in Section 5).

Finally, based upon the above results, the following shortcut can be suggested. With the help of symmetry projection, symmetry-adapted wave functions and the corresponding expression for the tunneling splitting energy gap can be obtained in the well established ‘old’ way of the perturbation approach of Bersuker [2,4]. The corresponding tunneling integral, $H_{12} = -\Gamma \cos \varphi_B$, is a product of the tunneling rate Γ and the Berry-phase factor, $-\cos \varphi_B$. In the WKB approximation, the tunneling rate is expressed by equation (54) as an exponent of the corresponding action along the classical path connecting two neighboring wells. The latter can be approximated by the line of steepest descend from the saddle point of the potential barrier to the minimum at the bottom of the well. The Berry-phase factor, $\cos \varphi_B$, equals 1 or -1 , depending on the sign of the overlap integral, $\langle \psi_1 | \psi_2 \rangle$ of the frozen electron wave functions in the wells. If $\langle \psi_1 | \psi_2 \rangle$ is positive, then $\cos \varphi_B = 1$. If $\langle \psi_1 | \psi_2 \rangle$ is negative, and the loop includes odd number of steps on the corresponding Petersen graph, then $\cos \varphi_B = -1$, and the order of tunneling levels is opposite to the regular, non-JT case.

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REFERENCES

- [1] I. B. Bersuker, *Opt. Spektroskop.*, 1961, **11**, 319–324, [English transl.: *Opt. Spectrosc. (USSR)*].
- [2] I. B. Bersuker, *Zh. Eksp. Teor. Fiz.*, 1962, **43**, 1315–1322, [English transl.: *Sov. Phys. – JETP*].
- [3] M. C. M. O'Brien, *Proc. R. Soc. Lond. Ser. A*, 1964, **281**, 323–339.
- [4] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, Berlin, 1989.
- [5] C. P. Moate, M. C. M. O'Brien, J. L. Dunn, C. A. Bates, Y. M. Liu and V. Z. Polinger, *Phys. Rev. Lett.*, 1996, **77** (21), 4362–4365.
- [6] V. Polinger, R. Huang, C. A. Bates and J. L. Dunn, *J. Chem. Phys.*, 2002, **117** (9), 4340–4347.
- [7] V. Z. Polinger, *Fiz. Tverd. Tela*, 1974, **16**, 2578–2583, [English transl.: *Sov. Phys. – Solid State*, 1975, **16** (9), 1676–1679].
- [8] V. Z. Polinger, P. J. Kirk, J. L. Dunn and A. Bates, *J. Phys.: Condens. Matter*, 1993, **5**, 2213–2232.
- [9] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals*, McGraw-Hill, New York, 1965.
- [10] A. Auerbach and S. Kivelson, *Phys. Rev. Lett.*, 1984, **53** (5), 411–414.
- [11] A. Auerbach and S. Kivelson, *Nucl. Phys. B*, 1985, **257**, 799–858.
- [12] Z. H. Huang, T. E. Feuchtwang, P. H. Cutler and E. Kazes, *Phys. Rev. A*, 1990, **41** (1), 32–41.
- [13] M. Razavy and A. Pimpale, *Phys. Rep.*, 1988, **168**, 305–370.
- [14] G. Herzberg and H. C. Longuet-Higgins, *Discuss. Faraday Soc.*, 1963, **35** (7), 77–82.
- [15] F. Ham, *Phys. Rev. Lett.*, 1987, **58**, 725–728; F. Ham, *J. Phys.: Condens. Matter*, 1990, **2**, 1163–1177.
- [16] H. Koizumi and I. B. Bersuker, *Phys. Rev. Lett.*, 1999, **83**, 3009.
- [17] H. Koizumi, I. B. Bersuker, J. Boggs and V. Z. Polinger, *J. Chem. Phys.*, 2000, **112**, 8470.
- [18] G. Bevilacqua, I. B. Bersuker and L. Martinelli, in *Vibronic Interactions: Jahn–Teller Effect in Crystals and Molecules* (eds M. D. Kaplan and G. O. Zimmerman), NATO Science Series, Kluwer, Dordrecht, 2001, Vol. 39, p. 229.
- [19] R. Dagis and I. B. Levinson, *Group Theoretical Properties of Adiabatic Potentials in Molecules*, *Optika i Spektroskopiia: Sbornik Statei*, Nauka, Leningrad, 1967, Vol. 3, pp. 3–8.
- [20] B. P. Martinenas and R. S. Dagis, *Teor. Eksp. Khim.*, 1969, **5** (1), 123–125, [English transl.: *Theor. Exp. Chem. (USA)*].
- [21] A. Ceulemans, *J. Chem. Phys.*, 1987, **87**, 5374–5385.
- [22] G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol III. *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Van Nostrand, Toronto, 1966, Table 60.
- [23] R. L. Flurry, Jr., *Symmetry Groups, Theory and Chemical Applications*, Prentice-Hall, Englewood Cliffs, NJ, 1980, Appendix 4.
- [24] U. Öpik and M. H. L. Pryce, *Proc. R. Soc. Lond. Ser. A*, 1957, **238**, 425–447.
- [25] A. F. Devonshire, *Proc. R. Soc. Lond. Ser. A*, 1936, **153**, 601–621.
- [26] I. B. Bersuker, *Phys. Lett.*, 1966, **20**, 589–590.
- [27] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory*, 3rd ed., Butterworth-Heinemann, 1981, Vol. 3, Section 50, problem 3.
- [28] M. C. M. O'Brien, *Tunneling in Several Dimensions: The Jahn–Teller Systems $T \otimes t_2$ and $H \otimes h$* , Department of Physics, Oxford University, 1997, Unpublished preprint.
- [29] G. I. Bersuker and V. Z. Polinger, *Zh. Eksp. Teor. Fiz.*, 1981, **80** (5), 1798–1809, [English transl.: *Sov. Phys. JETP*, 1981, **53** (5), 930–936].
- [30] M. C. M. O'Brien, *J. Phys.: Condens. Matter*, 1990, **2**, 5539–5553.

- [31] M. Caner and R. Englman, *J. Chem. Phys.*, 1966, **44** (6), 2305–2306.
- [32] A. Ceulemans and P. W. Fowler, *J. Chem. Phys.*, 1990, **93** (2), 1227–1234.
- [33] L. L. Boyle and Y. M. Parker, *Mol. Phys.*, 1980, **39**, 95.
- [34] J. D. Louck, *J. Mol. Spectrosc.*, 1960, **4**, 298.
- [35] S. P. Karkach and V. I. Osherov, *Mol. Phys.*, 1978, **36** (4), 1069–1084.

Tunneling Path and Ground State Crossover in Linear $T \otimes (e \oplus t_2)$ and Quadratic $G \otimes (g \oplus h)$ Jahn–Teller Systems

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Abstract

It was believed that vibronic coupling does not alter the symmetry and degeneracy of the ground state of a Jahn–Teller (JT) system. However this conjecture was found to be untrue in the case of the icosahedral $H \otimes h$ system, where in strong coupling the system has a ground vibronic state of A symmetry instead of the expected H symmetry. A physical explanation to account for this ground state crossover has been given very recently by the consideration of two kinds of tunneling paths on the adiabatic potential energy surface. One path between a pair of minima is favored at strong coupling while a path between a different pair of minima is favored in weak coupling. By using the WKB approximation, it was shown that different contributions to the tunneling splitting arise from the two different paths. This gives rise to the crossover of the ground vibronic states occurring at a certain value of the coupling strength. In the cubic $T \otimes (e \oplus t_2)$ JT system a crossover has also been proposed. However, only minima having trigonal symmetry occur when the t_2 mode dominates and thus only one type of tunneling path is present so that a crossover seems to be unlikely in the reported range of coupling constants. In a second example considered here, it is shown that in the icosahedral $G \otimes (g \oplus h)$ system a crossover is possible for certain combinations of linear and quadratic coupling constants. This crossover can be understood from the consideration of two kinds of competing paths between pairs of trigonal minima.

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1. INTRODUCTION

It is well known that vibronic coupling does not alter the symmetry of a Jahn–Teller (JT) system except in the static limit. This is because the coupling between the

electrons and the nuclei is an inner-system interaction so that, with or without the vibronic coupling, the Hamiltonian for this dynamic system has the same overall symmetry. Both the electronic and vibronic states belong to the irreducible representations of the symmetry group of the Hamiltonian of the system but there is no group-theoretical requirement for the ordering of these states. However, it had been supposed for a long time that the ground vibronic states should belong to the same irreducible representation as the electronic states from which they were derived. Also, all systems known had this property from analytical and numerical calculations. That is the ground vibronic states have the same degeneracy as the original electronic states. This assumption was mainly based on the argument that, for a JT system, there are several equivalent distortions that individually lower the symmetry. Tunneling between these equivalent distortions then restores the original higher symmetry of the system and hence, in most cases, the degeneracy of the ground vibronic states [1].

However, in 1996 it was found that the $H \otimes h$ JT system might have a singlet A ground vibronic state instead of the expected quintet H state [2]. The tunneling splitting energy gap between the lowest vibronic A singlet and vibronic H quintet associated with D_{3d} JT distortions was calculated analytically. With an increase in the coupling strength, the tunneling splitting changes from being positive to negative showing a crossover of the ground vibronic states from H symmetry to A symmetry. Both numerical phase tracking and an analysis of the degeneracies associated with the adiabatic potential energy surface (APES) showed that the geometrical phase (the Berry phase) change was absent for some paths between the well states. This absence of a phase change gives rise to the A ground state. Another independent calculation for the $H \otimes h$ JT system gave similar results and confirmed the crossover from H states to A state when the D_{3d} minima (or wells) are lowest in energy [3].

A ground state crossover was also reported in the quadratic $E \otimes e$ JT system [4]. These authors gave an explanation of the crossover by consideration of two competing paths on the ground APES using the WKB approximation. A non-degenerate ground state was also found in the $T \otimes t_2$ JT system with both linear and quadratic vibronic coupling including fourth-order terms [5]. The results were explained in terms of the requirements of the Berry phase and the properties of conical intersections. A detailed physical explanation of the ground state crossover in the $H \otimes h$ JT effect was given very recently in Ref. [6] also within the framework of the WKB approximation. In this explanation, the ground state crossover could be understood by considering two types of tunneling paths between two D_{3d} minima. One path having C_1 symmetry was *via* a point on the D_3 saddle continuum and the other path having C_2 symmetry was *via* a point on the T saddle continuum. There was a Berry phase change in the closed C_1 loop while there was no Berry phase change in the closed C_2 loop. The tunneling along these two paths is associated with different values of the ground state energy splitting. In weak coupling, tunneling along the C_1 path dominates and as a result the system has an H -type ground state. At intermediate-to-strong coupling strengths, the tunneling along the C_2 path is favored and the system has an A -type ground state.

The geometrical phase of the eigenstate of a quantum system has a change in sign along a circuit around a point of conical intersection in the potential surfaces [7,8]. Also Ham [9] studied the role of the Berry phase in connection with the ordering of the low-energy states of the $E \otimes e$ JT system. Similar work followed for the $T \otimes t_2$ JT system [10,11]. In both of these systems, the non-degenerate ground state is associated with a circuit in vibrational coordinate space in which there is no change in the sign of the Berry phase. The same argument holds in the icosahedral $H \otimes h$ problem in which a non-degenerate ground state is present together with a phase-free loop in parameter space [2,3,12]. A Berry phase analysis was also used in the $G \otimes (g \oplus h)$ system and in its subsystems $G \otimes g$ and $G \otimes h$ with respect to the ordering of the low-lying states [13,14].

The key point in providing an explanation of the non-degenerate ground state in the above examples is that two tunneling paths exist. When the path with a Berry phase change dominates, the tunneling in the system produces the normal degenerate ground state; on the other hand, when the phase-free path dominates, the tunneling produces a non-degenerate ground state. Another aspect in viewing this problem can be given. The tunneling splitting δ can be written as the sum of two terms, each one due to a different type of tunneling process. The tunneling along a path with a Berry phase change makes a positive contribution to δ whilst tunneling along a path without a Berry phase change makes a negative contribution to δ . When the latter tunneling process is favored, δ is negative and there is a crossover of the ground state.

In this paper, we consider possible tunneling paths in the $G \otimes (g \oplus h)$ and $T \otimes (e \oplus t_2)$ JT systems in which, in each case, a possible crossover has been suggested. Section 2 describes the WKB approximation in relation to JT systems. Sections 3 and 4 describe the analysis of the two systems and Section 5 summarizes the implications of these results.

2. THE WKB APPROXIMATION IN JAHN–TELLER PROBLEMS

Let us suppose that the potential barrier is much higher in energy than the vibronic JT state under consideration. It is appropriate therefore to apply the semi-classical WKB approximation to the tunneling problem in such systems. The action integral I_T is given by [15]:

$$I_T = \int_s \sqrt{\frac{2m}{\hbar}} (V(r) - E) ds \quad (1)$$

where m is the mass of the particle, E is the energy eigenvalue and $V(r)$ is the potential energy. The integration path s is chosen to minimize I_T . It also corresponds to the classical trajectory in the equivalent classical Hamiltonian.

The action integral I_T is an important quantity characterizing the tunneling problem. We consider here an example of tunneling in the simplest case namely

one-dimensional tunneling in a symmetric double quantum well. We assume a potential function in which both the height and shape of the energy minima are identical on both sides of the potential barrier. The splitting of the originally degenerate energy levels due to the overlap of the wave functions localized in the separate wells is called the tunneling splitting δ which is simply related to I_T by the equation [16]:

$$\delta = \hbar\omega \exp(-I_T) \quad (2)$$

where ω is the vibrational frequency of the particle in the single well.

In multi-dimensional tunneling, the result involves the interference of all possible tunneling paths as given by the Feynman path integral theory. Amongst all these paths, the ones with the smallest action integrals dominate and give the most probable classical trajectory. When a particle tunnels through a potential groove, the probability flow is a tube centered on the classical trajectory [17,18].

In this paper, we single out the classical trajectory as the tunneling path required and estimate the tunneling splitting by calculating the action integral along this path. It is an approximation yet we will see it is sufficient for our present discussion of the crossover in JT problems. This is especially the case in strongly coupled systems in which the potentials are steep and possible tunneling paths are close together forming a narrow tube.

In 1974, Polinger [19] used the WKB method for the $E \otimes e$ JT problem. Recently, it was also used in the explanation of the non-degenerate ground state for the same problem [4]. Further discussions were given by O'Brien [11] on the semi-classical method for both one-dimensional and multi-dimensional JT problems. All these semi-classical approaches simplified the multi-dimensional cases to one-dimensional problems.

For the $T \otimes t_2$ JT problem, the path of minimum action must be determined in a three-dimensional vibrational coordinate space. It can be calculated by a variational procedure [20]. The conditions that minimize the action integral I_T are given by the set of equations [21]:

$$\begin{aligned} \frac{\partial g}{\partial x} &= \frac{dx}{ds} \left(\frac{\partial g}{\partial x} \frac{dx}{ds} + \frac{\partial g}{\partial y} \frac{dy}{ds} + \frac{\partial g}{\partial z} \frac{dz}{ds} \right) + g \frac{d^2x}{ds^2} \\ \frac{\partial g}{\partial y} &= \frac{dy}{ds} \left(\frac{\partial g}{\partial x} \frac{dx}{ds} + \frac{\partial g}{\partial y} \frac{dy}{ds} + \frac{\partial g}{\partial z} \frac{dz}{ds} \right) + g \frac{d^2y}{ds^2} \\ \frac{\partial g}{\partial z} &= \frac{dz}{ds} \left(\frac{\partial g}{\partial x} \frac{dx}{ds} + \frac{\partial g}{\partial y} \frac{dy}{ds} + \frac{\partial g}{\partial z} \frac{dz}{ds} \right) + g \frac{d^2z}{ds^2} \end{aligned} \quad (3)$$

where

$$g(x, y, z) = \sqrt{\frac{2m}{\hbar^2} (V(x, y, z) - E')} \quad (4)$$

Here, $V(x, y, z)$ is the adiabatic potential and E' is the energy of the ground phonon state. The vibrational co-ordinates x, y, z are treated as functions of s , the arc length of the path. Because the system has a zero-point energy E' above the potential well, the boundary conditions are not unique.

For the computation of the tunneling path between a pair of wells, we use the method of O'Brien [20]. We thus choose one of the points on the mirror plane of the two wells as the starting point and extend the path until it reaches the boundary. Different paths with different starting points on the mirror plane have been computed using Maple by solving equation (3) and the path with the smallest value of the action integral was chosen as the most probable tunneling path. The paths computed in this way are shown in Fig. 1.

For JT problems of higher dimensions such as that for the $T \otimes (e \oplus t_2)$ problem, the adiabatic potential V is complicated and cannot be written down in an analytical form. However, in such problems, the least action path can be approximated by the minimum energy path (or path of steepest descent) on the adiabatic potential surface. It is the path for which the tangent to it is parallel to the gradient of the APES.

3. CROSSOVER AND TUNNELING PATHS IN THE LINEAR $T \otimes (e \oplus t_2)$ SYSTEM

The Hamiltonian for the linear cubic $T \otimes (e \oplus t_2)$ JT system is

$$\mathcal{H} = \mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{linear}} \quad (5)$$

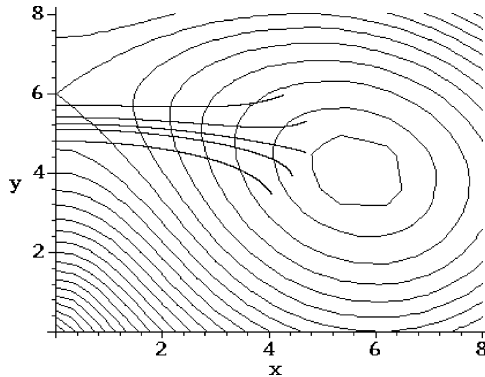


Fig. 1. The path and the contour plot of the lowest potential energy surface in the $T \otimes t_2$ system. By symmetry considerations, the 3D problem is reduced to a calculation in 2D (X, Y) coordinate space. The five paths have been computed with different initial conditions and the one (in the middle) that reaches the zero-point energy (the innermost ring) is the least action path.

with

$$\mathcal{H}_{\text{vib}} = -\frac{1}{2\mu}(P_\theta^2 + P_\varepsilon^2 + P_4^2 + P_5^2 + P_6^2) + \frac{\mu\omega_E^2}{2}(Q_\theta^2 + Q_\varepsilon^2) + \frac{\mu\omega_T^2}{2}(Q_4^2 + Q_5^2 + Q_6^2) \quad (6)$$

$$\mathcal{H}_{\text{linear}} = \begin{bmatrix} -V_E\left(\frac{1}{2}Q_\theta - \frac{\sqrt{3}}{2}Q_\varepsilon\right) & V_TQ_6 & V_TQ_5 \\ V_TQ_6 & -V_E\left(\frac{1}{2}Q_\theta + \frac{\sqrt{3}}{2}Q_\varepsilon\right) & V_TQ_4 \\ V_TQ_5 & V_TQ_4 & V_EQ_\theta \end{bmatrix} \quad (7)$$

in the x, y, z basis where $Q_\theta, Q_\varepsilon, Q_4, Q_5, Q_6$ are the vibrational co-ordinates, $P_\theta, P_\varepsilon, P_4, P_5, P_6$ are the corresponding conjugate momentum operators, μ is the particle mass and ω_E and ω_T are the frequencies for the e and t_2 vibrations respectively. V_E and V_T are the linear vibronic coupling constants.

Many authors, for example [22–25], have described calculations of the tunneling splitting in the $T \otimes (e \oplus t_2)$ JT system. Interestingly, a recent numerical calculation [26] showed that, for the first time, there appeared to be a crossover from a T ground state to an A ground state when t_2 vibrations dominate. Thus a new study of the tunneling paths under the WKB approximation is described here for the case in which the t_2 vibrations in this problem dominate.

The cubic $T \otimes (e \oplus t_2)$ JT system has three types of extremal points on the ground APES namely trigonal (D_{3d}), tetragonal (D_{4h}) and orthorhombic (D_{2h}) points. If the coupling to the e modes dominates, the D_{4h} points are minima and the D_{3d} points are saddle points. When the t_2 modes dominate, the D_{3d} points are minima and the D_{4h} points are saddle points. The D_{2h} points are always saddle points except in the equal coupling case. Because the ground vibronic state was found to have A symmetry when the t_2 mode vibrations dominate, we limit our discussion here to tunneling between trigonal minima.

Due to the complexity of the APES, the path of minimum action is difficult to determine. However, an alternative approximate procedure has been used instead, namely calculating the path of steepest descent between equivalent minima. There are two possible types of paths of steepest descent connecting D_{3d} wells; one is *via* a D_{2h} saddle point and the other *via* a D_{4h} saddle point. Yet we find that, when the t_2 vibrations dominate, there is no interchange between these two types of tunneling paths, as one *via* a D_{2h} saddle point is always favored. According to equation (2), there are two factors that should be considered in deciding the tunneling rate along a path. These are the collision frequency of the particle hitting the barrier and the value of the action integral along the path that determines the possibility of crossing the barrier. The collision frequency is determined from the curvature of the D_{3d} potential well, which is the same for both paths. Detailed

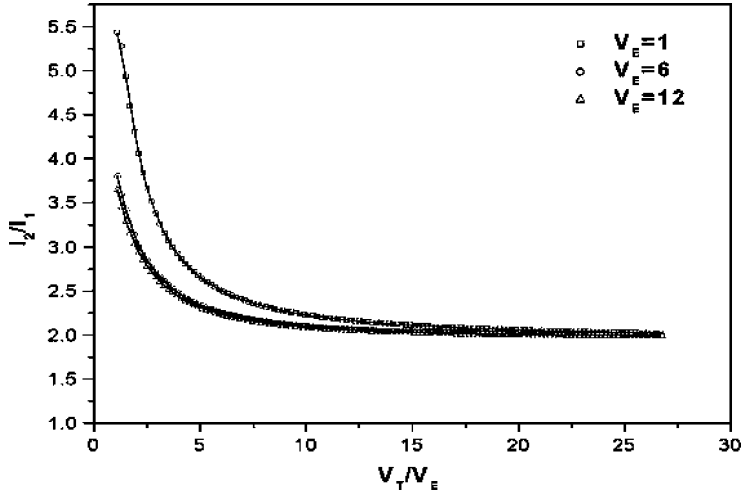


Fig. 2. The ratio of the action integrals I_2/I_1 as functions of V_T/V_E with different choices of V_E when t_2 mode dominates. Here I_1 and I_2 are respectively the action integral of the path *via* a D_{4h} saddle point and that of the path *via* a D_{2h} saddle point. As shown in the figure I_2 is always bigger than I_1 .

calculations show that the tunneling integral along the path *via* a D_{4h} saddle point always has a larger value than that along a D_{2h} saddle point for all values of the coupling constant when the t_2 mode dominates, as shown in Fig. 2.

Alternatively, this becomes clear when looking at the barrier height of the saddle points and the distances between the saddle points and the D_{3d} minima (Table 1). When the t_2 mode dominates, the D_{4h} saddle points have a higher potential energy and are at a larger distance from the minima than the D_{2h} saddle points as shown in the table. Thus the path through a point on the D_{4h} saddle should be avoided and only the path *via* a point on the D_{2h} saddle is physically possible.

Table 1. Comparison of the geometry of the two types of saddle points.

	D_{2h} saddle points	D_{4h} saddle points
Potential barrier	$E_1 = -\frac{1}{8} \frac{V_E^2}{\mu \omega_E^2} + \frac{1}{6} \frac{V_T^2}{\mu \omega_T^2}$	$E_2 = -\frac{1}{2} \frac{V_E^2}{\mu \omega_E^2} + \frac{2}{3} \frac{V_T^2}{\mu \omega_T^2}$
Distance from minimum	$S_1 = \frac{1}{4} \frac{V_E^2}{\mu^2 \omega_E^4} + \frac{V_T^2}{\mu^2 \omega_T^4}$	$S_2 = \frac{V_E^2}{\mu^2 \omega_E^4} + \frac{4}{3} \frac{V_T^2}{\mu^2 \omega_T^4}$

When the t_2 -mode dominates $\left(\frac{V_T^2}{\omega_T^2} > \frac{3}{4} \frac{V_E^2}{\omega_E^2} \right)$, $E_2 > E_1$ and $S_2 > S_1$.

An explanation therefore for the crossover in terms of two competing paths is not possible in this case. However, this conclusion might need modification were it possible to incorporate the centrifugal/Born–Huang term in the original Hamiltonian.

4. CROSSOVER AND TUNNELING PATHS IN THE QUADRATIC $G \otimes (g \oplus h)$ JT SYSTEM

The vibronic states and energy spectrum of the icosahedral $G \otimes (g \oplus h)$ JT system with linear couplings have been previously derived analytically [27]. The vibronic ground states for this JT system have possible symmetries of G , A and H . The observation that the tunneling splitting between the A and G states tends to zero in the strong coupling limits suggests that a quadratic term introduced into the system as a small perturbation may cause a crossover to occur. These ideas are examined here.

The vibronic Hamiltonian for this system is

$$\mathcal{H} = \mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{linear}} + \mathcal{H}_{\text{quad}} \quad (8)$$

where the vibrational terms are given by

$$\mathcal{H}_{\text{vib}} = \frac{1}{2} \sum_{\Lambda=G,H} \sum_{\lambda} \left(\frac{P_{\Lambda\lambda}^2}{\mu_{\Lambda}} + \mu_{\Lambda} \omega_{\Lambda}^2 Q_{\Lambda\lambda}^2 \right) \quad (9)$$

where λ is summed over the nine components of the g - and h -modes. The linear coupling terms are given by

$$\mathcal{H}_{\text{linear}} = \sum_{\Lambda=G,H} \sum_{\lambda} V_{\Lambda} C_{\Lambda\lambda}^{\Lambda} Q_{\Lambda\lambda} \quad (10)$$

and one of the quadratic terms is:

$$\mathcal{H}_{\text{quad}} = \sum_{\lambda} V_{\text{quad}} C_{G\lambda}^G R_{\lambda}^G \quad (11)$$

with

$$\begin{aligned} R_a^G &= \frac{\sqrt{30}}{10} (Q_{\theta}^2 + Q_{\varepsilon}^2) - \frac{\sqrt{30}}{15} (Q_{\xi}^2 + Q_{\eta}^2 + Q_{\zeta}^2), \\ R_x^G &= -\frac{\sqrt{3}}{3} Q_{\theta} Q_{\varepsilon} + Q_{\varepsilon} Q_{\xi} + \frac{\sqrt{6}}{3} Q_{\eta} Q_{\zeta}, \\ R_y^G &= -\frac{\sqrt{3}}{3} Q_{\theta} Q_{\eta} - Q_{\varepsilon} Q_{\eta} + \frac{\sqrt{6}}{3} Q_{\xi} Q_{\zeta} \end{aligned} \quad (12)$$

and

$$R_z^G = -\frac{2\sqrt{3}}{3} Q_{\theta} Q_{\zeta} + \frac{\sqrt{6}}{3} Q_{\xi} Q_{\eta} \quad (13)$$

in terms of the bases a , x , y , and z . In the above definitions, V_G , V_H , and V_{quad} are the coupling constants for the G , H linear terms and the quadratic term, respectively.

The $C_{A\lambda}^A$ are the Clebsch–Gordan (CG) coupling coefficients for the icosahedral system [28]. There is more than one quadratic term produced by the G and H modes. These quadratic terms can be derived from the CG coefficients. We add one of these terms to the Hamiltonian to show that the quadratic $G \otimes (g \oplus h)$ system can have a non-degenerate ground vibronic state with a realistic choice of coupling constants.

Ceulemans and Fowler [29] have derived the extremal properties of the APES surface of the $G \otimes (g \oplus h)$ system. There are four types of extrema: T minima (with α orbits), D_3 minima (with β orbits), D_3 saddle points (with γ orbits) and D_2 saddle points (with δ orbits). For a dominant JT stabilization from the G mode, the system has T minima (α orbits) only. For a dominant H mode, the system has D_3 minima (β orbits). The result of the linear problem shows the possibility of a non-degenerate ground state derived from D_3 well states. Thus here we consider only the situation when H modes dominate.

The energies of the vibronic states have been calculated analytically by the shift transformation method developed initially by Bates *et al.* [24]. Consider now the quadratic coupling term as a perturbation on the linear system. The resultant energies have similar forms to those of the linear system namely:

$$E_A = \frac{E'_{11} + 3E'_{12} + 6E'_{13}}{1 + 3S_{12} + 6S_{13}}, \quad E_G = \frac{E'_{11} - 2E'_{12} + E'_{13}}{1 - 2S_{12} + S_{13}} \quad (14)$$

Here E_A and E_G are the energies of the A and G vibronic states, respectively. The two overlaps S_{12} , S_{13} between the ground states within the D_3 well states are given by

$$S_{12} = -\frac{2}{3} \exp\left(-\frac{5}{54}k_G^2 - \frac{10}{27}k_H^2\right) \quad (15)$$

and

$$S_{13} = \frac{1}{6} \exp\left(-\frac{5}{108}k_G^2 - \frac{20}{27}k_H^2\right) \quad (16)$$

with

$$k_G = -\frac{V_G}{\sqrt{2\mu_G\hbar\omega_G^3}} \quad (17)$$

and

$$k_H = -\frac{V_H}{\sqrt{2\mu_H\hbar\omega_H^3}} \quad (18)$$

The matrix elements of H between the ground states in the wells are E'_{11} , E'_{12} , and E'_{13} . They are the sums of the corresponding matrix elements of the linear system E_{11} , E_{12} , and E_{13} and the corrections due to the contributions from the quadratic terms Δ_{11} , Δ_{12} , and Δ_{13} such that

$$E'_{11} = E_{11} + \Delta_{11}, \quad E'_{12} = E_{12} + S_{12}\Delta_{12} \quad \text{and} \quad E'_{13} = E_{13} + S_{13}\Delta_{13} \quad (19)$$

with

$$\begin{aligned} E_{11} &= 2\hbar\omega_G\left(1 - \frac{1}{36}k_G^2\right) + \frac{5}{2}\hbar\omega_H\left(1 - \frac{2}{9}k_H^2\right), \\ E_{12} &= S_{12}\left(\hbar\omega_G\left(2 - \frac{4}{27}k_G^2\right) + \frac{5}{2}\hbar\omega_H\left(1 - \frac{10}{27}k_H^2\right)\right) \end{aligned} \quad (20)$$

and

$$E_{13} = S_{13}\left(\hbar\omega_G\left(2 - \frac{11}{108}k_G^2\right) + \frac{5}{2}\hbar\omega_H\left(1 - \frac{14}{27}k_H^2\right)\right) \quad (21)$$

with

$$\Delta_{11} = -\frac{8\sqrt{10}}{81}k_H^2k_Q\hbar\omega_G, \quad \Delta_{12} = -\frac{4\sqrt{10}}{27}k_H^2k_Q\hbar\omega_G \quad (22)$$

and

$$\Delta_{13} = -\frac{16\sqrt{10}}{81}k_H^2k_Q\hbar\omega_G \quad (23)$$

Also

$$k_Q = \frac{V_{\text{quad}}}{2\mu\omega_G\omega_H} \quad (24)$$

The tunneling splitting between the lowest two vibronic states is thus given by

$$\delta = E_A - E_G \quad (25)$$

The above expressions for the energies are calculated by supposing that the D_3 extrema are absolute minima. When the D_3 extrema lie on the lowest sheet of the APES, the condition

$$\Delta = -\frac{2}{9}k_G^2\hbar\omega_G + \frac{16}{9}k_H^2\hbar\omega_H - \frac{16}{81}\sqrt{10}k_H^2k_Q\hbar\omega_G > 0 \quad (26)$$

should be fulfilled. Here Δ is the energy difference between the lowest two sheets of the APESs at the D_3 minima. It can be easily verified that, when $\Delta > 0$, the JT stabilization energy E_{JT} of the H mode is larger than that of the G mode and the D_3 extrema are absolute minima. Thus the energy expressions are valid when the condition given in equation (26) is satisfied. Figure 3 shows the region where δ is negative and the results are valid. This gives the range of coupling constants values when the crossover of the ground states from the G state to the A state occurs.

The crossover in the quadratic $G \otimes (g \oplus h)$ system can be explained by arguments similar to those given in Ref. [6]. In strong coupling, the overlaps S_{12} , S_{13} of the well states [equations (15) and (16)] are small so that the energy expression in equation (14) can be approximated to

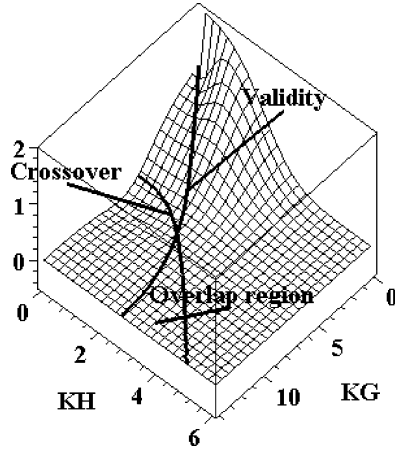


Fig. 3. The tunneling splitting δ (vertical axis) between the G and A states as a function of the linear coupling constants K_G and K_H for states associated with D_{3d} wells. The two curves on the surface mark the region where the G vibronic state crosses the A vibronic state and the region where the D_{3d} extrema are wells on the lowest APES, respectively. The region marked 'Overlap' is where δ has negative values and the ground state has A symmetry and the results are physically acceptable.

$$\begin{aligned} E_A &\approx E'_{11}(1 - 3S_{12} - 6S_{13}) + 3E'_{12} + 6E'_{13} \\ E_G &\approx E'_{11}(1 + 2S_{12} - S_{13}) - 2E'_{12} + E'_{13} \end{aligned} \quad (27)$$

Thus the tunneling splitting then approximates to

$$\delta \approx 5(E'_{12} - E'_{11}S_{12}) + 5(E'_{13} - E'_{11}S_{13}) \quad (28)$$

In the Born–Oppenheimer approximation, the n th well state $\Psi_n(r, Q)$ for the well centered at the point Q_n is given by the product of the electronic wave function $\varphi_0(r, Q)$ and the wave function $\Phi_0(Q - Q_n)$ of the nuclear vibrations so that

$$\Psi_n(r, Q) = \varphi_0(r, Q)\Phi_0(Q - Q_n) \quad (29)$$

where r and Q are the electronic and nuclear coordinates, respectively. In the strong coupling case, the potential well is precipitous and the function $\Phi_0(Q - Q_n)$ is a sharp function which enables us to approximate $\varphi_0(r, Q)$ to the electronic wave function at the minimum namely $\varphi_0(r, Q_n)$. By using such approximate wave functions as bases for the matrix elements, equation (28) becomes

$$\delta \approx 5s_{12}\Gamma_{12} + 5s_{13}\Gamma_{13} \quad (30)$$

where

$$s_{mn} = \langle \varphi_0(r, Q_m) | \varphi_0(r, Q_n) \rangle \quad (31)$$

and

$$\Gamma_{mn} = \langle \Phi_0(Q - Q_m) | \mathcal{H} | \Phi_0(Q - Q_n) \rangle - \langle \Phi_0(Q - Q_m) | \Phi_0(Q - Q_n) \rangle \times \langle \Phi_0(Q - Q_m) | \mathcal{H} | \Phi_0(Q - Q_m) \rangle \quad (32)$$

Here Γ_{mn} is a function of the nuclear coordinates only and represents the splitting due to the effect of tunneling between the potential well m and the well n . Also s_{mn} is the overlap of electronic wave functions at the bottom of the wells m and n .

An important feature of Γ_{mn} and s_{mn} in the $G \otimes (g \oplus h)$ JT system is that they both have one of two possible values amongst all pairs of wells. Each value corresponds to one type of tunneling. There are 10 D_3 potential wells. For each well, there are three neighboring wells and six other wells at a larger distance as illustrated in Fig. 4 and there exist two possible tunneling paths. For well 1, one kind of path goes to one of the nearest neighbor wells (labeled 2, 7, 8 in the figure) with a tunneling splitting Γ_{12} ; the other path goes to one of the next nearest neighbor wells (labeled 3, 4, 5, 6, 9, 10) with a corresponding tunneling splitting of Γ_{13} . The electronic overlaps are:

$$s_{12} = -\frac{2}{3}, \quad s_{13} = \frac{1}{6} \quad (33)$$

Thus

$$\delta \approx -\frac{10}{3}\Gamma_{12} + \frac{1}{6}\Gamma_{13} \quad (34)$$

The different signs for s_{12} and s_{13} show that the path from well 1 to well 2 has a Berry phase sign change and the path from well 1 to well 3 is Berry phase free.

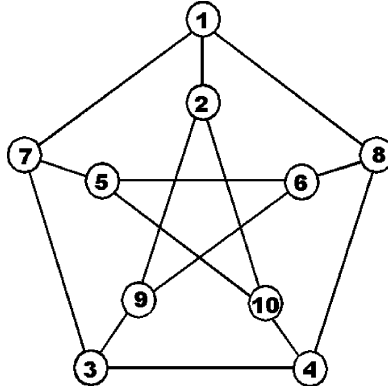


Fig. 4. The Petersen graph for the topology of the $G \otimes (g \oplus h)$ JT surfaces for preferential H coupling by Ceulemans and Fowler [29]. The numbered 10 vertices of the graph represent the 10 trigonal minima (β orbits). The centers of the edges represent the D_2 saddles (δ orbits). There are two types of tunneling between wells: one between adjacent wells (minima connected with edges in the graph); the other between non-adjacent wells.

Thus tunneling from well 1 to well 3 has a positive contribution to δ but tunneling from well 1 to well 2 has a negative contribution to δ , which makes the crossover possible.

5. CONCLUSIONS

We have analyzed the tunneling paths in the $T \otimes (e \oplus t_2)$ JT system and found that only one type of path is physically possible when the t_2 vibrational dominates, showing that a non-degenerate ground state is unlikely in this situation. As noted earlier, this conclusion may need modification if the non-adiabatic terms were considered. Calculations of the energies of the low-lying vibronic states of the $G \otimes (g \oplus h)$ JT problem in which quadratic coupling terms have been included as perturbations have also been described. A crossover from the degenerate ground state to the non-degenerate ground state was also found in this latter system with reasonable values of the coupling strengths. We have shown that the crossover is due to competing contributions of two types of tunneling paths on the APES associated with different Berry phase changes.

REFERENCES

- [1] I. B. Bersuker and V. Z. Polinger, in *Vibronic Interactions in Molecules and Crystals*, Springer, Berlin, 1989
- [2] C. P. Moate, M. C. M. O'Brien, J. L. Dunn, C. A. Bates, Y. M. Liu and V. Z. Polinger, *Phys. Rev. Lett.*, 1996, **77**, 4362.
- [3] P. De Los Rios, N. Manani and E. Tosatti, *Phys. Rev. B*, 1996, **54**, 7157.
- [4] H. Koizumi and I. B. Bersuker, *Phys. Rev. Lett.*, 1999, **83**, 3009.
- [5] H. Koizumi, I. B. Bersuker, J. E. Boggs and V. Z. Polinger, *J. Chem. Phys.*, 2000, **112**, 8470.
- [6] V. Z. Polinger, R. Huang, J. L. Dunn and C. A. Bates, *J. Chem. Phys.*, 2002, **117**, 4340.
- [7] G. Herzberg and H. C. Longuet-Higgins, *Discuss. Faraday Soc.*, 1963, **35**, 77.
- [8] M. V. Berry, *Proc. R. Soc. Lond. A*, 1984, **392**, 45.
- [9] F. S. Ham, *Phys. Rev. Lett.*, 1987, **58**, 725.
- [10] F. S. Ham, *J. Phys.: Condens. Matter*, 1990, **2**, 1163.
- [11] M. C. M. O'Brien, *J. Phys. A: Math. Gen.*, 1989, **22**, 1779.
- [12] N. Manini and P. De Los Rios, *Phys. Rev. B*, 2000, **62**, 29.
- [13] J. P. Cullene and M. C. M. O'Brien, *J. Phys.: Condens. Matter*, 1994, **6**, 9017.
- [14] C. C. Chancy and M. C. M. O'Brien, in *The Jahn–Teller Effect in C_{60} and Other Icosahedral Complexes*, Princeton, University Press Princeton, New Jersey, 1997, Chapter 4.
- [15] P. L. Kapur and R. Peierls, *Proc. R. Soc. A*, 1937, **163**, 606.
- [16] L. D. Landau, E. M. Lifshitz, *A Shorter Course of Theoretical Physics Mechanics*, Pergamon, Oxford, 1972, Vol. 1, Chapter 3, Section 10.
- [17] R. P. Feynman and A. R. Hibbs, in *Quantum Mechanics and Path Integrals*, McGraw-Hill, New York, 1965.
- [18] Z. H. Zhang, T. E. Feuchtwang, P. H. Cutler and E. Kazes, *Phys. Rev. A*, 1990, **41**, 32.
- [19] V. Z. Polinger, *Sov. Phys.: Solid State*, 1974, **16**, 2578.
- [20] M. C. M. O'Brien, *Tunneling in Several Dimensions: The Jahn–Teller Systems $T \otimes t_2$ and $H \otimes h$* , unpublished data.

- [21] R. Weinstock, in *Calculus of Variations*, McGraw-Hill, New York, Toronto, London, 1952, Chapter 3.
- [22] M. C. O'Brien, *Phys. Rev.*, 1969, **187**, 187.
- [23] I. B. Bersuker and V. Z. Polinger, *Sov. Phys. JEPT*, **39**, 1023.
- [24] C. A. Bates, J. L. Dunn and E. Sigmund, *J. Phys. C: Solid State Phys.*, 1987, **20**, 1965.
- [25] J. L. Dunn, *J. Phys. C: Solid State Phys.*, 1988, **21**, 383.
- [26] G. Bevilacqua, I. B. Bersuker and L. Martinelli, in *Vibronic Interactions: Jahn–Teller Effect in Crystals and Molecules* (eds M. D. Kaplan and G. O. Zimmerman), NATO Science Series II, Kluwer, The Netherlands, 2000, Vol. 39, p. 229.
- [27] M. Abou-Ghantous, P. B. Oliete, C. A. Bates, J. L. Dunn, V. Z. Polinger, R. Huang and S. P. Rough, *J. Phys.: Condens. Matter*, 2002, **14**, 4679.
- [28] P. W. Fowler and A. Ceulemans, *Mol. Phys.*, 1985, **54**, 767.
- [29] A. Ceulemans and P. W. Fowler, *Phys. Rev. A*, 1989, **39**, 481.

The Electronic Non-Adiabatic Coupling Terms: On the Connection between Molecular Physics and Field Theory

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Abstract

In this chapter we discuss the close relationship between the Born–Oppenheimer treatment of molecular systems and field theory as applied to elementary particles. The theory is based on the Born–Oppenheimer non-adiabatic coupling terms which are known to behave as vector potentials in electromagnetic dynamics. Treating the time-dependent Schrödinger equation for the electrons and the nuclei we show that enforcing diabatization produces for non-Abelian time-dependent systems the ‘four-component’ Curl equation as obtained by Yang and Mills (Phys. Rev. 95, 631 (1954)).

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1. INTRODUCTION

Mentioning gauge transformation or gauge invariance to nowadays theoretical chemists is just like mentioning it to the theoretical physicists about 70 years ago [1]. Gauge transformations were known to play a role in electromagnetic theory and even there only as a tool to simplify calculations [2]. Nowadays it is common knowledge that gauge transformations play a fundamental role in field theory, namely, serve as a tool to study the radiation field of elementary particles such as gravitational field, electro-magnetic field, massive vector meson field of the weak interactions and colored gluon field of the strong interaction. Having said all that it is not clear how these concepts have anything to do with the study of molecular systems, which are characterized by the fact that they are governed by the established Coulomb potentials and are well described by the Schrödinger equation (SE). It is true that one may think that since the Coulomb potentials have their origin in charged particles (i.e., electrons, protons) there could be a connection but it is well known that field theory is interested in what happens in the close vicinity of the electrons and even ‘inside’ the electrons but the study of molecular systems is not interested in this particular aspect at all.

An eventual connection is formed due to the Born–Oppenheimer–Huang (BOH) [3,4] treatment. Within this treatment Born and Oppenheimer distinguished between the fast moving electrons and the slow moving nuclei and presented the total wave function (of the nuclei and the electrons) in the form:

$$\Psi(e, \nu) = \sum_{j=1}^N \psi_j(\nu) \zeta_j(e|\nu) \quad (1)$$

where ν and e stand for nuclear and electronic coordinates, respectively, $\psi_j(\nu)$ is the j th nuclear-coordinate-dependent coefficient (recognized as the j th nuclear wave function) and $\zeta_j(e|\nu)$, is the j th electronic wave functions, assumed to be the eigenfunction of the electronic Hamiltonian $H_e(e|\nu)$:

$$(H_e(e|\nu) - u_j(\nu))\zeta_j(e|\nu) = 0; \quad j = 1, \dots, N \quad (2)$$

Here $u_j(\nu)$ is the j th (adiabatic) potential energy surface (PES) that governs the motion of the nuclei on this electronic level. Although being a straightforward treatment it was revealed, some time later by Longuet-Higgins (LH) [5–7], that the above mentioned BO eigenfunctions may possess an unexpected feature, namely, they are not always single-valued functions in *configuration space* once calculated for a *fixed set of electronic coordinates*. LH, without referring to the source of this multi-valuedness, went one step further and suggested to correct this deficiency in an *ad hoc* manner and multiplied the electronic eigenfunctions by a nuclear phase factor $\exp\{i(\theta/2)\}$ where θ is a polar angle defined in the range $[0, 2\pi]$ and in this way to enforce the single-valuedness. This, essentially harmless, idea was a few years later employed to construct an *ad hoc* framework for treating the nuclear dynamics [8]. Moreover, efforts were made to connect this feature with findings in

other areas in physics (e.g. the Aharonov–Bohm phase [9]). The main difficulty with this approach is that it was never analyzed physically and therefore the multi-valuedness was not attributed to any physical source.

As is noticed the above BOH treatment yields the adiabatic PES but as it turns out, it also yields another type of physical magnitudes, namely, the non-adiabatic coupling terms (NACT). Although some of the features of the NACTs are known for a long time, in particular the possibility of them becoming singular [10], they were never considered as magnitudes of fundamental importance. In fact even in processes like charge transfer [11] where one would expect them to play a dominant role they were ignored [12] due to the ingenious semi-classical Landau-Zener formula [13], which circumvented the need to employ the NACTs.

The NACTs are derivative couplings and as such are vectors (in contrast to PESs which are scalars) defined as follows:

$$\tau_{ji} = \langle \zeta_j | \nabla \zeta_i \rangle, \quad i, j = \{1, \dots\} \quad (3)$$

where the grad operator is expressed with respect to the nuclear coordinates. The NACTs become apparent following the derivation of the nuclear SE. Assuming the BOH eigenfunctions span a whole Hilbert space the relevant nuclear SE becomes [14]:

$$-\frac{\hbar^2}{2m}(\nabla + \boldsymbol{\tau})^2 \boldsymbol{\Psi} + (\mathbf{u} - E)\boldsymbol{\Psi} = 0 \quad (4)$$

where $\boldsymbol{\tau}$ is an anti-symmetric matrix which contains the NACTs defined in equation (3), $\mathbf{u}$ is a diagonal matrix that contains the nuclear PESs (introduced in equation (2)), $\boldsymbol{\Psi}$ is a column vector that contains the nuclear wave functions to be solved, e is the energy and m is the mass of the system (it is assume that the grad operator is defined with respect to mass scaled coordinates).

2. THE TREATMENT OF ATOM–ATOM SYSTEMS

As is noticed equation (4) becomes complicated if one keeps the NACTs. Born and Oppenheimer argued that in general the NACTs are relatively small (they are expected to be proportional to $(m_e/m)^{(1/2)}$, thus reducing their relative magnitudes by ~ 50 [15]) and therefore suggested to ignore them, at least, for low enough energies. In this way is formed the well known BO approximation. As for higher energies, it was suggested [14] to rigorously eliminate the NACTs (more details are given in Section 3) and in this way to maintain the simplicity of the approximated BO–SE. While studying diatom systems (characterized by a single radial nuclear coordinate, ρ) Smith managed to derive a new SE free of NACTs and reached what is known as the diabatic representation [16] (sometime later this transformation was

termed adiabatic-to-diabatic transformation (ADT)). Thus:

$$-\frac{\hbar^2}{2m} \nabla^2 \Phi + (\mathbf{W} - E) \Phi = 0 \quad (5)$$

where $\mathbf{W}$ is the diabatic potential matrix given in the form:

$$\mathbf{W} = \mathbf{A}^\dagger \mathbf{u} \mathbf{A} \quad (6)$$

Here $\mathbf{A}$, defined as the adiabatic-to-diabatic transformation matrix (ADTM), is the solution of the radial (single coordinate) first order differential equation [14]:

$$\frac{\partial}{\partial \rho} \mathbf{A} + \boldsymbol{\tau} \mathbf{A} = 0 \quad (7)$$

The Smith transformation as performed for the atom–atom systems is interesting but does not point at any unusual features just because the atom–atom system is too limited in its scope (possessing only one single radial coordinate). As we shall see next the novel features that show up due to the Smith ADT are closely related to the fact that the NACTs may become singular. However, the atom–atom systems are characterized by the non-crossing rule [17] which guarantees the analyticity of the NACTs and therefore prevents them from becoming singular. Thus, enhanced interest in the Smith ADT may take place only in case of poly-atomic systems characterized by several internal coordinates.

3. THE TREATMENT OF POLY-ATOMIC SYSTEMS – THE TIME-INDEPENDENT APPROACH

3.1. The non-adiabatic coupling term as a vector potential

Having singular NACTs is a computational difficulty but there is more to it than that. It turns out that the *singular* NACTs produce non-local effects thus bringing into molecular physics a new subject, namely, topological effects which are effects due to geometry. Geometry plays, in general, a passive role in physics by providing the stage on which physical processes take place. The same applies to molecular systems; however, once such a system contains singular NACTs this fact changes the geometrical aspect of the system and the processes to be treated. As will be seen the NACTs play the same role as the radiation fields in particle physics, in particular the better known electromagnetic vector potential.

Just by considering equation (4) one may speculate that the NACTs might be similar to the electromagnetic vector potential, $\mathbf{S}$. It is known from classical mechanics that the momentum $\mathbf{p}$ of a charged particle in an electromagnetic field changes to $\mathbf{p} \rightarrow \mathbf{p} + e\mathbf{S}$ – a substitution termed as the *minimal principle* [1]. Due to the correspondence principle the quantum mechanical minimal principle becomes $\nabla \rightarrow \nabla + i(e/\hbar)\mathbf{S}$. However, the NACTs in equation (4), when considering each element separately, do not combine with ∇ (because the

$\boldsymbol{\tau}$ -matrix is an anti-symmetric matrix) and therefore do not fulfill the minimal principle. Nevertheless, to see how the minimal principle can be fulfilled for the NACTs we consider the two-state case:

Recalling that $\boldsymbol{\tau}$ is given in the form:

$$\boldsymbol{\tau} = \begin{pmatrix} 0 & \tau_{12} \\ -\tau_{12} & 0 \end{pmatrix} \quad (8)$$

we transfer equation (4) employing the (constant) unitary transformation

$$\mathbf{G} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix} \quad (9)$$

so that it becomes [18]:

$$-\frac{\hbar^2}{2m}(\nabla + i\boldsymbol{\tau}_d)^2\boldsymbol{\Phi} + (\mathbf{w} - E)\boldsymbol{\Phi} = 0 \quad (10)$$

where $\boldsymbol{\tau}_d$ is a diagonal matrix:

$$\boldsymbol{\tau}_d = \begin{pmatrix} \tau_{12} & 0 \\ 0 & -\tau_{12} \end{pmatrix} \quad (11)$$

and $\mathbf{w}$ is the potential matrix:

$$\mathbf{w} = \frac{1}{2} \begin{pmatrix} w_1 + w_2 & w_1 - w_2 \\ w_1 - w_2 & w_1 + w_2 \end{pmatrix} \quad (12)$$

Due to this 2×2 constant transformation the minimal principle is fulfilled: $\nabla \rightarrow \nabla \pm i\boldsymbol{\tau}_{12}$ and $(\hbar/e)\boldsymbol{\tau}_{12}$ is recognized as a vector potential.

3.2. The diabatic representation

Just like the adiabatic framework, expressed in terms of equation (4), the diabatic one which avoids the NACTs altogether follows from the same basic observation, namely, that molecular systems contain fast and slow moving particles. However, instead of applying an electronic basis set which varies with the nuclear coordinates one may employ a single basis set as calculated at one point in configuration space. Following this idea it can be shown that the relevant SE is [19]:

$$-\frac{\hbar^2}{2m}\nabla^2\boldsymbol{\Theta} + (\mathbf{V} - E)\boldsymbol{\Theta} = 0 \quad (13)$$

where $\mathbf{V}$ is the potential matrix with the elements:

$$V_{ij}(\nu|\nu_0) = v_{ij}(\nu|\nu_0) + u_j(\nu_0)\delta_{ij} \quad (14)$$

and the $v_{ij}(\nu|\nu_0)$ element is defined as:

$$v_{ij}(\nu|\nu_0) = \langle \zeta_j(e|\nu_0) | U(e|\nu) - U(e|\nu_0) | \zeta_i(e|\nu_0) \rangle \quad (15)$$

where $U(e|\nu)$ is the sum of all Coulomb potentials

To summarize this part we notice that nuclear dynamics may be described either by employing the adiabatic SE in equation (4) or the diabatic one in equation (13). Both are suited for this task and the results, if solved using a large enough basis set, should be identical.

3.3. The adiabatic-to-diabatic transformation

The fact that the molecular system can be described within two different frameworks indicates that there must be a relation between them. Such relations are usually formed *via* a unitary transformation matrix $\mathbf{A}$ and since we talk about the adiabatic framework and the diabatic framework it is natural to term it as the ADT. Considering equation (4) we replace Ψ by Φ where the two are related:

$$\Psi = \mathbf{A}\Phi \quad (16)$$

Substituting equation (16) in equation (4), performing the usual algebra and demanding the elimination of the τ -matrix yields the following results:

- (a) The new (diabatic) SE is

$$-\frac{\hbar^2}{2m} \nabla^2 \Phi + (\mathbf{W} - E)\Phi = 0 \quad (17)$$

where the diabatic potential $\mathbf{W}$ is given by an equation similar to equation (6).

- (b) The ADT matrix has to be a solution of the first order differential equation [20]:

$$\nabla \mathbf{A} + \boldsymbol{\tau} \mathbf{A} = 0 \quad (18)$$

Equation (18) has to be solved along contours [20,21].

Assuming a contour, Γ , it can be shown that a solution in a given region, Λ , (in configuration space) is possible if the τ -matrix fulfills the following relation [19,20]:

$$\text{Curl } \boldsymbol{\tau} - [\boldsymbol{\tau} \times \boldsymbol{\tau}] = 0 \quad (19)$$

or more explicitly:

$$\frac{\partial}{\partial p} \boldsymbol{\tau}_q - \frac{\partial}{\partial q} \boldsymbol{\tau}_p - [\boldsymbol{\tau}_q, \boldsymbol{\tau}_p] = 0, \quad p, q = 1, n \quad (20)$$

where $\boldsymbol{\tau}_p$ and $\boldsymbol{\tau}_q$ are the p th and the q th components of $\boldsymbol{\tau}$ and n stands of the number of internal coordinates.

Equation (19) can be extended to include the points where the $\boldsymbol{\tau}$ matrix elements are singular [18,19]:

$$\mathbf{H} = \text{Curl } \boldsymbol{\tau} - [\boldsymbol{\tau} \times \boldsymbol{\tau}] \quad (21)$$

and in this form $\mathbf{H}$ acts like a Yang–Mills (YM) field [1,22,23] as derived for the conservation of the isotopic spin. Moreover just like in case of YM field here too the field is maintained by its sources namely the points of degeneracy [24] where the NACTs become singular [18,19]. Another interesting feature to be mentioned is that, just like in case of YM field, here too, equation (21) holds for the non-Abelian case. For the two-state case equation (21) reduces to:

$$\mathbf{H} = \text{Curl } \boldsymbol{\tau} \Rightarrow \mathbf{H} = \text{Curl } \boldsymbol{\tau}_{12} \quad (22)$$

because the 2×2 components of the $\boldsymbol{\tau}$ -matrix commute with each other which implies that the system becomes Abelian as is the case for the electromagnetic field.

Equation (19) is the sufficient condition for equation (18) to have a solution. The question to be asked is under what circumstances is equation (19) fulfilled. It can be shown that if the BO adiabatic eigenfunctions form a sub-Hilbert space equation (19) is satisfied [19,25]. In other words the diabatization can be carried out only for a group of states which form a sub-Hilbert space.

3.4. The quantization of the non-adiabatic coupling matrix

The fact that the BO treatments forms two frameworks, the adiabatic and the diabatic ones, and the fact that the two are related through a unitary transformation introduces one of the most exciting results of the present approach, namely, the *quantization* of the NACM. As we shall see the quantization is an outcome of the requirement that the diabatic potential matrix $\mathbf{W}$ as given in equation (6) has to be single-valued just like the diabatic potential matrix $\mathbf{V}$ given in equations (14) and (15). There is also a practical reason why $\mathbf{W}$ has to be single-valued because otherwise it is impossible to obtain any sensible solution for the nuclear SE.

In order to be able to calculate $\mathbf{W}$ we have first to calculate $\mathbf{A}$, namely, to derive the solution of equation (18). As mentioned earlier such a solution can be obtained along a given contour Γ . One way of writing the solution of equation (18) is [21]:

$$\mathbf{A}(s, s_0 | \Gamma) = \wp \exp \left(- \int_{s_0}^s ds' \cdot \boldsymbol{\tau}(s' | \Gamma) \right) \mathbf{A}(s_0) \quad (23)$$

where the dot stands for a scalar product between $\boldsymbol{\tau}(s)$ and a differential vector, ds , along Γ , and $\wp$ is a path ordering operator introduced to indicate that this integral has to be carried out in a given order [21]. Next we consider equation (23) for a closed contour Γ and define accordingly a new matrix – the $\mathbf{D}(\Gamma)$ -matrix:

$$\mathbf{D}(\Gamma) = \wp \exp \left(- \oint_{\Gamma} ds \cdot \boldsymbol{\tau}(s) \right) \quad (24)$$

It was shown by Baer and Alijah that the single-valuedness of $\mathbf{W}$ in the region surrounded by Γ is guaranteed if $\mathbf{D}(\Gamma)$ is diagonal [26]. Next, since $\mathbf{D}(\Gamma)$, just like

$\mathbf{A}(s|I)$, is a unitary matrix this implies that:

$$\mathbf{D}_{jk}(I) = \delta_{jk} \exp(i\chi_k(I)) \quad (25)$$

where the $\chi_k(I)$ s are real phases which usually are multiples of π .

Returning to the beginning of this Section we established the following: the *necessary* condition for the $\mathbf{A}$ -matrix to yield single-valued diabatic potentials is that the $\mathbf{D}$ -matrix, defined in equation (24), is diagonal and has, in its diagonal, numbers of norm 1. Since we consider only real electronic eigenfunctions these numbers can be either $(+1)$ s or (-1) s. The number of (-1) s in the diagonal is assigned as K and is termed as the topological number and since it may vary from contour to contour we write $K(I)$.

Following equation (23) it is also obvious that the $\mathbf{A}$ -matrix is not necessarily single-valued because the $\mathbf{D}$ -matrix, as was just proved, is not necessarily a unit matrix.

The quantization feature becomes transparent in the two-state case for which $\mathbf{A}$ can be written as:

$$\mathbf{A} = \begin{pmatrix} \cos \gamma_{12} & \sin \gamma_{12} \\ -\sin \gamma_{12} & \cos \gamma_{12} \end{pmatrix} \quad (26)$$

Here γ_{12} is called the ADT angle and it was shown to be [20]:

$$\gamma_{12}(I) = \int_{s_0}^s ds' \cdot \boldsymbol{\tau}_{12}(s'|I) \quad (27)$$

Accordingly we define $\alpha_{12}(I)$ as the value of γ_{12} calculated for the closed contour, I :

$$\alpha_{12}(I) = \oint_I ds \cdot \boldsymbol{\tau}_{12}(s) \quad (28)$$

and the corresponding $\mathbf{D}$ -matrix becomes:

$$\mathbf{D}(I) = \begin{pmatrix} \cos \alpha_{12} & \sin \alpha_{12} \\ -\sin \alpha_{12} & \cos \alpha_{12} \end{pmatrix} \quad (29)$$

Since $\mathbf{D}(I)$ has to be a diagonal matrix with $(+1)$ s and (-1) s, it is seen that $\alpha_{12}(I)$ has to fulfill the condition $\alpha_{12}(I) = n\pi$ where n is either odd or even (or zero) and therefore the only two possibilities for $\mathbf{D}$ are as follows:

$$\mathbf{D} = (-1)^k \mathbf{I} \quad (30)$$

where k is an integer. Recalling the definition for $K(I)$ it is seen that for a two-state system $K(I) = 0, 2$. Although in principle, each case may give a different k -value in fact the number of k -values is quite small. It can be shown to be either zero or an even number (see Ref. [19], Section 7). Thus, in case of two states it can be $K = 0, 2$ and the same applies to three states. The numbers $K = 1, 3$ are not allowed.

Along this analysis we hardly referred to points of degeneracy – also known as the points of conical intersections or simply conical intersections (CI) [15,27]. It can be shown that line integrals as presented in equation (28) yields a unit matrix if the closed

contour, Γ , does not surround any CI [28]. The situation changes once the region surrounded by Γ contains several CIs – either between the same two (adjacent) states or between several different pairs of (adjacent) states. For instance, if in case of two states, Γ surrounds one CI then $\alpha_{12} = \pi$, and if it surrounds two CIs between the same two states then we get either $\alpha_{12} = 0$ or 2π , etc. Further complications are expected in case of three (or more) states: Here we have situations where Γ surrounds CIs between one pair of states only (e.g. between the first and the second states) or some CIs between the first and the second state and several more between the second and the third states etc. (for a detailed discussion on this subject, see Ref. [29]).

In the numerical part, we discuss a few results related to CIs of the three lower electronic states for the $\text{H} + \text{H}_2$ system [30]. It was revealed that for a fixed HH distance, R_{HH} , these three states form either three or four CIs: one or two, between the two lower states and two, between the two upper states. The example to be discussed is formed by fixing $R_{\text{HH}} = 0.74 \text{ \AA}$ and presented in Fig. 1. For this

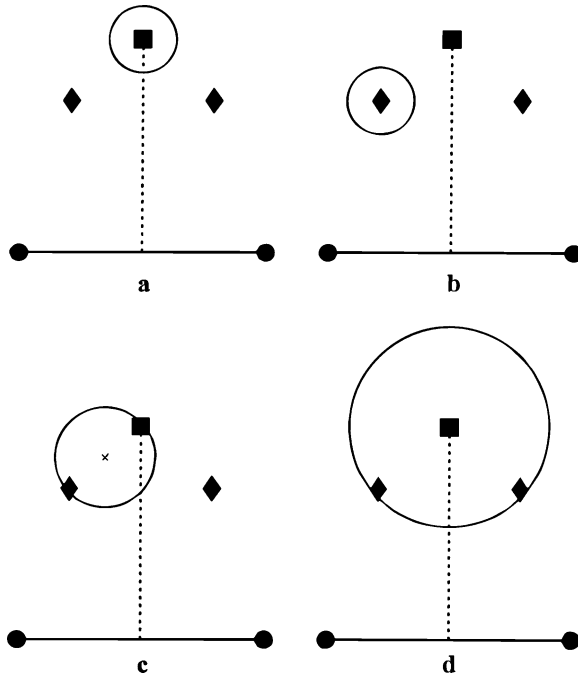


Fig. 1. The CIs and the contours for the $\text{H} + \text{H}_2$ system as calculated for $R_{\text{HH}} = 0.74 \text{ \AA}$. Full circles stand for the two fixed hydrogens, (full) squares stand for (1,2) CIs; (full) diamonds stand for (2,3) CIs and circles describe the closed contours. The straight line perpendicular to the HH axis connects the mid-point between the two hydrogens and the D_{3h} (1,2) CI point. (a) A circle surrounding the D_{3h} (1,2) CI; (b) A circle surrounding the C_{2v} (2,3) CI; (c) A circle surrounding the D_{3h} (1,2) CI and a C_{2v} (2,3) CI; (d) A circle surrounding the D_{3h} (1,2) CI and the two C_{2v} (2,3) CIs.

Table 1. Topological results as obtained for various contours surrounding conical intersections of the H + H₂ system as obtained for $R_{\text{HH}} = 0.74 \text{ \AA}$

Contour No.	$q \text{ (\AA)}$	α_{12}	α_{23}	D_{11}	D_{22}	D_{33}
a	0.10	3.145	0.0000	-0.9997	-0.9997	+1.0000
b	0.10	0.350	3.153	+0.9999	-0.9999	-1.0000
c	0.15	1.827	2.997	-0.9989	+0.9989	-1.0000
d	0.30	1.867	0.000	-0.9857	-0.9855	+0.9999

(a) Surrounding the $D_{3h}(1, 2)$ CI.

(b) Surrounding the sideway $C_{2v}(2, 3)$ CI.

(c) Surrounding two CI: the $D_{3h}(1, 2)$ CI and a $C_{2v}(2, 3)$ CI.

(d) Surrounding three CIs: the $D_{3h}(1, 2)$ CI and the two $C_{2v}(2, 3)$ CI.

situation we encounter the well known equilateral D_{3h} CI which couples the two lower states and the two C_{2v} CIs which couple the two higher states and are located on both sides of the D_{3h} symmetry line. Also shown in the figure are the various (circular) contours along which the line integral calculations were carried out. The two-state results, expressed in terms of the topological angles α_{12} and α_{23} and the three-state results expressed in terms of the three diagonal elements of the topological $\mathbf{D}$ -matrix are presented in Table 1. It is noticed that the two-state quantization (when the corresponding α_{12} and/or α_{23} become π) are obtained only for circles surrounding one CI and having a small enough radius $q (< 0.1 \text{ \AA})$. As q increases and two or three CIs become surrounded by a given circle the two-state quantization breaks down (thus, neither α_{12} nor α_{23} are equal to π) but, as is noticed the three-state quantization sets in (i.e., $\mathbf{D}_{jj} = \pm 1$) and seems to hold at least for the considered q -values (as large as $q = 0.3 \text{ \AA}$).

4. THE TREATMENT OF POLY-ATOMIC SYSTEMS – THE TIME-DEPENDENT APPROACH

4.1. Introductory comments

The starting point is the TD-SE for the total wave-function, Ψ [31,32]:

$$i\hbar \frac{\partial \Psi}{\partial t} = \left(-\frac{\hbar^2}{2m} \nabla^2 + \mathbf{H}_e \right) \Psi \quad (31)$$

and, following BOH, Ψ is presented in the form:

$$\Psi = \zeta^T \psi \quad (32)$$

(here ζ^T is a row vector, in contrast to ζ which is a column vector) and we assume

that ζ fulfills the following TD equation, namely:

$$i\hbar \frac{\partial \zeta}{\partial t} = \mathbf{H}_e \zeta \quad (33)$$

Substituting equations (32) and (33) in equation (31) yields the following TD equation for the nuclear wave-functions:

$$i\hbar \zeta^T \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 (\zeta^T \Psi) \quad (34)$$

As is noticed this equation is entirely dominated by the kinetic operator.

4.2. The time-dependent equation for the electronic component

Our next step is to write equation (33) in a more explicit way. In what follows it is assumed that each electronic ‘adiabatic’ wave function fulfills, independently, equation (33). Thus:

$$i\hbar \frac{\partial |\zeta_k\rangle}{\partial t} = \mathbf{H}_e |\zeta_k\rangle \quad (35)$$

where equation (35) is solved for the initial function which is identified with k th electronic eigenfunction of $\mathbf{H}_e$ at $t = 0$, i.e., $|\zeta_k(e|t = 0, \nu)\rangle$. To solve equation (35) the TD $|\zeta_k(e|t, \nu)\rangle$ is expanded in terms of the eigenfunctions of $\mathbf{H}_e$ as calculated at $t = 0$. Thus:

$$|\zeta_k(e|t, \nu)\rangle = \sum_{j=1}^L |\zeta_j(e|t = 0, \nu)\rangle \omega_{jk}(t|\nu) \quad (36)$$

Substituting equation (36) in equation (35) yields – for a sub-Hilbert space – the differential equation for $\omega(t|\nu)$:

$$i\hbar \frac{\partial \omega(t|\nu)}{\partial t} = \tilde{\mathbf{H}}_e(t|\nu) \omega(t|\nu) \quad (37)$$

where

$$\tilde{\mathbf{H}}_e(t|\nu)_{jk} = \langle \zeta_j(e|t = 0, \nu) | \mathbf{H}_e(e|t, \nu) | \zeta_k(e|t = 0, \nu) \rangle \quad (38)$$

The solution of equation (37) is given in the form:

$$\omega(t|\nu) = \wp \exp\left(-\frac{i}{\hbar} \int_0^t \tilde{\mathbf{H}}_e(t'|\nu) dt'\right) \quad (39)$$

where $\wp$ is now time-ordering operator (see also Ref. [211]) and it can be seen that at $t = 0$ the matrix $\omega(t|\nu)$ is the unit matrix. It is well noticed that $\omega(t|\nu)$, as presented in equation (39), is a unitary matrix.

4.3. The adiabatic time-dependent equation for the nuclear wave functions

Returning to equation (34) and evaluating the right hand side, one obtains

$$i\hbar\zeta^T \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \{ \zeta^T \nabla^2 \Psi + 2 \nabla \zeta^T \nabla \Psi + (\nabla^2 \zeta^T) \Psi \} \quad (40)$$

Multiplying equation (40) (from the left hand side) by $\zeta^\dagger(e|t, \nu)$ and integrating over the electronic coordinates we obtain:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} (\nabla + \tilde{\tau})^2 \Psi \quad (41)$$

where $\tilde{\tau}$ is a TD, *dressed*, non-adiabatic coupling matrix given in the form:

$$\tilde{\tau} = \omega^\dagger \tau \omega + \omega^\dagger \nabla \omega \quad (42)$$

Equation (41) which stands for the general adiabatic time-dependent nuclear equation is by itself of an interesting form because it misses the expected PES matrix.

Equation (41) is the required form of the (adiabatic) SE which will be diabitized in Section 4.4.

4.4. The time-dependent adiabatic-to-diabatic transformation

We apply again the ADT as presented in equation (16). Substituting equation (16) in equation (41) yields the following expression:

$$i\hbar \mathbf{A} \frac{\partial \Phi}{\partial t} = -\frac{\hbar^2}{2m} [\mathbf{A} \nabla^2 + 2(\mathbf{G}\mathbf{A}) \nabla + (\mathbf{G}^2 \mathbf{A})] \Phi - i\hbar \frac{\partial \mathbf{A}}{\partial t} \Phi \quad (43)$$

Here $\mathbf{G}$ is an operator which acts only on $\mathbf{A}$ and is given in the form:

$$\mathbf{G} = \nabla + \tilde{\tau} \quad (44)$$

To continue we add and subtract a yet undetermined matrix $\mathbf{B}$ multiplied by $\mathbf{A}\Phi$, so that equation (43) becomes

$$i\hbar \mathbf{A} \frac{\partial \Phi}{\partial t} = -\frac{\hbar^2}{2m} [\mathbf{A} \nabla^2 + 2(\mathbf{G}\mathbf{A}) \nabla + (\mathbf{G}^2 \mathbf{A})] \Phi + (\mathbf{F} - \mathbf{B}) \mathbf{A} \Phi \quad (45)$$

where $\mathbf{F}$ is an operator which acts only on $\mathbf{A}$ and is defined as:

$$\mathbf{F} = -i\hbar \frac{\partial}{\partial t} + \mathbf{B} \quad (46)$$

The $\mathbf{A}$ -matrix is chosen to be a simultaneous solution of the two following equations:

$$\mathbf{G}\mathbf{A} = 0 \quad (47a)$$

and

$$\mathbf{F}\mathbf{A} = 0 \quad (47b)$$

The derivation of this matrix follows by demanding that the elements of the solution-matrix of equations (47a) and (47b), once derived, have to be analytic functions at every point in a given ‘four-dimensional’ space–time region. This means that each element of the $\mathbf{A}$ -matrix has to be differentiable to any order with respect to all the spatial coordinates and with respect to time. In addition, analyticity requires the fulfillment of the following two conditions:

- (1) The results of two consecutive differentiations of the $\mathbf{A}$ -matrix with respect to two spatial coordinates, p and q , does not depend on the order of differentiation [20]. This requirement leads to a set of conditions similar to equation (19) (or (20)) but where $\boldsymbol{\tau}$ is replaced by $\tilde{\boldsymbol{\tau}}$ (see equation (42)).
- (2) The results of two consecutive differentiations of the $\mathbf{A}$ -matrix, one with respect to *time* and the other with respect to any spatial coordinate p , does not depend on the order of differentiation. This requirement implies

$$\frac{\partial}{\partial t}(\nabla\mathbf{A}) - \nabla\left(\frac{\partial}{\partial t}\mathbf{A}\right) = 0 \quad (48)$$

Substituting equations (44) and (46) in equations (47a) and (47b), activating the grad operator with respect to equation (47b) and differentiating equation (47a) with respect to t , subtracting the second equation from the first and demanding that equation (48) is fulfilled leads to the following equation that has to be fulfilled:

$$\{\nabla\mathbf{B} - \mathbf{B}\tilde{\boldsymbol{\tau}} - (\tilde{\mathbf{H}}_e\tilde{\boldsymbol{\tau}} - \tilde{\boldsymbol{\tau}}\tilde{\mathbf{H}}_e) + \nabla\tilde{\mathbf{H}}_e + \tilde{\boldsymbol{\tau}}\mathbf{B}\}\mathbf{A} = 0 \quad (49)$$

where $\tilde{\mathbf{H}}_e$ is defined as:

$$\tilde{\mathbf{H}}_e = \boldsymbol{\omega}^\dagger \tilde{\mathbf{H}}_e \boldsymbol{\omega} \quad (50)$$

It is noticed that the expression in the curled parentheses becomes identically zero if $\mathbf{B} = -\tilde{\mathbf{H}}_e$.

Having this result equations (47a) and (47b) become

$$\begin{aligned} \nabla\mathbf{A} + \tilde{\boldsymbol{\tau}}\mathbf{A} &= 0 \\ i\hbar\frac{\partial\mathbf{A}}{\partial t} + \tilde{\mathbf{H}}_e\mathbf{A} &= 0 \end{aligned} \quad (51)$$

which can be written in terms of a ‘four’ component vector:

$$\tilde{\nabla}\mathbf{A} + \tilde{\boldsymbol{\tau}}\mathbf{A} = 0 \quad (51')$$

where $\tilde{\nabla}$ is a ‘four’ component grad operator reminiscent of the expression [22]:

$$\tilde{\nabla} = \left\{ \frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, \dots, \frac{\partial}{\partial q_n}, i\hbar\frac{\partial}{\partial t} \right\} \quad (52)$$

and, similarly, $\tilde{\boldsymbol{\tau}}$ is recognized as a ‘four’ component vector–matrix:

$$\tilde{\boldsymbol{\tau}} = \{\tilde{\boldsymbol{\tau}}_{q_1}, \tilde{\boldsymbol{\tau}}_{q_2}, \dots, \tilde{\boldsymbol{\tau}}_{q_n}, \tilde{\mathbf{H}}_e\} \quad (53)$$

Here $\tilde{\mathbf{H}}_e$ is the time component of $\tilde{\boldsymbol{\tau}}$. It is important to mention that in our case we do not have necessarily ‘four’ components but in general $(n + 1)$ components.

The corresponding ‘four’ component non-Abelian Curl equation which guarantees the existence of a solution for equation (51')) takes the form:

$$\frac{\partial}{\partial \mu'} \tilde{\boldsymbol{\tau}}_\mu - \frac{\partial}{\partial \mu} \tilde{\boldsymbol{\tau}}_{\mu'} - [\tilde{\boldsymbol{\tau}}_\mu, \tilde{\boldsymbol{\tau}}_{\mu'}] = 0, \quad \mu, \mu' = p, q, t/(i\hbar) \quad (54)$$

where p and q are spatial coordinates and $\tilde{\boldsymbol{\tau}}_t$, stands for the time component of $\tilde{\boldsymbol{\tau}}$, namely, $\tilde{\mathbf{H}}_e$. Equation (54) is reminiscent of the ‘four-component’ Yang–Mills non-Abelian Curl equation [22]. We would like also to mention that Engelman and Yahalom briefly discussed the possibility to extend the present author’s spatial Curl-equation to include the relevant time component [23] similar to equation (54).

It can be shown that the solution of equation (51) is a unitary matrix and as a result the diabatic SE is (see equation (45)) becomes

$$i\hbar \frac{\partial \Phi}{\partial t} = \left(-\frac{\hbar^2}{2m} \nabla^2 + \mathbf{W} \right) \Phi \quad (55)$$

where $\mathbf{W}$ is the ‘missing’ potential matrix:

$$\mathbf{W} = \mathbf{A}^\dagger \tilde{\mathbf{H}}_e \mathbf{A} \quad (56)$$

Equation (56) is similar to equation (6) except that $\tilde{\mathbf{H}}_e$ is not diagonal.

5. CONCLUSIONS

In this article, we discussed to what extent the time-dependent theory as applied to molecular systems is similar to field theory as applied to elementary particle [31,32]. Starting from the time-dependent Hamiltonian, which contains the electronic and the nuclear motions we followed the BO treatment with the aim of reaching the adiabatic SE for the nuclei. The result is equation (41) which essentially contains, in addition to the usual first order time derivative term, only a (shifted) kinetic energy term. This equation is characterized by two features: (1) it does not contain the usual potential energy term; (2) the momentum operator is not shifted by the regular NACM $\boldsymbol{\tau}$ but by a kind of an extended dressed NACM $\tilde{\boldsymbol{\tau}}$ as presented in equation (42). So far, the results are an outcome of straightforward algebra. The more interesting part emerges once we proceed one step further and carryout the diabatization. In the time-independent framework the diabatization enforced the curl equation given in equation (20) (or (21)) and later revealed the quantization of the NACM as presented in equations (24) and (25).

The diabaticization within the time-dependent framework produced the expected potential matrix $\mathbf{W}$ presented in equation (56) but enforced the ‘four vector’ curl equation which is given in equation (54). This set of equations contains not only derivatives with respect to the spatial coordinates but also with respect to time. In fact this non-Abelian curl equation is completely identical to YM curl equation which has its origin in field theory.

The similarity between the two final expressions as derived in two different frameworks is a surprise because the physical systems are so different. However, the question is if we should be surprised. After all the basic assumption in both frameworks is the *minimal principle* which states that in order to employ the ordinary SE for charged particles all one has to shift ∇ by $\nabla \rightarrow \nabla + i(e/\hbar)\mathbf{S}$ where $\mathbf{S}$ is a vector potential.

As a final comment we would like to mention that the derivations as presented here apply for time-dependent perturbation caused, e.g. by (strong) electric fields which are characterized by having a zero vector potential. In case the perturbation is caused by magnetic fields [33] the corresponding vector potential has to be included according to the *minimal principle*.

REFERENCES

- [1] L. O’Raifeartaigh, *Dawning of Gauge Theory*, Princeton University Press, Princeton, NJ, 1997.
- [2] J. D. Jackson, *Classical Electrodynamics*, 3rd edn, Wiley, New York, 1998, Chap. 6.
- [3] M. Born and J. R. Oppenheimer, *Ann. Phys. (Leipzig)*, 1927, **84**, 457.
- [4] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford University, New York, 1954.
- [5] H. C. Longuet-Higgins, U. Opik, M. H. L. Pryce and R. A. Sack, *Proc. R. Soc. Lond. Ser. A*, 1958, **244**, 1.
- [6] H. C. Longuet-Higgins, *Adv. Spectrosc.*, 1961, **2**, 429.
- [7] G. Herzberg and H. C. Longuet-Higgins, *Discuss. Faraday Soc.*, 1963, **35**, 77; H. C. Longuet-Higgins, *Proc. R. Soc. Lond. Ser. A*, 1975, **344**, 147.
- [8] C. A. Mead, *Chem. Phys.*, 1980, **49**, 23.
- [9] Y. Aharonov and D. Bohm, *Phys. Rev.*, 1959, **115**, 485.
- [10] H. Hellmann, *Einführung in die Quantenchemie*, Franz Deuticke, Leipzig, 1937; R. Feynman, *Phys. Rev.*, 1939, **56**, 340.
- [11] M. Baer, in *State-to-State Ion Molecule Reaction Dynamics*, *Adv. Chem. Phys.* (eds M. Baer and C. Y. Ng), Vol. 2, 1992, 82, 187.
- [12] A. Bjerre and E. Nikitin, *Chem. Phys. Lett.*, 1967, **1**, 179; R. K. Preston and J. C. Tully, *J. Chem. Phys.*, 1971, **54**, 4297; J. C. Tully and R. K. Preston, *J. Chem. Phys.*, 1971, **55**, 562.
- [13] C. Zener, *Proc. R. Soc. Lond. Ser. A*, 1932, **137**, 696; L. D. Landau, *Phys. Z. Sowjetunion*, 1932, **2**, 46; H. Nakamura and C. Zhu, *Comments At. Mol. Phys.*, 1996, **32**, 249.
- [14] F. T. Smith, *Phys. Rev.*, 1969, **179**, 112.
- [15] B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, New York, 1989.
- [16] W. Lichten, *Phys. Rev.*, 1967, **164**, 131.
- [17] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, Pergamon Press, Oxford, 1965, pp. 262–266.
- [18] M. Baer, *Chem. Phys. Lett.*, 2001, **349**, 84.
- [19] M. Baer, *Phys. Rep.*, 2002, **358**, 75, Appendix D.
- [20] M. Baer, *Chem. Phys. Lett.*, 1975, **35**, 112.

- [21] M. Baer, *Mol. Phys.*, 1980, **40**, 1011.
- [22] C. N. Yang and S. N. Mills, *Phys. Rev.*, 1954, **95**, 631.
- [23] R. Englman and A. Yablonovitch, in *The Role of Degenerate States in Chemistry*, *Adv. Chem. Phys.* (eds M. Baer and G. D. Billing), Wiley, New York, 2002, Vol. 124, p. 197.
- [24] M. Baer and G. D. Billing (eds), *The Role of Degenerate States in Chemistry*, *Adv. Chem. Phys.*, Wiley, New York, 2002, Vol. 124.
- [25] M. Baer, *Chem. Phys. Lett.*, 2000, **259**, 123.
- [26] M. Baer and A. Alijah, *Chem. Phys. Lett.*, 2000, **319**, 489; M. Baer, *J. Phys. Chem. A*, 2000, **104**, 3181.
- [27] R. Englman, *The Jahn–Teller Effect in Molecules and Crystals*, Wiley (Interscience), New York, 1972.
- [28] M. Baer, *Phys. Rep.*, 2002, **358**, 75, Appendix C.
- [29] M. Baer, *Chem. Phys. Lett.*, 2000, **329**, 450.
- [30] G. Halasz, A. Vibok, A. M. Mebel and M. Baer, *J. Chem. Phys.*, 2003, **118**, 3052; see also G. Halasz, A. Vibok, A. M. Mebel and M. M. Baer, *Chem. Phys. Lett.*, 2002, **358**, 163.
- [31] R. Baer, D. J. Kouri, M. Baer and D. K. Hoffman, *J. Chem. Phys.* (in press).
- [32] M. Baer, *J. Phys. Chem. A*, 2003, **107**, 4724.
- [33] I. H. Zimmermann, J. M. Yuan and T. F. George, *J. Chem. Phys.*, 1977, **66**, 2638; I. Last, M. Baer, I. H. Zimmermann and T. F. George, *Chem. Phys. Lett.*, 1983, **101**, 163; I. Last and M. Baer, *J. Chem. Phys.*, 1985, **82**, 4954.

Nonadiabatic Coupling: General Features and Relation to Molecular Properties

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Abstract

The general features of the nonadiabatic coupling and its relation to molecular properties are surveyed. Some consequences of the ‘equation of motion’, formally expressing a ‘smoothness’ of a given molecular property within the diabatic basis, are demonstrated. A particular emphasis is made on the relation between a ‘smoothness’ of the electronic dipole moment and the generalized Mulliken–Hush formula for the diabatic electronic coupling.

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1. INTRODUCTION

Myriads of molecular processes evolve on two or more adiabatic potential energy surfaces (PESs) approaching each other rather closely and eventually intersecting along crossing seam(s) [1]. Such a crossing was first thought by Landau [2], Zener [3], and Stueckelberg [4] to be a primary source of inelastic transitions. Its treatment within the Born–Oppenheimer [5] or Born–Huang–Oppenheimer approximation [6], based on a partitioning of the total Hamiltonian into the

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electronic Hamiltonian H_{el} and the kinetic energy operator T_{n} of the nuclei, and taking the large difference in masses of electrons and nuclei into account, naturally demands the separate solution of electronic and nuclear problems. The former induces a parametric dependence of the Hilbert space $\mathfrak{H}_{\text{el}}$ of electronic wave functions on the nuclear geometry, either ‘frozen’ (the nuclei are clamped) or ‘moving’.

A physically sound model of a ‘moving’ nuclear geometry of a given molecular system, evolving on two or more potential energy surfaces, leads to the appearance of a so-called nonadiabatic coupling (NAC) in the nuclear Schrödinger equation, which is actually responsible for coupling of the PESs under study [1,7–18 and references therein]. The NAC is a nonlocal off-diagonal operator, which becomes singular along the crossing seam, and hence it grossly complicates a solution of the nuclear Schrödinger equation. Traditionally, such a problem has been thought to be resolved by choosing, instead of the *adiabatic* basis in $\mathfrak{H}_{\text{el}}$, consisting of the eigenfunctions of H_{el} , another one, a so-called *diabatic* [1,7–20], which removes either the singular component of the NAC (a *diabatic I* basis) or it completely (*diabatic II* or *strictly diabatic* basis).

Adiabatic and diabatic bases are interconverted by some orthogonal transformations [1,7–18]. Despite wide use of the idea of a diabatic basis, the existence of a strictly diabatic one or, in other words, the existence of such orthogonal transformation that transforms the adiabatic basis to the latter, has recently become a rather debated topic [21–24] since the seminal works by McLachlan [7], Baer [12], Mead and Truhlar [13], and Cederbaum, Köoppel, Domcke and co-workers [14]. Mead and Truhlar [13a] particularly proved that, on the one hand, there does exist only a *diabatic I* basis for the two electronic states, coupled to the bath of the others (the generalized two-state problem or simply the two-state problem in the present context), where the so-called longitudinal component of the NAC, embodying its singularity, is eliminated and, on the other hand, a *strictly diabatic* basis does not exist because the transverse component of the NAC cannot be removed (see also Ref. [12a]). Their work has led to the development of some approximate computational techniques to handle the removable and nonremovable components of the nonadiabatic coupling and to defining approximate (‘quasidiabatic’, ‘most diabatic’, ‘locally diabatic’) basis sets which ‘rigorously’ eliminates the NAC singularity at a conical intersection and at an intersection of seams [25–43 and references therein]. Among them, in particular, are the so-called block-diagonalization method developed by Cederbaum and co-workers [14, 40a–d] and Domcke and co-workers [40e–f], the use of quasidegenerate perturbation theory as suggested by Spiegelmann and Malrieu [39] and the occupation probabilities of natural spin orbitals [38].

The other techniques can be divided into a few categories (see also Ref. [14c]). One of them goes back to the idea first coined by Mulliken [41], Hush [42] and Lichten [8] of using molecular properties to determine the diabatic basis and is actually based on the Werner–Meyer–Macías–Riera formula [32,33] for the adiabatic-to-diabatic mixing angle in terms of electronic dipole moments. This

formula received a wide range of applications [34] including its generalization to quadrupole moments. A similar formula that expresses the mixing angle in terms of angular momentum operator for the states $1^2A'$, $2^2A'$, and $2^2A''$ was derived by Rebertrost and Lester [35] and was further applied by Peyerimhoff and co-workers [34d] and Alexander [36]. We may refer to this category as being related to a smoothness of molecular property [37]. Another category requires a smoothness of wave functions or, equivalently, its configurational uniformity. This approach has been developed by Ruedenberg and his co-workers [28] (see also recent work by Nakamura and Truhlar [43]).

2. NONADIABATIC COUPLING: KEY PROPERTIES

NAC appears in the nuclear Schrödinger equation in the following manner. Let us first deal with the electronic eigenvalue problem

$$H_{\text{el}}\Phi_k(\mathbf{r}; \mathbf{R}) = E_k(\mathbf{R})\Phi_k(\mathbf{r}; \mathbf{R}) \quad (1)$$

where $H_{\text{el}} = T_{\text{el}} + V_{\text{ee}} + V_{\text{en}} + V_{\text{nn}}$ is the sum of the electronic kinetic energy operator T_{el} , interelectronic Coulomb potential V_{ee} and electron–nuclear and nuclear–nuclear Coulomb interaction potentials V_{en} and V_{nn} , respectively, and where $\mathbf{r}$ and $\mathbf{R}$ collectively stand for the coordinates of the N electrons and of the $\alpha = 1, \dots, M$ nuclei, respectively, of the given system (their spins are excluded). In equation (1), $\Phi_k(\mathbf{r}; \mathbf{R})$ is the real valued k th electronic eigenfunction of H_{el} corresponding to the eigenvalue E_k . All Φ_k form an *adiabatic* basis set. Together with E_k , they parametrically depend on the nuclear configuration space $\mathfrak{R}_n^{3M}$. Such parametric dependence is indicated by a semicolon.

Applying the gradient operator $\nabla_{\mathbf{R}_\alpha}$ with $\alpha \in \{1, \dots, M\}$ to equation (1), one obtains

$$\begin{aligned} & (\nabla_{\mathbf{R}_\alpha} H_{\text{el}})\Phi_k(\mathbf{r}; \mathbf{R}) + H_{\text{el}}[\nabla_{\mathbf{R}_\alpha} \Phi_k(\mathbf{r}; \mathbf{R})] \\ &= [\nabla_{\mathbf{R}_\alpha} E_k(\mathbf{R})]\Phi_k(\mathbf{r}; \mathbf{R}) + E_k(\mathbf{R})[\nabla_{\mathbf{R}_\alpha} \Phi_k(\mathbf{r}; \mathbf{R})] \end{aligned} \quad (2)$$

and (see, e.g. Ref. [44])

$$\mathbf{f}_{kl}^{(\alpha)} = \langle\langle \Phi_k | \nabla_{\mathbf{R}_\alpha} \Phi_l \rangle\rangle = \frac{\langle\langle \Phi_k | \nabla_{\mathbf{R}_\alpha} H_{\text{el}} | \Phi_l \rangle\rangle}{E_l - E_k} \quad (3)$$

The double bracket notation in equation (3) implies the integration over the electronic configuration space $\mathfrak{R}_{\text{el}}^{3N}$. By definition, $\mathbf{f}_{kl}^{(\alpha)}$ is the α th nonadiabatic coupling between the electronic states k and l .

Nonadiabatic couplings $\mathbf{f}_{kl}^{(\alpha)}$ for all pairs of electronic eigenstates Φ_k and Φ_l form a matrix $\mathbf{F}^{(\alpha)}$ with non-zero off-diagonal matrix elements $\mathbf{F}_{kl}^{(\alpha)} = \mathbf{f}_{kl}^{(\alpha)} \cdot \mathbf{f}_{kl}^{(\alpha)}$ is a vector field and, therefore, according to Helmholtz theorem [45] (see also, e.g. Ref. [46])

and application to the H_3 system in Ref. [47]), it is decomposed into two components

$$\mathbf{f}_{kl}^{(\alpha)} = \mathbf{f}_{kl}^{(\alpha)\parallel} + \mathbf{f}_{kl}^{(\alpha)\perp} \quad (4)$$

The former one $\mathbf{f}_{kl}^{(\alpha)\parallel}$, called the longitudinal or irrotational one, is defined by its curl, $\nabla_{\mathbf{R}} \times \mathbf{f}_{kl}^{(\alpha)\parallel}$, and is identically zero (the ‘flow source’). It is thus represented as $\mathbf{f}_{kl}^{(\alpha)\parallel} = \nabla_{\mathbf{R}_\alpha} P_{kl}^{(\alpha)\parallel}$ where $P_{kl}^{(\alpha)\parallel}$ is some ‘scalar potential’ determined as [46]

$$P_{kl}^{(\alpha)\parallel} = -\frac{1}{4\pi} \int d^3 \mathbf{r}' \frac{\nabla' \cdot \mathbf{f}_{kl}^{(\alpha)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (5)$$

The other, transverse or rotational, or solenoidal component, $\mathbf{f}_{kl}^{(\alpha)\perp}$ is divergenceless (the ‘vortex source’), i.e., $\nabla_{\mathbf{R}_\alpha} \cdot \mathbf{f}_{kl}^{(\alpha)\perp} = 0$. Therefore, $\mathbf{f}_{kl}^{(\alpha)\perp} = \nabla_{\mathbf{R}_\alpha} \times \mathbf{P}_{kl}^{(\alpha)\perp}$, where $\mathbf{P}_{kl}^{(\alpha)\perp}$ is a ‘vector potential’. In other words, $\mathbf{f}_{kl}^{(\alpha)\perp}$ defines the vorticity field belonging to the field $P_{kl}^{(\alpha)\perp}$. The latter *a priori* fulfills a so-called incompressibility condition $\nabla_{\mathbf{R}_\alpha} \cdot \mathbf{P}_{kl}^{(\alpha)\perp} = 0$ [46]. Hence, $\mathbf{P}_{kl}^{(\alpha)\perp}$ can be replaced by $\mathbf{P}_{kl}^{(\alpha)\perp} + \nabla_{\mathbf{R}_\alpha} g$, where the gauge g is arbitrary, without changing $\mathbf{f}_{kl}^{(\alpha)\perp}$. A particular choice of g is a so-called gauge origin produced by $g = \frac{1}{2} \mathbf{f}_{kl}^{(\alpha)\perp} \times (\mathbf{R} - \mathbf{R}') \cdot \mathbf{R}_\alpha$. Such gauge invariance of the transverse component is interesting in view of the recent work by Buenker and Li [48] on the independence of NAC on the choice of the origin of the coordinate frame.

Similarly to equation (5), one writes the formula derived by Stokes and Helmholtz [46],

$$\mathbf{P}_{kl}^{(\alpha)\perp} = -\frac{1}{4\pi} \int d^3 \mathbf{r}' \frac{\nabla' \times \mathbf{f}_{kl}^{(\alpha)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (6)$$

It is also worth noticing ansatz [46d,49] consisting of

$$\mathbf{P}_{kl}^{(\alpha)\perp} = \mathbf{v}a + \nabla \times (\mathbf{v}b) \quad (7)$$

where a and b are scalar functions and $\mathbf{v}$ is the carrier field.

The decomposition (4) is valid if the vector field $\mathbf{f}_{kl}^{(\alpha)}$ is finite and it is unique if $\nabla_{\mathbf{R}_\alpha} \mathbf{P}_{kl}^{(\alpha)\perp} = 0$, $\lim_{R_\alpha \rightarrow \infty} P_{kl}^{(\alpha)\parallel} = 0$, and if $\lim_{R_\alpha \rightarrow \infty} \mathbf{P}_{kl}^{(\alpha)\perp} = 0$ for all α [50]. Notice also another representation of an arbitrary vector field, particularly the NAC vector field, in terms of three scalar fields [51],

$$\mathbf{f}_{kl}^{(\alpha)} = \mathbf{L}\psi + \nabla \times \mathbf{L}\chi + \nabla\phi \quad (8)$$

where $\mathbf{L} = -i\mathbf{r} \times \nabla$ is the angular momentum operator, and ψ and χ are the Debye potentials and ϕ the scalar potential. The two first terms on the right hand side of equation (8) thus give the angular-momentum representation of the transverse component of NAC.

Using equation (4) and the representation of the NAC transverse and longitudinal components in terms of the potentials $P^{\parallel}$ and $P^{\perp}$, one then easily obtains

$$\nabla_{\mathbf{R}_\alpha} \cdot [P_{kl}^{(\alpha)\parallel} \nabla_{\mathbf{R}_\alpha} \times \mathbf{P}_{kl}^{(\alpha)\perp}] = \nabla_{\mathbf{R}_\alpha} \cdot P_{kl}^{(\alpha)\parallel} \cdot \nabla_{\mathbf{R}_\alpha} \times \mathbf{P}_{kl}^{(\alpha)\perp} \quad (9)$$

Integrating equation (9) over $\mathfrak{R}_\alpha^3$ and applying the Ostrogradsky–Gauss’ theorem yields [24c]

$$\int_{\mathfrak{R}_\alpha^3} d^3\mathbf{R}_\alpha \mathbf{f}_{kl}^{(\alpha)\parallel} \cdot \mathbf{f}_{kl}^{(\alpha)\perp} = 0 \quad (10)$$

Equation (10) represents a so-called orthogonality between the longitudinal and transverse components of the vector field $\mathbf{f}_{kl}^{(\alpha)}$.

Acting upon curl operator of $\mathbf{f}_{kl}^{(\alpha)}$ given by equation (3), one derives the following expression [13a] (see also Ref. [29g])

$$\nabla_{\mathbf{R}_\alpha} \times \mathbf{f}_{kl}^{(\alpha)} = \langle\langle \nabla_{\mathbf{R}_\alpha} \Phi_k | \times | \nabla_{\mathbf{R}_\alpha} \Phi_l \rangle\rangle = \sum_n \mathbf{f}_{kn}^{(\alpha)} \times \mathbf{f}_{nl}^{(\alpha)} \quad (11)$$

Equation (11) is actually a particular case of the theorem proved in Section 49 of Ref. [52].

Let us now consider a subclass of NACs satisfying the so-called curl condition [12] (see also Refs. [18,53]):

$$\nabla_{\mathbf{R}} \times \mathbf{f} = 0 \quad (12)$$

(the superscript and subscript α are hereafter removed). Using equation (12), the singularity of NAC can be linked to a pseudo-magnetic field $\mathbf{H} \equiv \nabla_{\mathbf{R}} \times \mathbf{f}$, determining the vorticity of $\mathbf{f}$, which is defined along a seam [54] and nonvanished therein if equation (12) holds. It has been also proved [55] and shown numerically [29c,56] that the circulation of a given $\mathbf{f}$ along an arbitrary loop C , enclosed a seam, is quantized, i.e.,

$$\oint_C \mathbf{f} \cdot d\mathbf{s} = n\pi \quad (13)$$

where n is an integer. If the curl condition (12) is fulfilled, then, according to Stokes’ theorem, the circulation along a closed path C that bounds a surface S is equal to the flux of $\mathbf{f}$ through S , viz.,

$$\oint_C \mathbf{f} \cdot d\mathbf{s} = \int_S \nabla_{\mathbf{R}} \times \mathbf{f} \cdot d\mathbf{S} \quad (14)$$

and hence vanishes if C does not enclose any singularity. The explicit form of the

NACs that simultaneously obey both conditions (12) and (13) has recently been derived by Avery *et al.* [57].

Notice finally that the perturbation theory approach for calculating NAC corrections has been developed in Ref. [58].

3. ORTHOGONAL TRANSFORMATION AND TWO-STATE PROBLEM

The two-state problem assumes that the two given adiabatic electronic eigenstates Φ_1 and Φ_2 of H_{el} are coupled to each other but not to the rest of the electronic eigenstates (a so-called ‘bath’). In other words, the quantum treatment is confined to the Hilbert subspace $\{\Phi_1, \Phi_2\}$ spanned on Φ_1 and Φ_2 and H_{el} acts thereupon as $P_{12}H_{\text{el}}P_{12}$ where $P_{12} = |\Phi_1\rangle\langle\Phi_1| + |\Phi_2\rangle\langle\Phi_2|$ is the projector onto $\{\Phi_1, \Phi_2\}$. Rotating Φ_1 and Φ_2 via a two-dimensional orthogonal transformation,

$$\begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix} = \begin{pmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{pmatrix} \begin{pmatrix} \Phi_1 \\ \Phi_2 \end{pmatrix} \quad (15)$$

where α determines the mixing or rotation angle, one obtains ‘new’ wave functions Ψ_1 and Ψ_2 which in general are no longer the eigenfunctions of H_{el} . The nonadiabatic couplings in the ‘old’ and ‘new’ two-dimensional bases are linked to each other as

$$\langle\langle \Psi_2 | \nabla_{\mathbf{R}} \Psi_1 \rangle\rangle = \langle\langle \Phi_2 | \nabla_{\mathbf{R}} \Phi_1 \rangle\rangle - \nabla_{\mathbf{R}} \alpha$$

or equivalently

$$\mathbf{f}_{21}^{\Psi} = \mathbf{f}_{21}^{\Phi} - \nabla_{\mathbf{R}} \alpha \quad (16)$$

The ‘new’ NAC $\mathbf{f}_{21}^{\Psi}$ vanishes if the mixing angle satisfies the equation

$$\nabla_{\mathbf{R}} \alpha = \mathbf{f}_{21}^{\Phi} \quad (17)$$

Such an angle α is called the mixing angle of the adiabatic-to-diabatic transformation (ADT) for the two-state problem.

Let us now consider the generalized two-state problem which assumes that two given adiabatic electronic eigenstates Φ_1 and Φ_2 are coupled to the ‘bath’ $\{\Phi_1, \Phi_2\}^{\perp}$ defined as the complementary subspace to $\{\Phi_1, \Phi_2\}$ in $\mathfrak{H}_{\text{el}}$ (for the inclusion of the third state see, e.g. Refs. [59–66]), i.e.,

$$\mathfrak{H}_{\text{el}} = \{\Phi_1, \Phi_2\} \oplus \{\Phi_1, \Phi_2\}^{\perp} \quad (18)$$

Their rotation upon the angle α , similar to that defined by equation (15), gives the

following relation between the ‘old’ and ‘new’ NACs

$$\langle\langle \Psi_2 | \nabla_{\mathbf{R}} \Psi_1 \rangle\rangle = \langle\langle \Phi_2 | \nabla_{\mathbf{R}} \Phi_1 \rangle\rangle - \nabla_{\mathbf{R}} \alpha$$

or, equivalently

$$\mathbf{f}_{21}^{\Psi} = \mathbf{f}_{21}^{\Phi} - \nabla_{\mathbf{R}} \alpha \quad (19)$$

Equations (16) and (19) are formally identical. It is suggested that α satisfies equation (17) for the two-state problem and $\tilde{\alpha}$ the similar one for the generalized two-state problem. Applying now the curl operator to both sides of the first equations in equations (16) and (19) and substituting $\alpha = \tilde{\alpha}$ in the last one, one readily obtains that, in the former case, this results in the identity $0 = 0$ because the right hand side of equation (11) vanishes for the two-state problem. In the latter case, one finds that the substitution $\alpha = \tilde{\alpha}$ and curl operation, applied to the first equation in equation (19), do not commute, viz., replacing α by $\tilde{\alpha}$ eliminates the right hand side of the first equation in equation (19) and a further application of the curl to the resultant equation yields

$$\nabla_{\mathbf{R}} \times \mathbf{f}_{21}^{\Psi} = 0 \quad (20)$$

Acting initially, however, by the curl upon the first equation in (19), one derives

$$\nabla_{\mathbf{R}} \times \mathbf{f}_{21}^{\Psi} = \nabla_{\mathbf{R}} \times \mathbf{f}_{21}^{\Phi} \quad (21)$$

A further substitution $\alpha = \tilde{\alpha}$ in equation (21) leaves it unchanged because $\nabla_{\mathbf{R}} \times (\nabla_{\mathbf{R}} \alpha)$ is identically zero. One arrives at the discrepancy between equation (20), whose right hand side is identically zero, and equation (21), whose right hand side, identical, on the one hand, to the left hand side of equation (20), is, on the other, nonvanishing due to equation (11). Generally speaking, the latter must be non-zero for the generalized two-state problem except for the case when the curl condition (12) holds. Such inconsistency is a quintessence of the Mead–Truhlar theorem [13a] on the non-existence of a strictly diabatic basis for the generalized two-state problem obtained via a two-dimensional orthogonal transformation of the two adiabatic states. According to equation (21), the ‘new’ basis still absorbs the nonvanishing transverse component of the NAC of the ‘old’ one. Notice finally that due to the following formula (see, for example, Ref. [29g])

$$\begin{aligned} \nabla_{\mathbf{R}} \times \mathbf{f}_{kl} = & - \sum_{m \neq k, l} \frac{\langle\langle \Psi_k(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}} H_{el}(\mathbf{r}; \mathbf{R}) | \Psi_n(\mathbf{r}; \mathbf{R}) \rangle\rangle}{E_m(\mathbf{R}) - E_k(\mathbf{R})} \\ & \times \frac{\langle\langle \Psi_n(\mathbf{r}'_e; \mathbf{R}_n) | \nabla_{\mathbf{R}} H_{el}(\mathbf{r}'_e; \mathbf{R}_n) | \Psi_n(\mathbf{r}; \mathbf{R}) \rangle\rangle}{E_m(\mathbf{R}) - E_l(\mathbf{R})} \end{aligned} \quad (22)$$

the transverse component of NAC is not singular unless there appears (at least) an intersection of one of the coupled potential energy surfaces under study with a third one belonging to the ‘bath’. Within the degenerate perturbation theory, this was shown by Mead [13b] and Matsunaga and Yarkony [29e] (see also comments on p. 7372 of Ref. [26a]). Thus, the only singular part of $\mathbf{f}_{12}^\phi$ is its longitudinal component and it is actually removable by the two-dimensional orthogonal transformation (15). The ADT angle α then obeys the inhomogeneous Poisson equation

$$\nabla_{\mathbf{R}}^2 \alpha = \langle\langle \nabla_{\mathbf{R}} \Psi_1 | \nabla_{\mathbf{R}} \Psi_2 \rangle\rangle + \langle\langle \Psi_1 | \nabla_{\mathbf{R}}^2 \Psi_2 \rangle\rangle \quad (23)$$

This is precisely the ADT angle that performs the two-dimensional orthogonal transformation from the *adiabatic* to *diabatic I* bases. Concluding, with this derivation we emphasize the sufficiency of a two dimensional orthogonal transformation to remove the singular component of the nonadiabatic coupling between two intersecting potential energy surfaces.

4. ‘EQUATION OF MOTION’ AND DIABATIC ‘SMOOTHNESS’ OF MOLECULAR PROPERTY

Consider some molecular property defined by the matrix $\mathbf{A}$ with the elements $A_{ij} = \langle\langle \Psi_i | A(\mathbf{r}, \mathbf{R}) | \Psi_j \rangle\rangle$ of a Hermitian operator A . One then easily derives that this matrix $\mathbf{A}$ obeys the following ‘equation of motion’ [37],

$$\nabla_{\mathbf{R}} A_{ij} = [\mathbf{A}, \mathbf{F}]_{ij} + \langle\langle \Psi_i | \nabla_{\mathbf{R}} A(\mathbf{r}, \mathbf{R}) | \Psi_j \rangle\rangle \quad (24)$$

where the standard notation $[\cdot, \cdot]$ for commutation bracket is used. Interestingly, equation (24) structurally resembles a time-dependent Schrödinger equation in Heisenberg representation.

If A depends on the electronic variables, equation (24) is simplified as

$$\nabla_{\mathbf{R}} A_{ij} = [\mathbf{A}, \mathbf{F}]_{ij} \quad (25)$$

Assuming that a strictly diabatic basis exists and defining the corresponding matrix elements $A_{ij}^d = \langle\langle \Psi_i^d | A(\mathbf{r}, \mathbf{R}) | \Psi_j^d \rangle\rangle$, one arrives at

$$\nabla_{\mathbf{R}} A_{ij}^d = 0 \quad (26)$$

Equation (26) expresses a ‘smoothness’ of matrix elements of Hermitian operator A in a strictly diabatic basis. It is the key formula for deriving the expression of the ADT angle in terms of a given molecular property [37].

5. MOLECULAR PROPERTIES AND TWO-STATE DIABATIZATION

In this section we demonstrate the usage of a ‘smoothness’ of molecular property expressed by equation (26) for determining the corresponding ADT mixing angle. Let us begin with the two-state problem described by the given wave functions Ψ_1 and Ψ_2 . Under two-dimensional rotation (15), matrix $\mathbf{A}$ of a given Hermitian electronic operator A undergoes the following transformation

$$\mathbf{A}^\Phi \equiv \mathbf{U}_2^{-1} \mathbf{A} \mathbf{U}_2 = \begin{pmatrix} \frac{1}{2}(A_{11}+A_{22}) + \frac{1}{2}(A_{11}-A_{22})\cos 2\alpha + A_{12}\sin 2\alpha & A_{12}\cos 2\alpha - \frac{1}{2}(A_{11}-A_{22})\sin 2\alpha \\ A_{12}\cos 2\alpha - \frac{1}{2}(A_{11}-A_{22})\sin 2\alpha & \frac{1}{2}(A_{11}+A_{22}) - \frac{1}{2}(A_{11}-A_{22})\cos 2\alpha - A_{12}\sin 2\alpha \end{pmatrix} \quad (27)$$

where $\mathbf{A}^\Phi$ is the matrix representation of $\mathbf{A}$ in the basis formed by Φ_1 and Φ_2 . If the mixing angle obeys equation (17), $\mathbf{A}^\Phi$ is equal to A^{dl} . Therefore, it satisfies the two-state analogue of equation (25) that can be used to determine the ADT mixing angle without integrating equation (17). To show this, let us rewrite the two-state equation (25) for a problem in a case when A only describes a given electronic property:

$$\nabla_{\mathbf{R}} \begin{pmatrix} A_{11} & A_{12} \\ A_{12} & A_{22} \end{pmatrix} = \begin{pmatrix} -2\mathbf{f}_{12}A_{12} & \mathbf{f}_{12}(A_{11} - A_{22}) \\ \mathbf{f}_{12}(A_{11} - A_{22}) & 2\mathbf{f}_{12}A_{12} \end{pmatrix} \quad (28)$$

Defining $A_{\pm} \equiv A_{11} \pm A_{22}$, equation (28) becomes rewritten as

$$\begin{aligned} \nabla_{\mathbf{R}} A_{12} &= \mathbf{f}_{12} A_{-} \\ \nabla_{\mathbf{R}} A_{+} &= 0 \\ \nabla_{\mathbf{R}} A_{-} &= -4\mathbf{f}_{12} A_{12} \end{aligned} \quad (29)$$

Therefore, the two-state analogue of equation (25) takes the following form

$$\begin{aligned} \nabla_{\mathbf{R}} A_{12}^\Phi &= (\nabla_{\mathbf{R}} A_{12} - A_{-} \nabla_{\mathbf{R}} \alpha) \cos 2\alpha - \frac{1}{2} (\nabla_{\mathbf{R}} A_{-} + 4A_{12} \nabla_{\mathbf{R}} \alpha) \sin 2\alpha \\ \nabla_{\mathbf{R}} A_{11}^\Phi &= -\nabla_{\mathbf{R}} A_{22}^\Phi \\ &= (\nabla_{\mathbf{R}} A_{12} - A_{-} \nabla_{\mathbf{R}} \alpha) \sin 2\alpha + \frac{1}{2} (\nabla_{\mathbf{R}} A_{-} + 4A_{12} \nabla_{\mathbf{R}} \alpha) \cos 2\alpha \end{aligned} \quad (30)$$

Equation (30) has the following general solution for the ADT mixing angle [37]

$$\tan 2\alpha = \frac{A_{-} + 2\lambda A_{12}}{\lambda A_{-} - 2A_{12}} \quad (31)$$

where λ is a numerical constant determined by the auxiliary condition that the

adiabatic and diabatic representations agree at a given value of $\mathbf{R}$. Equation (31) can be also rewritten as $\tan 2\alpha = \tan(2\alpha_0 + \cot^{-1}\lambda)$ where $\tan 2\alpha_0$ is the particular solution of equation (31), viz., $\tan 2\alpha_0 = 2A_{12}/A_-$ obtained under $\lambda = \infty$. Such a particular solution for the mixing angle was first derived by Werner and Meyer [33] for the two lowest states of the diatomic molecule LiF with A as the electronic dipole moment and Macías and Riera [32] under the assumption of a vanishing off-diagonal element of matrix $\mathbf{A}$ in diabatic basis (for recent discussions of the present approach see Refs. [18,43,67]).

6. ‘SMOOTHNESS’ OF THE ELECTRONIC DIPOLE MOMENT AND THE GENERALIZED MULLIKEN–HUSH APPROACH

Consider the electronic dipole moment matrix $\mathbf{M} = (\mathbf{m}_{kl} = \langle\langle \Psi_k | r | \Psi_l \rangle\rangle)_{kl}$ and project it on a given direction in $\Re^3$. This gives the matrix $\mathbf{m} = (m_{kl})_{kl}$. Imposing a ‘smoothness’ condition of this matrix within the two-state diabatic basis, one readily obtains the ADT mixing angle in terms of the electronic dipole moment [32, 33,37,68]

$$\tan 2\alpha_{\text{dipole}} = \frac{m_- + 2\lambda m_{12}}{\lambda m_- - 2m_{12}} \quad (32)$$

and the matrix elements of the electronic dipole moment in the *diabatic I* basis [62]

$$m_{11}^{\text{dI}} = \frac{m_+}{2} \pm \frac{1}{2} \begin{cases} \lambda \sqrt{\frac{m_-^2 + 4m_{12}^2}{1 + \lambda^2}}, & |\lambda| \geq \frac{2m_{12}}{m_-} \\ \frac{4m_- - m_{12} - \lambda(m_-^2 - 4m_{12}^2)}{\sqrt{(1 + \lambda^2)(m_-^2 + 4m_{12}^2)}}, & \text{otherwise} \end{cases} \quad (33)$$

$$m_{22}^{\text{dI}} = \frac{m_+}{2} \mp \frac{1}{2} \begin{cases} \lambda \sqrt{\frac{m_-^2 + 4m_{12}^2}{1 + \lambda^2}}, & |\lambda| \geq \frac{2m_{12}}{m_-} \\ \frac{4m_- - m_{12} - \lambda(m_-^2 - 4m_{12}^2)}{\sqrt{(1 + \lambda^2)(m_-^2 + 4m_{12}^2)}}, & \text{otherwise} \end{cases} \quad (34)$$

$$m_{12}^{\text{dl}} = \mp \frac{1}{2} \begin{cases} \lambda \sqrt{\frac{m_-^2 + 4m_{12}^2}{1 + \lambda^2}}, & |\lambda| \geq \frac{2m_{12}}{m_-} \\ \frac{4\lambda m_- - m_{12} - m_-^2 + 4m_{12}^2}{\sqrt{(1 + \lambda^2)(m_-^2 + 4m_{12}^2)}}, & \text{otherwise} \end{cases} \quad (35)$$

Let us further rotate the two-state adiabatic Hamiltonian by the mixing angle α_{dipole} . This yields

$$\begin{aligned} H_{11}^{\text{dl}} &= E_0 \pm \frac{\Delta E}{2} \frac{\lambda m_- - 2m_{12}}{\sqrt{(1 + \lambda^2)(m_-^2 + 4m_{12}^2)}} \\ H_{22}^{\text{dl}} &= E_0 \mp \frac{\Delta E}{2} \frac{\lambda m_- - 2m_{12}}{\sqrt{(1 + \lambda^2)(m_-^2 + 4m_{12}^2)}} \\ H_{12}^{\text{dl}} &= \mp \frac{\Delta E}{2} \frac{m_- + 2\lambda m_{12}}{\sqrt{(1 + \lambda^2)(m_-^2 + 4m_{12}^2)}} \end{aligned} \quad (36)$$

where $E_0 = (E_1 + E_2)/2$ and the energy offset $\Delta E = E_1 - E_2$. The substitution $\lambda = \infty$ in equation (36), which actually corresponds to a vanishing off-diagonal diabatic dipole moment, finally results in the generalized Mulliken–Hush formula for the diabatic electronic coupling [41,42,62,68,69,70]

$$|H_{12}^{\text{dl}_0}| = \frac{m_{12}}{\sqrt{m_-^2 + 4m_{12}^2}} \Delta E \quad (37)$$

which is the major factor determining the rate of the electron transfer. In the general case, the last equation in (36) provides the expression of the electronic coupling which takes the off-diagonal diabatic dipole moment into account, and hence is useful, for instance, for estimating such coupling in polarizable solvents [71].

7. SUMMARY

In the present survey, we have focused on the key general features of the nonadiabatic coupling and its relationship to molecular properties and reviewed some consequences of the ‘equation of motion’, earlier derived in Ref. [37], which formally expresses a nice property of a ‘smoothness’ of a given molecular property within the diabatic basis. The latter distinguishes the diabatic basis from the others, the adiabatic one in particular. We have also shown and discussed the relation between a ‘smoothness’ of the electronic dipole moment and the generalized

Mulliken–Hush formula for the diabatic electronic coupling. We suggest that the latter approach might be rather useful to thoroughly investigate multistate effects on the electronic diabatic coupling recently pursued by Cave and co-workers [66].

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REFERENCES

- [1] (a) B. H. Lengsfeld and D. R. Yarkony, in *State-Selected and State-to-State Ion–Molecule Reaction Dynamics: Part 2 Theory*, *Adv. Chem. Phys.* (eds M. Baer and C.-Y. Ng), Wiley, New York, 1992, Vol. 82, p. 1; (b) D. R. Yarkony, in *Modern Electronic Structure Theory* (ed. D. R. Yarkony), World Scientific, Singapore, 1995; (c) D. R. Yarkony, *J. Phys. Chem.*, 1996, **100**, 18612; (d) D. R. Yarkony, *Rev. Mod. Phys.*, 1996, **68**, 985; (e) D. R. Yarkony, *Acc. Chem. Res.*, 1998, **31**, 511; (f) D. R. Yarkony, *Theor. Chem. Acc.*, 2000, **103**, 242; (g) D. R. Yarkony, *J. Phys. Chem. A*, 2001, **105**, 6277, and references therein.
- [2] L. D. Landau, *Physik Z. Sowjetunion*, 1932, **2**, 46.
- [3] C. Zener, *Proc. R. Soc. Lond. A*, 1932, **137**, 696.
- [4] E. C. G. Stueckelberg, *Helv. Phys. Acta*, 1932, **5**, 369.
- [5] (a) M. Born and J. R. Oppenheimer, *Ann. Phys. (Leipzig)*, 1927, **84**, 457; (b) M. Born, *Nachr. Akad. Wiss. Göttingen, II Math-Physik. Kl.*, 1951, **6**; See also J. C. Tully, *Theor. Chem. Acc.*, 2000, **103**, 173.
- [6] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Clarendon Press, Oxford, 1954, Appendix VIII.
- [7] (a) W. D. Hobey and A. D. McLachlan, *J. Chem. Phys.*, 1960, **33**, 1695; (b) A. D. McLachlan, *Mol. Phys.*, 1961, **4**, 417.
- [8] (a) W. Lichten, *Phys. Rev.*, 1963, **131**, 229; (b) W. Lichten, *Phys. Rev.*, 1965, **139**, A27; (c) W. Lichten, *Phys. Rev.*, 1967, **164**, 131.
- [9] D. R. Bates, *Proc. R. Soc. Lond. A*, 1960, **257**, 22.
- [10] E. E. Nikitin, in *Chemische Elementarprozesse* (ed. H. Hartmann), Springer, Berlin, 1968.
- [11] F. T. Smith, *Phys. Rev.*, 1969, **179**, 111.
- [12] (a) M. Baer, *Chem. Phys. Lett.*, 1975, **35**, 112; (b) M. Baer, *Chem. Phys.*, 1976, **15**, 49; (c) Z. H. Top and M. Baer, *Chem. Phys.*, 1977, **25**, 1; (d) M. Baer, *Mol. Phys.*, 1980, **40**, 1011.
- [13] (a) C. A. Mead and D. G. Truhlar, *J. Chem. Phys.*, 1982, **77**, 6090; (b) C. A. Mead, *J. Chem. Phys.*, 1983, **78**, 807; (c) T. C. Thompson and C. A. Mead, *J. Chem. Phys.*, 1985, **82**, 2408; (d) B. C. Garrett, D. G. Truhlar and C. F. Melius, in *Energy Storage and Redistribution in Molecules* (ed. J. Hinze), Plenum, New York, 1983, 375; (e) T. C. Thompson, D. G. Truhlar and C. A. Mead, *J. Chem. Phys.*, 1985, **82**, 2392.
- [14] (a) H. Köppel, W. Domcke and L. S. Cederbaum, *Adv. Chem. Phys.*, 1984, **72**, 59; (b) T. Pacher, L. S. Cederbaum and H. Köppel, *Adv. Chem. Phys.*, 1993, **84**, 293; (c) W. Domcke and G. Stock, *Adv. Chem. Phys.*, 1997, **100**, 1.

- [15] V. Sidis, in *State-Selected and State-to-State Ion–Molecule Reaction Dynamics: Part 2 Theory*, *Adv. Chem. Phys.* (eds M. Baer and C.-Y. Ng), Wiley, New York, 1992, Vol. 82, p. 73.
- [16] A. Kuppermann, in *Dynamics of Molecules and Chemical Reactions* (eds R. E. Wyatt and J. Z. H. Zhang), Marcel Dekker, New York, 1996, p. 411.
- [17] C. A. Mead, *Rev. Mod. Phys.*, 1992, **64**, 51.
- [18] M. Baer, *Phys. Rep.*, 2002, **358**, 75.
- [19] The term diabatic states was first introduced by R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 1375; See also W. H. Miller, *Faraday Discuss.*, 1998, **110**, 1.
- [20] T. F. O'Malley, *Adv. At. Mol. Phys.*, 1971, **7**, 223.
- [21] M. Baer, *J. Chem. Phys.*, 1997, **107**, 2694.
- [22] B. K. Kendrick, C. A. Mead and D. G. Truhlar, *J. Chem. Phys.*, 1999, **110**, 7594; See also M. Baer, *J. Chem. Phys.*, 2000, **112**, 6089.
- [23] M. Baer, *Chem. Phys. Lett.*, 2000, **322**, 520.
- [24] (a) B. K. Kendrick, C. A. Mead and D. G. Truhlar, *Chem. Phys. Lett.*, 2000, **330**, 629; (b) M. Baer, *Chem. Phys. Lett.*, 2000, **330**, 633; (c) E. S. Kryachko and A. J. C. Varandas, *Int. J. Quantum Chem.*, 2002, **89**, 255; (d) See also Corrigendum and Addendum, *Int. J. Quantum Chem.* (to appear).
- [25] C. A. Mead, *J. Chem. Phys.*, 1983, **78**, 807.
- [26] (a) T. Pacher, L. S. Cederbaum and H. Köppel, *J. Chem. Phys.*, 1988, **89**, 7367; (b) T. Pacher, C. A. Mead, L. S. Cederbaum and H. Köppel, *J. Chem. Phys.*, 1989, **91**, 7057.
- [27] F. X. Gadéa and M. Péliissier, *J. Chem. Phys.*, 1990, **93**, 545.
- [28] (a) K. Ruedenberg and G. J. Atchity, *J. Chem. Phys.*, 1993, **99**, 3799; (b) G. J. Atchity and K. Ruedenberg, *Theor. Chem. Acc.*, 1997, **97**, 47; (c) J. Ivanic, G. J. Atchity and K. Ruedenberg, *J. Chem. Phys.*, 1997, **107**, 4307.
- [29] (a) G. Parlant, J. Rostas, G. Taieb and D. R. Yarkony, *J. Chem. Phys.*, 1990, **93**, 6403; (b) S. Han, H. Hettema and D. R. Yarkony, *J. Chem. Phys.*, 1995, **102**, 1955; (c) D. R. Yarkony, *J. Chem. Phys.*, 1996, **105**, 10456; (d) Yarkony, *J. Phys. Chem. A*, 1997, **101**, 4263; (e) N. Matsunaga and D. R. Yarkony, *Mol. Phys.*, 1998, **93**, 79; (f) R. G. Sadygov and D. R. Yarkony, *J. Chem. Phys.*, 1998, **109**, 20; (g) E. Kryachko and D. R. Yarkony, *Theor. Chem. Acc.*, 1998, **100**, 154; (h) D. R. Yarkony, *J. Phys. Chem. A*, 1998, **102**, 8073; (i) D. R. Yarkony, *J. Chem. Phys.*, 2000, **112**, 2111.
- [30] (a) A. Thiel and H. Köppel, *J. Chem. Phys.*, 1999, **110**, 9371; (b) H. Köppel, J. Gronki and S. Mahapatra, *J. Chem. Phys.*, 2001, **115**, 2377.
- [31] (a) R. Thürwachter and P. Halvick, *Chem. Phys.*, 1997, **221**, 33; (b) V. M. García, M. Reguero, R. Caballo and J. P. Malrieu, *Chem. Phys. Lett.*, 1997, **281**, 161; (c) D. Simah, B. Hartke and H.-J. Werner, *J. Chem. Phys.*, 1999, **111**, 4523.
- [32] (a) A. Macías and A. Riera, *J. Phys. B*, 1978, **11**, L489; (b) A. Macías and A. Riera, *Int. J. Quantum Chem.*, 1980, **17**, 181.
- [33] H. J. Werner and W. Meyer, *J. Chem. Phys.*, 1981, **74**, 5802.
- [34] (a) C. Petrongolo, R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys. Lett.*, 1985, **115**, 249; (b) H. Thummel, R. Klotz and S. D. Peyerimhoff, *Chem. Phys.*, 1989, **135**, 229; (c) C. Petrongolo, G. Hirsch and R. J. Buenker, *Mol. Phys.*, 1990, **70**, 825; (d) M. Peric, R. J. Buenker and S. D. Peyerimhoff, *Mol. Phys.*, 1990, **71**, 673; (e) G. Hirsch, R. J. Buenker and C. Petrongolo, *Mol. Phys.*, 1990, **70**, 835; (f) M. Peric, R. J. Buenker and S. D. Peyerimhoff, *Z. Phys. D*, 1992, **24**, 177; (g) M. Terao, C. Harel, A. Salin and R. J. Allan, *Z. Phys. D*, 1988, **7**, 319; (h) A. J. Dobbyn and P. J. Knowles, *Mol. Phys.*, 1997, **91**, 1107; (i) R. J. Cave and M. D. Newton, *J. Chem. Phys.*, 1997, **106**, 9213; (j) N. Khelifi, W. Zraft, B. Oujia and F. X. Gadea, *Phys. Rev. A*, 2002, **65**, 042513.
- [35] (a) F. Rebertrost and J. W. A. Lester, *J. Chem. Phys.*, 1975, **63**, 3737; (b) F. Rebertrost and J. W. A. Lester, *J. Chem. Phys.*, 1976, **64**, 3879; (c) F. Rebertrost and J. W. A. Lester, *J. Chem. Phys.*, 1977, **67**, 3367.
- [36] (a) M. Alexander, *J. Chem. Phys.*, 1993, **99**, 6014; (b) M. Alexander and M. Yang, *J. Chem. Phys.*, 1995, **103**, 7956; (c) M. H. Alexander, *J. Chem. Phys.*, 1998, **108**, 4467.
- [37] E. S. Kryachko and D. R. Yarkony, *Int. J. Quantum Chem.*, 2000, **76**, 235.
- [38] (a) J. Hendeković, *Chem. Phys. Lett.*, 1982, **90**, 193; (b) J. Hendeković, *Croat. Chem. Acta*, 1983, **56**, 375; (c) J. Kucar, M. Pavlovic and J. Hendeković, *Int. J. Quantum Chem.*, 1987, **32**, 699.

- [39] (a) F. Spiegelmann and J. P. Malrieu, *J. Phys. B*, 1984, **17**, 1235; (b) F. Spiegelmann and J. P. Malrieu, *J. Phys. B*, 1984, **17**, 1259.
- [40] (a) L. S. Cederbaum, H. Köppel and W. Domcke, *Int. J. Quantum Chem. Quantum Chem. Symp.*, 1981, **15**, 251; (b) T. Pacher, L. S. Cederbaum and H. Köppel, *J. Chem. Phys.*, 1988, **89**, 7367; (c) L. S. Cederbaum, J. Schirmer and H. D. Meyer, *J. Phys. A*, 1989, **22**, 2427; (d) T. Pacher, H. Köppel and L. S. Cederbaum, *J. Chem. Phys.*, 1991, **95**, 6668; (e) W. Domcke and C. Woywood, *Chem. Phys. Lett.*, 1993, **216**, 362; (f) W. Domcke, C. Woywod and M. Stengle, *Chem. Phys. Lett.*, 1994, **226**, 257.
- [41] R. S. Mulliken, *J. Am. Chem. Soc.*, 1952, **74**, 811.
- [42] N. S. Hush, *Progr. Inorg. Chem.*, 1967, **8**, 391.
- [43] (a) H. Nakamura and D. G. Truhlar, *J. Chem. Phys.*, 2001, **115**, 10353; (b) H. Nakamura and D. G. Truhlar, *J. Chem. Phys.*, 2002, **117**, 5576.
- [44] (a) S. H. Lin, *J. Chem. Phys.*, 1966, **44**, 3759; (b) S. H. Lin and R. Bersohn, *J. Chem. Phys.*, 1968, **48**, 2732.
- [45] H. L. F. v. Helmholtz, *Crelles J.*, 1858, **55**, 25; See also G. Stokes, *Trans. Cambridge Phil. Soc.*, 1849, **9**, 1.
- [46] (a) W. K. H. Panofsky and M. Phillips, *Classical Electricity and Magnetism*, Addison-Wesley, Reading, MA, 1962; (b) D. H. Kobe, *Am. J. Phys.*, 1985, **54**, 552; (c) R. Aldrovandi and J. G. Pereira, *An Introduction to Geometrical Physics*, World Scientific, Singapore, 1995; (d) S. Grossmann, *Mathematischer Einführungskurs für die Physik*, Teubner, Stuttgart, 2000; (e) P. M. Morse and H. Feshbach, *Methods of Theoretical Physics*, McGraw-Hill, New York, 1953, Part I; (f) R. Plonsey and R. Collin, *Principles and Applications of Electromagnetic Fields*, McGraw-Hill, New York, 1961; (g) R. B. McQuistan, *Scalar and Vector Fields: A Physical Interpretation*, Wiley, New York, 1965.
- [47] R. Abrol and A. Kuppermann, *J. Chem. Phys.*, 2001, **115**, 4640.
- [48] R. J. Buenker and Y. Li, *J. Chem. Phys.*, 2000, **112**, 8318; See also A. K. Belyaev, A. Dalgarno and R. McCarroll, *J. Chem. Phys.*, 2002, **116**, 5395.
- [49] U. Brosa and S. Grossmann, *Eur. Phys. J., B*, 2002, **26**, 121.
- [50] See, e.g., G. Dassios and I. V. Lindell, *J. Phys. A*, 2002, **35**, 5139, and references therein.
- [51] (a) C. G. Gray, *Am. J. Phys.*, 1978, **46**, 169; (b) P. R. Wallace, *Can. J. Phys.*, 1951, **29**, 393.
- [52] H. B. Phillips, *Vector Analysis*, Wiley, New York, 1946.
- [53] (a) A. M. Mebel, M. Baer, V. M. Rozenbaum and S. H. Lin, *Chem. Phys. Lett.*, 2001, **336**, 135; (b) M. Baer, A. M. Mebel and G. D. Billing, *J. Phys. Chem. A*, 2002, **106**, 6499; (c) M. Baer and R. Engelman, *Chem. Phys. Lett.*, 2001, **335**, 85.
- [54] (a) M. Baer, *Chem. Phys. Lett.*, 2001, **349**, 84; (b) M. Baer, *Chem. Phys. Lett.*, 2002, **360**, 243.
- [55] (a) M. Baer and A. Alijah, *Chem. Phys. Lett.*, 2000, **319**, 389; (b) M. Baer, *J. Phys. Chem. A*, 2000, **104**, 318; (c) M. Baer, S. H. Lin, A. Alijah, S. Adhikari and G. D. Billing, *Phys. Rev. A*, 2000, **62**, 032506; (d) S. Adhikari, G. D. Billing, A. Alijah, S. H. Lin and M. Baer, *Phys. Rev. A*, 2000, **62**, 032507.
- [56] (a) G. Chaban, M. S. Gordon and D. R. Yarkony, *J. Phys. Chem. A*, 1997, **101**, 7953; (b) A. Mebel, M. Baer and S. H. Lin, *J. Chem. Phys.*, 2000, **112**, 10703.
- [57] J. Avery, M. Baer and G. D. Billing, *Mol. Phys.*, 2002, **100**, 1011.
- [58] (a) J. M. Hutson and B. J. Howard, *Mol. Phys.*, 1980, **41**, 1113; (b) V. Špirko and J. Čížek, *J. Chem. Phys.*, 1995, **102**, 8906; (c) V. Špirko, J. Čížek and L. Skála, *J. Chem. Phys.*, 1995, **102**, 8916; (d) V. Špirko and J. Čížek, *J. Chem. Phys.*, 1997, **106**, 6338; (e) V. Špirko, M. Rozložník and J. Čížek, *Phys. Rev. A*, 2000, **61**, 014102; (f) F. Dufey and S. Fischer, *Phys. Rev. A*, 2001, **63**, 042510; (g) F. Dufey, *J. Chem. Phys.*, 2001, **115**, 7375.
- [59] R. Meiswinkel and H. Köppel, *Chem. Phys.* **144**, 1990, 117.
- [60] A. Alijah and M. Baer, *J. Phys. Chem. A*, 2000, **104**, 389.
- [61] J. N. Murrell, *J. Am. Chem. Soc.*, 1959, **81**, 5037.
- [62] R. S. Mulliken and W. B. Person, *Molecular Complexes: A Lecture and Reprint Volume*, Wiley, New York, 1969.
- [63] M. Bixon, J. Jortner and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1994, **116**, 7349.

- [64] I. R. Gould, R. H. Young, L. J. Mueller, A. C. Albrecht and S. Farid, *J. Am. Chem. Soc.*, 1994, **116**, 8176–8188.
- [65] J. Herbich and A. Kapturkiewicz, *J. Am. Chem. Soc.*, 1988, **110**, 1014.
- [66] M. Rust, J. Lappe and R. J. Cave, *J. Phys. Chem. A*, 2002, **106**, 3930.
- [67] (a) M. Baer and A. M. Mebel, *Int. J. Quantum Chem.*, 2001, **85**, 315; (b) M. Baer, *J. Phys. Chem. A*, 2001, **105**, 2198.
- [68] E. S. Kryachko, *J. Phys. Chem. A*, 1999, **103**, 4368.
- [69] (a) N. S. Hush, *Electrochim. Acta*, 1968, **13**, 1005; (b) J. R. Reimers and N. S. Hush, *J. Phys. Chem.*, 1991, **95**, 47.
- [70] (a) M. D. Newton, *Chem. Rev.*, 1991, **91**, 767; (b) M. D. Newton and R. J. Cave, in *Molecular Electronics* (eds. J. Jortner and M. Ratner), Blackwell Science, New York, 1997, 73; (c) R. J. Cave and M. D. Newton, *Chem. Phys. Lett.*, 1996, **249**, 15; (d) R. J. Cave and M. D. Newton, *J. Chem. Phys.*, 1997, **106**, 9213; (e) C. Creutz, M. D. Newton and N. Sutin, *J. Photochem. Photobiol. A: Chem.*, 1994, **82**, 47; (f) R. J. Cave, M. D. Newton, K. Kumar and M. B. Zimmt, *J. Phys. Chem.*, 1995, **99**, 17501; (g) C. M. Elliott, D. L. Derr, S. Ferrere, M. D. Newton and Y.-P. Liu, *J. Am. Chem. Soc.*, 1996, **118**, 5221; (h) E. Culier, S. Daniels, E. Vinson and R. J. Cave, *J. Phys. Chem. A*, 2002, **106**, 11240, and references therein.
- [71] (a) R. A. Marcus, *Annu. Rev. Phys. Chem.*, 1964, **15**, 155; (b) V. G. Levich and R. R. Dogonadze, *Dokl. Akad. Nauk SSSR*, 1959, **124**, 9; (c) H. Kim and J. T. Hynes, *J. Phys. Chem.*, 1990, **94**, 2736; (d) D. V. Matyushov and B. M. Ladanyi, *J. Phys. Chem. A*, 1997, **102**, 5027; (e) See Appendix of (d); (f) D. Lu, G. Chen, J. W. Perry and W. A. Goddard, III, *J. Am. Chem. Soc.*, 1994, **116**, 10679, and references therein.

Jahn–Teller Effect in the Excited State: Anomalous Temperature Dependence of the Zero-Phonon Line

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Abstract

We are studying a zero-phonon line (ZPL) in the optical spectra of impurity centers in crystals, taking into account the strong Jahn–Teller effect in the excited state. We have found that, if this effect brings the system close to the dynamical instability, then at low temperatures the usual T^7 -dependence of the homogeneous width of the ZPL is replaced by the T^3 -dependence. One example of such a case is given by a center with a strong linear E–e Jahn–Teller effect. In this case the dynamical motion in the relaxed E-state is on the verge of the dynamical instability with respect to a shift along the bottom of the trough of the adiabatic potential. The first excited state of the nitrogen-containing centers in diamond crystals belongs to this type of states. Our experimental study of the emission of this center from E-state indeed has revealed the T^3 -type temperature broadening of the ZPL at low temperature.

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1. INTRODUCTION

The temperature dependence of the homogeneous width of zero-phonon lines (ZPLs) in the optical spectra of the impurity centers in crystals is determined by

the dephasing of the electronic excitation. Usually the main contribution to this process is given by the change of the local springs on the electronic transition in the center. This change causes the Raman-type processes when one phonon is absorbed and another phonon of a close energy is emitted at the optical transition. At low temperatures only low-energy acoustic phonons remarkably contribute to these processes. The ordinary temperature dependence of the ZPL broadening given by this mechanism at low temperatures $T \ll T_D$ is $\gamma \propto T^7$ [1–8] (here T_D is the Debye temperature).

The mechanism of the ZPL broadening described above holds for nondegenerate electronic levels. For degenerate levels an additional dephasing mechanism, caused by the Jahn–Teller effect, should be taken into account. In this case also at low temperatures the main contribution to the broadening of the ZPL is given by acoustic phonons. If the corresponding vibronic interaction is weak (this case is usually referred to as the dynamic Jahn–Teller effect), then one can apply the standard perturbation theory. In this case one finds the T^5 law of the broadening of ZPLs at low temperatures [9].

If the nondiagonal Jahn–Teller interaction is strong, then one cannot apply the perturbation theory. However, in this case, if one restricts oneself with the consideration of the ZPL only, then one can neglect all the sheets of the surface of the adiabatic potential (AP) of the degenerate state except the lowest one. It also suffices to include into consideration only one (any) minimum of the AP, while in this case only a small area of the configurational space actually contributes to the optical transitions of the ZPL; an account of other equivalent minima gives the same broadening. However, in this case a correct consideration of the Raman broadening mechanism caused by the change of the quadratic vibronic interaction is needed, while in the case of strong Jahn–Teller effect the elastic springs in the Jahn–Teller minimum differ essentially from those in the initial electronic state.

A change of the elastic springs on the electronic transition results in the change of the local density of states of phonons on the transition. If the quadratic interaction, being responsible for the change of the springs, is weak, then the change of the phonon density is also small and it may be neglected (in the standard theory it is neglected [3,4]). If the quadratic interaction is not weak, then the change of the local density of states of phonons becomes important. If there is a bond, which is remarkably softened on the electronic transition, then the local density of states of phonons also strongly shifts towards low frequencies. This can remarkably affect the temperature dependence of the ZPL at low temperatures. To describe the ZPL in this case, a nonperturbative theory [5,6,10] should be used. Later, this theory will be applied to a case wherein in one of electronic states the system gets to the verge of the dynamical instability. We will show (see also [10]) that in this case the width of the ZPL at low temperatures is described by the T^3 law.

One well-known example of the physical system where the described approach can be applied is the A_1 –E optical transition in trigonal centers with the E–e-type Jahn–Teller interaction. In this case the AP in the electronic E-state has a shape of the Mexican hat [11–14]. If the E–e-type Jahn–Teller interaction is strong, then the Mexican hat is large and the AP has a long minimum line along the trough. In this

case the system has no rigidity with respect to the dynamical motion along this line. The inclusion of quadratic vibronic coupling terms produces three minima in the trough. However, if this interaction is small, then the system in the relaxed E-state remains close to the dynamical instability.

If there are several AP minima of close energy, then at low temperatures one should take into account two-phonon-assisted transitions between these minima. In Ref. [15] (see also Ref. [14]) it was found that the rate of these transitions depends on temperature as T^3 . However, as it was already mentioned above, in Ref. [9] it was found that the contribution of the two-phonon-assisted transitions between different Jahn–Teller minima of the AP to the ZPL width at low temperatures is described by the T^5 law. Note that an increase of the Jahn–Teller interaction leads to a decrease of the rate of these transitions. Therefore, in the strong Jahn–Teller interaction limit this broadening mechanism becomes unimportant.

One more possibility to explain the T^3 dependence of the ZPL width has been proposed in Ref. [16]. It was found here that in defect-rich crystals the modulation of the ZPL frequency by the fluctuating entire field produced by defects leads to the given dependence.

One example of a concrete system where one observes optical spectrum caused by the A_1 –E electronic transition is the N–V center in diamond. This center consists of a substitutional N atom and three nearest C atoms (one of the nearest C atoms is replaced by the vacancy) and it has a trigonal symmetry. The ZPL line at 637 nm of this center corresponds to the electronic transition between the triplet ^3A and the ^3E electronic states. In the standard model of this center the electronic states of the center come from the occupation and the splitting of the a_1 and t_2 levels arising from three C radicals. The crystalline field of a trigonal symmetry splits the t_2 level into a number of states including the ground (A_1) state and the first excited E-state (see, e.g. Refs. [17–25]). Our experimental study of the optical transition between the E and the A_1 electronic states indeed showed the T^3 dependence of the ZPL width at low temperatures.

An important property of this N–V system is a small level spacing in the excited electronic state [25]. This leads to a remarkable vibronic mixing of these levels. One of the results of this mixing (called as the pseudo-Jahn–Teller effect) is the softening of the AP of the lowest excited state (E-state). In [10] this softening has been considered as a reason for the T^3 broadening of the ZPL at low temperatures. However, it is not very probable that this effect (which most probably takes place in the excited state of the N–V center in diamond) by itself brings the system exactly to the verge of the dynamical instability. Here we consider another possibility to explain the observed T^3 broadening of the ZPL – the Jahn–Teller effect in the excited E-state which is enhanced by the pseudo-Jahn–Teller effect. In this scenario the pseudo-Jahn–Teller effect ‘helps’ to get the system to a state being close to the verge of the dynamical instability due to enlargement of the Jahn–Teller distortion with the softening (decreasing) of the elastic springs. The above-mentioned softening of the excited E-state of the N–V centers, which is caused by the vibronic mixing of this state with the other excited states of higher (but close) energies, has an independent experimental support: a remarkable reduction of the barrier for the tunneling motion of the N atom in this state [26].

In this communication we will give a description of the vibronic E–e interaction in an optical center in a crystal near one of the minima of the trough of the deformed (due to the quadratic vibronic coupling) Mexican-hat-type AP. We will also present a derivation of the nonperturbative formula describing the temperature dependence of the ZPL in the case of an arbitrary change of the elastic springs on the electronic transition. Then we will study a case when the excited state is close to the dynamical instability. Finally, we will apply the obtained general results to the ZPLs in N–V centers in diamond.

2. STRONG JAHN–TELLER EFFECT: OPTICAL A_1 –E TRANSITION

Here we consider an optical transition between A_1 and E electronic states of a center of a trigonal symmetry. To describe the vibrations of the center we use the collinear-configurational approximation [27] in which only the central forces are taken into account in the optical center (taking account of deviations from this approximation, see later). If one restricts oneself to the linear vibronic coupling in the e state, then in this approximation the potential energy operators in the A_1 and E electronic states can be presented in the form:

$$U_1 = \sum_{nn'} \sum_{i=1,2} D_{nn'} Q_{ni} Q_{n'i} / 2 + w_1 (q_1^2 + q_2^2) / 2 \quad (1)$$

$$U_2 = U_1 \cdot I + v(\sigma_1 q_1 + \sigma_2 q_2) + (w_2 - w_1)(q_1^2 + q_2^2) / 2$$

Here w_1 and w_2 are the positive elastic springs ($w_{1,2} > 0$), q_i , $i = 1, 2$ is the symmetrized difference of the central displacements of the central atom and its nearest neighboring atoms, i denotes the row of the e -representation, Q_{ni} are all the other displacements of the crystal, being orthogonal to q_1 and q_2 , I is the second-order unit matrix, σ_1 and σ_3 are the Pauli matrices. The configurational coordinates q_1 and q_2 can be expanded into the normal coordinates x_{ij} and x_{2j} of the e -representation as follows:

$$q_m = \sum_j e_j x_{m,j}, \quad m = 1, 2 \quad (2)$$

The AP of the A_1 -electronic state in the q_1, q_2 -space is the rotatory paraboloid. The AP of the E -state is given by the matrix V_2 in the diagonal representation it has the form of the Mexican hat [11–14]. The vibronic E -state is invariant with respect to the rotation of the q_1, q_2 -surface on the arbitrary angle ϕ with the simultaneous rotation of the electronic basis states on the angle 2ϕ . In polar coordinates $\rho = (q_1^2 + q_2^2)^{1/2}$ and $\phi = \arctan(q_2/q_1)$ the APs do not depend on ϕ :

$$V_1 = w_1 \rho^2, \quad V_2 = -b\rho + w_2 \rho^2 / 2$$

(we take into account only the lowest sheet of the AP of the E -state).

We consider the dependence of the potential surfaces V_1 and V_2 on q_1 and q_2 in the vicinity of the point $\rho = \rho_0 = |v|/w_2$, $\phi = 0$. This point lies on the minimum line of

the Mexican hat. The dependence of the potentials on q_1 and q_2 near this point is as follows:

$$V_1 \approx w_1(q_1^2 + q_2^2)/2$$

$$V_2 \approx w_2[(q_1 - \rho_0)^2 + (q_1 - \rho_0)q_2^2/\rho_0 - \rho_0^2]/2$$

Note that in the vicinity of the point considered, the potential V_2 up to quadratic terms included does not depend on q_2 ; i.e., this potential is on the verge of the dynamical instability with respect to a shift in the q_2 direction. Note also that the Jahn–Teller distortion parameter ρ_0 increases if the quadratic interaction parameter w_2 decreases. The reason for such a decrease may be, as it was already noticed above, the pseudo-Jahn–Teller effect.

The difference of the APs of the E- and A_1 -electronic states in the vicinity of the point $\rho = \rho_0 = |v|/w_2$, $\phi = 0$ equals

$$V \approx vq_1 + (w_2 - w_1)q_1^2/2 - w_1q_2^2/2$$

If one takes into account also the quadratic vibronic interaction in the E-state, then the ϕ -dependent term appears in the AP of this state [11–14]:

$$V_2 = -v\rho + w_2\rho^2/2 + c\rho^2 \cos(3\phi)$$

As a rule, the $\propto \cos(3\phi)$ - term is small. With account of this term, the difference of the potentials of the E- and A_1 -electronic states near a minimum/maximum of the deformed Mexican hat has a form

$$V \approx vq_1 + (w_2 - w_1)q_1^2/2 - w_1q_2^2/2 \pm |c|(q_1^2 - 9q_2^2/2) \quad (3)$$

where, as a rule, $|c| \ll w_2$. Note that for different signs in equation (3) the definition of the angle ϕ and, correspondingly, the coordinates q_1 and q_2 are different.

Above the collinear-configurational approximation (1) was used. If one wants to take into account the deviations from this approximation then in equation (3) the term $V' = \sum_{ni} w_n Q_{ni} q_i$ should be added.

3. ZERO-PHONON LINE: POSITION AND WIDTH

To describe the effect of the change of the elastic springs on the optical spectrum of an impurity center, we use the adiabatic approximation. In this approximation, phonons are described by different phonon Hamiltonians in different electronic states. The optical spectrum, which corresponds to a transition between different electronic states is determined by the expression $\tilde{I}(\omega) = \text{const} \times \omega^{2\mp 1} I(\omega)$ [28], where the ‘–’ sign corresponds to the absorption spectrum and the ‘+’ sign stands for the emission spectrum,

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t - \gamma^{(0)}|t|} F(t)$$

$\gamma^{(0)}$ is the natural line-width, corresponds to $\hbar = 1$, $F(t) = \langle M e^{it(H+V)} M e^{-itH} \rangle$ is the Fourier transform of the spectrum, and $\langle \dots \rangle = A v_i \langle i | \dots | i \rangle$ denotes a quantum-statistical averaging over the initial states, H and $H + V$ are vibrational Hamiltonians of the initial (ground) and the final (excited) electronic state (we use $\hbar = 1$ units). Below we restrict ourselves to the consideration of the ZPL only. This allows us to use the Condon approximation, which accounts only for the constant term in the expansion of the electronic matrix element M with respect to the normal coordinates x_j : $M \approx M_0 = \text{const}$. We normalize M_0 to unity. Then

$$F(t) = \langle e^{it(H+V)} e^{-itH} \rangle \quad (4)$$

We also restrict ourselves to the harmonic approximation

$$H = \sum_j (-\partial^2 / \partial x_j^2 + \omega_j^2 x_j^2) / 2, \quad V = \omega_0 + (vq) + (qwq) / 2 \quad (5)$$

where ω_0 is the frequency of the electronic transition, x_j is the coordinate of the j th normal oscillator, $q = \sum_j e_j x_j$ is the vector of configurational coordinates, v and w are the vectorial and the tensorial set of the parameters of vibronic interaction. Note that equations (4) and (5) are also applicable to the case of degenerate electronic levels, e.g. to optical transitions between a nondegenerate to a degenerate levels. However in the latter case one should consider v and w to be $n \times n$ matrices, where n is the degeneracy of the final electronic state.

3.1. Large time asymptotic of the Fourier transform

In the case of the A_1 –E optical transition one can present H and V as the sum of the independent terms belonging to different representations. In this case the Fourier transform $F(t)$ is the product of the multipliers belonging to these representations. We are interested in the multiplier, which describes the contribution of the e -vibrations. Here we consider the case of strong Jahn–Teller effect. ZPL in this case is described by the optical transitions for configurational coordinates q_1 and q_2 in the vicinity of the AP minima. This means that one can use equation (4) with V given by equation (3). In this approximation the configurational coordinates q_1 and q_2 contribute to $F(t)$ independently. Later we consider a contribution of one of these coordinates and omit the index of the line of the representation.

We are interested only in the temperature dependence of the position and the width of the ZPL. We suppose that coordinates q in the linear term (vq) in equation (5) are orthogonal to the coordinates contributing to the quadratic term $(qwq)/2$. In this case the linear term does not contribute to these characteristics of the ZPL. This allows us to exclude this term from the further consideration.

We apply the Feynman formula:

$$e^{it(H+V)} e^{-itH} = \hat{T} \exp \left(i \int_0^t ds V(s) \right) \quad (6)$$

where $\hat{T}$ is the time-ordering operator, $V(s) = wq^2(s)/2$. By using the well-known cumulant expansion [28], this formula can be presented in the form:

$$F(t) = e^{g(t)}$$

where

$$g(t) = i\omega_0 t + \sum_{n=1}^{\infty} (i\omega)^n \langle \hat{T} \hat{f}_t^n \rangle_c / n!, \quad \hat{f}_t = \frac{1}{2} \int_0^t q^2(s) ds \quad (7)$$

where $\langle \dots \rangle_c$ denotes the cumulant averaging (in this averaging one should include only the connected diagrams [29]). To calculate

$$\langle \hat{T} \hat{f}_t \hat{f}_t \dots \rangle_c = \int_0^t ds \int_0^t ds' \dots \langle \hat{T} q^2(s) q^2(s') \dots \rangle_c$$

one can use the Bloch–DeDomicis theorem on pair correlations. Note that two coordinate operators have the same time. Starting with the pairing of the operator $q(s_1)$ with the operator $q(s_2)$ and proceeding step by step so that the next pairing involves the same time operator, which was paired at the last step, one gets

$$\langle \hat{T} \hat{f}_t^n \rangle_c = \frac{(n-1)!}{2} \int_0^t ds_1 \int_0^t ds_2 \dots \int_0^t ds_n D(s_1 - s_2) D(s_2 - s_3) \dots D(s_n - s_1) \quad (8)$$

where $D(s - s') = \langle \hat{T} q(s) q(s') \rangle$. The function under the integral depends on the time difference. This allows one to replace the integration limits 0 and t , respectively by $-t/2$ and $t/2$. In the spectral representation one gets

$$\begin{aligned} \langle \hat{T} \hat{f}_t^n \rangle_c &= (-i)^n \frac{(n-1)!}{2} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \dots \int_{-\infty}^{\infty} d\omega_n D(\omega_1) D(\omega_2) \dots D(\omega_n) \\ &\quad \varphi_t(\omega_1 - \omega_2) \varphi_t(\omega_2 - \omega_3) \dots \varphi_t(\omega_n - \omega_1) \end{aligned} \quad (9)$$

where

$$D(t) = (-i/2\pi) \int_{-\infty}^{\infty} d\omega e^{i\omega t} D(\omega), \quad \varphi_t(\omega) = \frac{1}{2\pi} \int_{-t/2}^{t/2} ds e^{-i\omega s} \quad (10)$$

The ZPL, being the narrowest line of the spectrum is determined by the large time asymptotic of the Fourier transform. In the large t limit $\varphi_t(\omega) \simeq \delta(\omega)$. Taking also into account that $\varphi_t(0) \simeq t/2\pi$, one gets in the large t limit [5,6]

$$g(t) = (i\omega_0 + i\delta - \gamma)t$$

where

$$i\delta - \gamma = \int_{-\infty}^{\infty} (d\omega/4\pi) \sum_n w^n D^n(\omega) / n = - \int_{-\infty}^{\infty} (d\omega/4\pi) \ln(1 - wD(\omega)) \quad (11)$$

is the contribution of the quadratic vibronic interaction to the ZPL frequency and width. If more than one configurational coordinate contribute to V , including the case when one takes into account the deviations from the collinear-configurational

approximation, then the factor $1 - wD(\omega)$ should be replaced by $\det\{1 - wD(\omega)\}$. If different configurational coordinates q_m belong to different representations (or different rows of one representation), then $\delta + i\gamma$ is given by the additive contributions of different coordinates.

A simple calculation gives $D(\omega) = G(\omega) + 2i\pi\bar{n}(|\omega|)I(|\omega|)$, where

$$G(\omega) = \int_0^\infty \frac{d\omega' \rho(\omega')}{\omega^2 - \omega'^2 - i0_+} \quad (12)$$

is the Green function of the displacement q in the spectral representation [30,31], $I(\omega) = \rho(\omega)/2\omega$, $\rho(\omega) = \sum_j e_j^2 \delta(\omega - \omega_j)$ is the local phonon density of states in the initial level, $\bar{n}(\omega) = 1/(\exp(\omega/k_B T) - 1)$. One can see that $D(\omega) = D(-\omega)$.

3.2. Low temperature

Let us separate the $T = 0$ part and the temperature-dependent part of γ and δ . The first part equals

$$\delta_0 + i\gamma_0 = \frac{i}{4\pi} \int_{-\infty}^\infty d\omega \ln(1 - wG(\omega)) \quad (13)$$

The temperature-dependent part of the $g(t)/t$ -function is as follows:

$$\gamma_T - i\delta_T = \int_0^\infty (d\omega/2\pi) \ln(1 - 2i\pi w\bar{n}(\omega)I(\omega))(1 + wG_1(\omega)) \quad (14)$$

where $G_1(\omega)$ is the Green function in the final (excited) electronic level; this function satisfies the Lifshitz (Dyson) equation $G_1(\omega) = G(\omega)(1 + wG_1(\omega))$, which gives $1 + wG_1(\omega) = 1/(1 - wG(\omega))$. At low temperatures (small ω and $n(\omega)$ under the integral (2)) one gets

$$\gamma_T \approx \pi w^2 \int_0^\infty d\omega \bar{n}(\omega)I(\omega)G_1(\omega) \quad (15)$$

$$\delta_T \approx w \int_0^\infty d\omega \bar{n}(\omega)I(\omega)(1 + w \operatorname{Re} G_1(\omega)) \quad (16)$$

where $\Gamma_1(\omega) = \operatorname{Im} G_1(\omega)/\pi$ is the weighted phonon density of states of the excited level. Equation (15) for the ZPL width holds both for absorption and emission. To obtain an equation for the position of ZPL in emission, one should change in equation (16) the sign of w in the brackets and permute $G(\omega)$ and $G_1(\omega)$. However, it will not change the value of (this statement holds for any temperature [6]).

Electronic state are dynamically stable if there are no poles of the phonon Greens functions $G(\omega)$ and $G_1(\omega)$ at imaginary ω (i.e., if $G(\omega)$ and the resolvent

$1/(1 - wG(\omega))$ have no poles at $\omega^2 < 0$). In this case, $\gamma_0 = 0$ which can immediately be seen from the following form of equation (13):

$$\delta_0 + i\gamma_0 = \frac{1}{4\pi} \int_{-\infty}^{\infty} d\omega \arctan\left(\frac{w \operatorname{Im} G(\omega)}{1 - w \operatorname{Re} G(\omega)}\right) \quad (17)$$

Here the argument of the arctan does not diverge at any ω . Therefore the integral (17) is real (i.e., $\gamma_0 = 0$). Note that equation (17) is well known in the lattice dynamics; it describes the contribution of an impurity to the phonon part of the free energy of the crystal (in $\hbar = 1$ units) at $T = 0$, supposing that the impurity does not change the point symmetry of the crystal lattice [30].

If the weakening is of the elastic spring at the electronic transition is so strong that the condition $w < w_{\text{cr}} = 1/\operatorname{Re} G(0)$ is fulfilled then the resolvent in equation (17) (as well as the Green function of the final state $G_1(\omega)$) has a pole at the negative ω^2 (imaginary ω). In this case, the excited state is dynamically unstable and γ_0 is finite. To find γ_0 we take into account that the function $G(\omega)$ can be analytically continued into the upper half of the complex plane (above the line $\operatorname{Im} \omega = 0_{+\operatorname{sign}(\omega)}$). Therefore, the pole contribution to the integral (13) can be written in the form:

$$\gamma_0 = -(1/4\pi) \int_C d\omega \ln(1 + wG_1(\omega))$$

where the subscript C denotes that integration has been performed around the upper half-plane. Note that in this case the final state of the transition under consideration does not correspond to the zero-point state of the excited level; it corresponds to the maximum of a potential barrier (not to a minimum). Strictly speaking, this spectral line is not a real ZPL; the latter is situated to the red and it may have rather a small intensity.

We consider the case when $w/w_{\text{cr}} - 1$ is small. Then the poles of the resolvent $1/(1 - wG(\omega))$ are situated at small $|\omega|$, where $|G(\omega)|$ is also small. Then $\ln(1 + wG_1(\omega)) \approx wG_1(\omega)$. In three-dimensional crystals for small ω , $\operatorname{Re} G(\omega) \approx G(0) - \beta\omega^2$, $\operatorname{Im} G(\omega) \approx \alpha\omega^3$, where α and β are positive parameters. The poles are situated at $\omega = \pm i\Gamma_0$ with $\Gamma_0 \approx \sqrt{(w_{\text{cr}} - w)/\beta w_{\text{cr}}^2}$.

3.3. Close to dynamical instability

Here we consider the case when the elastic springs in the excited state are remarkably weakened (the weakening of the springs in the ground state can be regarded analogously).

Therefore, $\gamma_0 \approx -w_{\text{cr}} \operatorname{Im} G(i\Gamma_0)/4\Gamma_0$, which gives

$$\gamma_0 \approx \frac{\alpha(w_{\text{cr}} - w)}{4\beta^2 w_{\text{cr}}^2} \theta(w_{\text{cr}} - w) \quad (18)$$

In the case $0 < (w - w_{\text{cr}})/w_{\text{cr}} \ll 1$ the width of the ZPL at $T = 0$ is finite.

Here we are interested in the low temperature behavior of the ZPL if the excited state is close to dynamical instability. We must account for the acoustic phonons. First we consider the limiting case $w = w_{\text{cr}}$. Taking into account that, with account of the acoustic phonons, for small ω $\text{Re}(G(\omega) - G(0)) \approx -\beta\omega^2$, $\text{Im } G(\omega) \approx \alpha\omega^3$, we get (see equation (14))

$$\gamma_T \approx \frac{\alpha^2}{\pi} \int_0^\infty \frac{d\omega \omega^6 n(\omega)}{\alpha^2 \omega^6 + \beta^2 \omega^4} \approx 2\zeta(3)\alpha^2 k_B^3 T^3 / \pi\beta^2 \quad (19)$$

where $\zeta(\nu)$ is the ζ -function; $\zeta(3) \approx 1.202$. From this expression it follows that, if the system gets close to the stability limit $w = w_{\text{cr}}$, then the temperature broadening of the ZPL at low temperatures is described by the T^3 law. In this limit the temperature shift of the ZPL is:

$$\delta_T \approx \frac{\alpha\beta}{\pi} \int_0^\infty \frac{d\omega \omega^5 n(\omega)}{\alpha^2 \omega^6 + \beta^2 \omega^4} \approx \pi\alpha k_B^2 T^2 / 6\beta \quad (20)$$

Note that the shift is to the blue. We remind that in standard model (which works at small $|w/w_{\text{cr}}|$) the sign of the shift depends on the sign of w .

Let us consider now the case when $w \neq w_{\text{cr}}$. We apply the Debye model

$$G(\omega) = -(5/2\omega_D^2)(2/3 + 2\Omega^2 + \Omega^3 \ln((1 + \Omega)/(1 - \Omega)) - i\pi\Omega^3)$$

Here $\Omega = \omega/\omega_D$, ω_D is the Debye frequency, $n(\Omega) = 1/[\exp(\Omega T_D/T) - 1]$, $T_D = \hbar\omega_D/k_B$ is the Debye temperature (in this model $\gamma_0 \approx (\pi\omega_D/24)(w/w_{\text{cr}} - 1)\theta(w_{\text{cr}} - w)$). The results of numerical calculations of the temperature dependence of the width and position of ZPL are given in Fig. 1.

One sees that, if $|w_{\text{cr}}/w - 1| \ll 1$ then $\gamma_T \propto T^3$, $\delta_T \propto T^2$. For $|w| < |w_{\text{cr}}|$ the temperature shift of the ZPL at low temperatures is red; however at higher temperatures and/or for very small $|w_{\text{cr}}/w - 1|$ it is changed to blue. Note the enhancement of γ_T at $w_{\text{cr}}/w \sim 1.02$; it is due to the low frequency peak in $\Gamma_1(\omega)$ which corresponds to the pseudolocal mode appearing in the excited state for such parameters.

In real systems a number of coordinates usually contribute to γ and δ ; not all of them can be related to softening modes. Therefore, one should expect that at low temperatures and $|(w - w_{\text{cr}})/w_{\text{cr}}| \ll 1$ the ZPL width can be described by the equations $\gamma \approx \gamma_0 + aT^3 + bT^7$, where the $\propto T^7$ term accounts for the contribution of hard modes (a and b are positive parameters). The temperature dependence of the position of the ZPL can be approximated by the equation $\delta_T \approx \mu T^2 - \nu T^4$, where the sign of μ may be positive or negative. The term $\propto T^4$ accounts for the contribution of hard modes. The sign of ν is positive if the elastic springs are reduced with excitation.

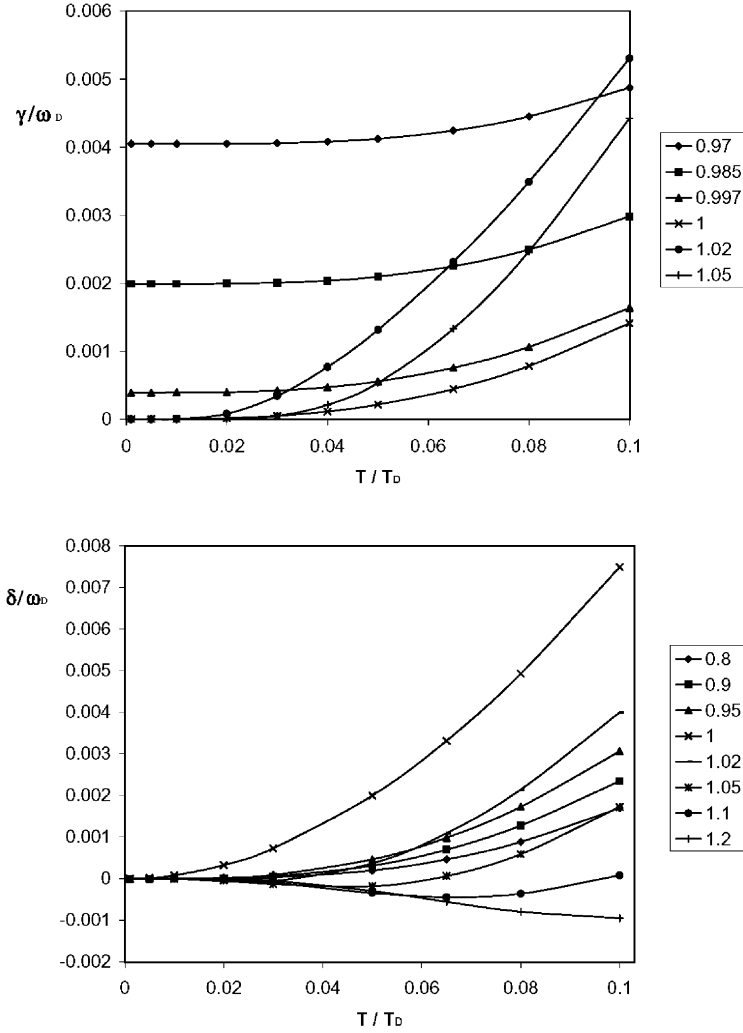


Fig. 1. Temperature dependence of the homogeneous width γ (a) and position δ (b) (in ω_D units) of a zero-phonon line in the Debye model for different values of the interaction parameter w_{cr}/w indicated in the right-side boxes. The instability limit corresponds to $w_{cr}/w = 1$.

4. APPLICATION TO A_1 –E TRANSITION

According to equation (3) the vibronic interaction V of the A_1 – E optical transition is the additive function of two terms depending respectively on q_1 and q_2 . Here we are interested only in the contribution of the q_2 -term to the width and position of the ZPL. This term is purely quadratic, which allows one to apply the presented

above theory of ZPL. In the collinear-configurational approximation (1) the Lifshitz equation gives the following relations:

$$G(\omega) = \frac{G_0(\omega)}{1 - w_1 G_0(\omega)}, \quad G_1(\omega) = \frac{G_0(\omega)}{1 \pm 9|c|G_0(\omega)}$$

where $G_0(\omega)$ is the contribution to $G(\omega)$ which does not account for the local quadratic vibronic interaction V_1 . The sign ‘ $-$ ’ corresponds to a minimum in the AP of the E-state, being dynamically stable; the sign ‘ $+$ ’ correspond to a saddle point of this AP, which have higher energy and is dynamically unstable.

From the physical consideration it is clear that in the $w_1 = 0$ limit the optical center in the initial state is just on the verge of the dynamical instability. This means that the relation $w_1 G_0(0) = 1$ holds for the model under consideration. Besides, if $c = 0$ then $G_2(\omega) = G_0(\omega)$; i.e., the excited state is (as it should be) on the verge of the dynamical instability. Consequently in the case of strong linear Jahn–Teller effect at low temperatures the ZPL is described by equations (19) and (20). Consequently the width of the ZPL in the case of the optical transition A_1 –E with the strong linear Jahn–Teller effect in the E-state increases with temperature as T^3 .

If c remarkably differs from zero then there are three equivalent minima and three equivalent saddle points on the trough of the deformed Mexican hat [see equation (3)], which are described by different signs in equation (3) for V . Therefore one can observe two ZPL, which corresponds to transitions into the vicinity of a minimum and into vicinity of a saddle point. The frequency difference of these lines is $v^2|c|/(w_2^2 - c^2)$. The lower frequency line corresponds to the optical transition into a minimum, which is dynamically stable. The higher frequency line corresponds to the optical transition into a saddle point, which is dynamically unstable. The temperature dependence of these lines at low temperatures are described by equations (15) and (16) with $w = -(w_1 \pm 9|c|)$ (the sign ‘ $+$ ’ in the brackets corresponds to the line with higher frequency). The width of the line with lower frequency at $T = 0$ is equal to zero; the width of the higher frequency line at $T = 0$ differs from zero; it is described by equation (17) with $w_{cr} - w = 9|c|$.

5. EXPERIMENTAL

In our experimental study high-quality diamond films with a low (< 1 ppm) content of nitrogen atoms were used. ZPL of fluorescence of N–V centers at 637 nm in temperature interval from 2 to 200 K was measured. It occurred, at 2 K the shape of ZPL is a pure Gaussian, while at 10 K it starts broadening and deviation from Gaussian (in general, a Voigt-like shape) occurs. We considered the spectrum measured at 2 K as the inhomogeneous distribution function of 3E–3A electronic transitions and deconvoluted at higher temperatures measured spectra with Lorentzians to find homogeneous width of transitions. These procedures lead to the ‘homogeneous’ width 8 cm^{-1} of line at 2 K. It should be mentioned, that this

agrees qualitatively with experimental value, estimated from single molecule experiment [32]. The obtained in this way temperature dependence between 2 and 200 K (see Fig. 2a) can indeed be rather well described by the equation $\gamma \approx \gamma_0 + aT^3 + bT^7$ with $\gamma_0 = 8 \text{ cm}^{-1}$, $a = 2.88 \times 10^{-6} \text{ cm}^{-1} \text{ K}^{-3}$ and $b = 7.8 \times 10^{-16} \text{ cm}^{-1} \text{ K}^{-7}$. Note that the full width of the ZPL at 200 K is 41 cm^{-1} ; thereby 23 cm^{-1} (the main contribution to the temperature broadening) comes from the $\propto T^3$ term, 10 cm^{-1}

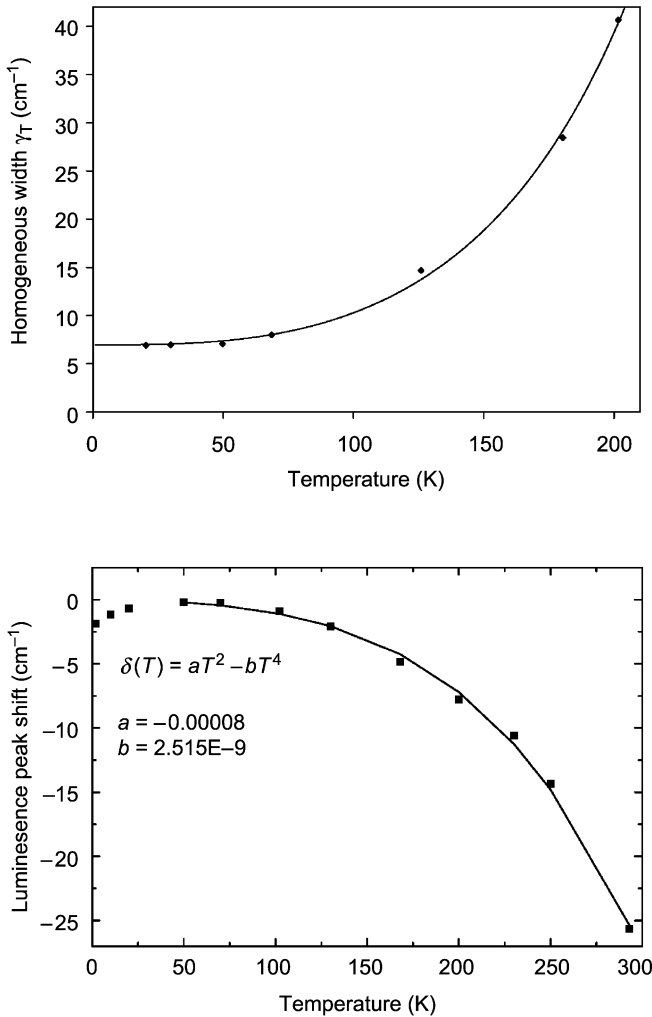


Fig. 2. Temperature dependence of the homogeneous width (a) and the peak shift (b) of the 637 nm zero-phonon line in luminescence spectrum of N–V centers in diamond films; points: experiment; the line: theoretical approximations according to the laws $\gamma = \gamma_0 + aT^3 + bT^7$ and $\delta = \mu T^2 - \nu T^4$.

are given by the $\propto T^7$ term. At present the origin of the residual width 8 cm^{-1} is not clear.

Shift of ZPL was also carefully experimentally investigated (see Fig. 2b). At temperatures from 2 up to 40 K the line shifts to the blue, while at higher temperatures the red shift is observed. This part of the shift is well described by the law $\delta_T = \mu T^2 - \nu T^4$ with $\mu = -8.0 \times 10^{-5}$, $\nu = 2.515 \times 10^{-9}$. Note that for $50 \text{ K} < T < 100 \text{ K}$ the $\propto T^2$ term dominates, while at higher temperatures the main term is $\propto T^4$.

Consequently both the temperature broadening and the main part of the shift of the ZPL of the N–V centers at 637 nm ZPL are well described by presented theory supposing that strong softening of the elastic springs in the excited state takes place (see Figs 2a and b). Only relatively small blue shift at $T < 40 \text{ K}$ most probably has another origin: it can be explained by repopulation between strain-induced sublevels of the excited 3E state [32].

6. CONCLUSION

The consideration given above shows that an account of the acoustic phonons in the case of a strong linear Jahn–Teller effect in the E-electronic state of a trigonal center leads to the T^3 -type law of the temperature broadening of the ZPL. The reason for such a law is the strong softening of the local springs of the optical center in the relaxed E-state. This softening causes a strong shift of the local density of states of acoustic phonons towards smaller frequencies, which remarkably enlarges the contribution of low-frequency phonons to the ZPL width (as compared to the case when no remarkable softening occurs and when the T^7 dependence of the ZPL line is expected). In the nitrogen-vacancy centers the Jahn–Teller interaction is, probably, enlarged by the pseudo-Jahn–Teller effect, causing an additional softening of the elastic forces. The latter softening has an independent experimental support: a remarkable reduction of the barrier for the tunneling motion of the N atom on the electronic transition. Speaking about the physical reasons for the remarkable pseudo-Jahn–Teller effect, one can assume that this is caused by the vibronic interaction, which mixes the lowest excited state with other excited states of close energies.

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REFERENCES

- [1] R. H. Silsbee, *Phys. Rev.*, 1962, **128**, 1726.
- [2] D. E. McCumber and M. D. Sturge, *J. Appl. Phys.*, 1963, **34**, 1622.
- [3] D. E. McCumber and M. D. Sturge, *Phys. Rev.*, 1964, **134**, 299.

- [4] M. A. Krivoglaz, *Sov. Phys. Solid State*, 1964, **6**, 1340.
- [5] D. F. Levenson, *Phys. Stat. Sol. (b)*, 1971, **43**, 739.
- [6] L. S. Osad'ko, *Sov. Phys. Usp.*, 1979, **22**, 311.
- [7] J. L. Skinner and D. Hsu, *Chem. Phys.*, 1986, **65**, 1.
- [8] V. Hizhnyakov, K. Seranski and U. Schurath, *Chem. Phys.*, 1992, **163**, 249.
- [9] V. Hizhnyakov and I. Tehver, in *Physics of Impurity Centers of Crystals* (ed. G. Zavt), Academy of Sciences of the Estonian SSR, Institute of Physics and Astronomy, Tallinn, 1972, p. 607.
- [10] V. Hizhnyakov, H. Kaasik and I. Sildos, *Phys. Stat. Sol. (b)*, 2002, **234**, 644.
- [11] H. C. Languet-Higgins, in *Advances in Spectroscopy* (ed. H. W. Thomson), Interscience, New York, 1961, Vol. II, p. 429.
- [12] R. Englman, *The Jahn–Teller Effect in Molecules and Crystals*, Wiley, London, New York, Sydney, Toronto, 1972.
- [13] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Nauka, 1983, (in Russian).
- [14] F. S. Ham, Jahn–Teller effects in electron paramagnetic resonance spectra, in *Electron Paramagnetic Resonance*, edited by S. Geshwind, Plenum, New York, 1972, pp. 1–119.
- [15] R. Pirc, R. Zeks and P. Gosar, *J. Phys. Chem. Solids*, 1966, **27**, 1219.
- [16] V. Hizhnyakov and P. Reineker, *J. Chem. Phys.*, 1999, **111**, 8131.
- [17] G. Davies and M. F. Hamer, *Proc. R. Soc. London A*, 1978, **348**, 285.
- [18] A. Halperin and O. Nawi, *J. Phys. Chem. Solids*, 1967, **28**, 2175.
- [19] R. Bauer, A. Osvet, I. Sildos and U. Bogner, *J. Lumin.*, 1993, **56**, 57–60.
- [20] I. Sildos, A. Suisalu, A. Osvet, V. Kiisk and V. Ralchenko, *Abstracts of the Ninth European Conference on Diamond, Diamond-like Materials, Nitrides and Silicon Carbide*, 13–18 September, 1998, Crete, Greece, p. 24.
- [21] C. Wei, K. Holliday, A. J. Meixner, M. Croci and U. O. Wild, *J. Lumin.*, 1991, **500**, 89.
- [22] S. J. Breuer and P. R. Briddon, *Phys. Rev. B*, 1995, **51**, 6984.
- [23] A. Lenef, S. W. Brown, D. A. Redman, S. C. Rand, J. Shigly and E. Fritsch, *Phys. Rev. B*, 1996, **53**, 13427.
- [24] J. P. Goss, R. Jones, P. R. Briddon, G. Davies, A. T. Collins, A. Mainwood, J. A. van Wyk, J. M. Baker, M. E. Newton, A. M. Stoneham and S. C. Lawson, *Phys. Rev. B*, 1997, **56**, 16031.
- [25] J. P. D. Martin, *J. Lumin.*, 1999, **81**, 237.
- [26] A. P. Nizovtsev, S. Ya. Kilin, C. Tietz, F. Jelezko and J. Wrachtrup, *Physica B*, 2001, **308–310**, 608.
- [27] A. Nitzan and J. Jortner, *Mol. Phys.*, 1973, **25**, 713; A. Nitzan, S. Mukamel and J. Jortner, *J. Chem. Phys.*, 1976, **63**, 200.
- [28] M. Lax, *J. Chem. Phys.*, 1952, **20**, 1752.
- [29] R. Kubo, *J. Phys. Soc. Jpn*, 1962, **17**, 1100.
- [30] A. A. Maradudin, E. W. Montroll and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation*, Academic, New York, 1963.
- [31] F. Jelezko, C. Tietz, A. Gruber, I. Popa, A. Nizovtsev, S. Kilin and J. Wrachtrup, *Single Mol.*, 2001, **2**, 255.
- [32] V. Kiisk, V. Palm, A. Suisalu and I. Sildos, *J. Lumin.*, 2000, **86**, 389.

Critical Dependence of Multiphonon Transitions on Interaction Strength and Temperature

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Abstract

A non-perturbative theory of the multiphonon relaxation of a localized vibrational mode, caused by a high-order anharmonic interaction with the nearest atoms of the crystal lattice, is proposed. It relates the rate of the process to the time-dependent non-stationary displacement correlation function of atoms. A non-linear integral equation for this function is derived and solved numerically for 3- and 4-phonon processes. We have found that the rate exhibits a critical behavior: it sharply increases near a specific (critical) value(s) of the interaction.

The temperature dependence of non-radiative transitions, caused by linear diagonal and quadratic non-diagonal vibronic interactions, is also investigated on the basis of the non-perturbative quantum theory. It was found that the usual increase of the transition rate with temperature does not hold near some critical values of the non-diagonal interaction and temperature. At these critical values the rate is high (comparable to the mean phonon frequency) and its temperature dependence has a maximum. The results may be important for understanding the mechanisms of catalysis in chemical reactions.

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1. INTRODUCTION

Multiphonon transitions in molecular systems and in solids are usually described by the perturbation theory [1–12]. This theory works only if the interaction causing the process is weak. However, very often this interaction is rather strong. To explain the results of measurements in such a case, a non-perturbative theory is needed.

Such a theory has been recently developed in Refs. [13,14] and has found first experimental confirmation [15].

In this paper, the multiphonon relaxation of a local vibrational mode and the non-radiative electronic transitions in molecular systems and in solids are considered using this non-perturbative theory. Results of model calculations are presented. According to the obtained results, the rate of these processes exhibits a critical behavior: it sharply increases near specific (critical) value(s) of the interaction. Also the usual increase of the non-radiative transition rate with temperature is reversed at certain value of the non-diagonal interaction and temperature. For a weak interaction, the results coincide with those of the perturbation theory.

2. RELAXATION OF A LOCALIZED VIBRATIONAL MODE

Physical processes in solids usually involve the relaxation of the vibrational energy. The vibrational quanta of light impurity molecules in crystals may exceed many times the maximal energy of phonons. In such a case the energy relaxation of a molecule takes place as a multiphonon emission. Pulse laser sources give a possibility to study these processes in the time domain (see, e.g. [3,4,9] and references therein). If one considers the relaxation of lower vibrational levels, then the interaction of the molecular vibration with phonons is usually weak and the process can be explained in terms of a standard perturbation theory [2,5–7,11,12]. However, modern methods allow one to excite molecules to very high vibrational levels [9]. In such cases the anharmonic interaction is strong. To interpret the results of measurements in these cases, a non-perturbative theory of multiphonon relaxation is needed. The goal of this communication is to propose such a theory.

When considering the decay of a non-stationary state of a quantum subsystem interacting with the medium, one usually proceeds from the calculation of the time dependence of the characteristics of the subsystem (e.g. its density matrix). Here we apply another method [13], which is based on the consideration of the rate of creation of phonons in a non-stationary state (here in the excited state of the localized mode). This method was originally proposed for a non-perturbative description of the two-phonon relaxations of a classical localized mode; in Ref. [14] it was extended to the two-phonon quantum transitions between two levels of arbitrary origin. According to this method the transition rate is strongly enhanced near the critical value(s) V_{cr} of the non-diagonal interaction V and it is remarkably reduced when this interaction is strong (above V_{cr}). This kind of dependence of a two-phonon relaxation on V was observed in Ref. [15], where a sharp maximum of the relaxation rate at the vibrational level number $n = 22$ of a Xe_2^* molecule was found in a hot luminescence spectrum of a self-trapped exciton in the solid Xe (in this case $V \propto n^{1/2}$).

To explain the idea of the method [13,14], let us consider a two-phonon decay of a highly excited local mode caused by the interaction $\hat{H}_{int} = \hat{Q} \sum_{ii'} V_{3,ii'} \hat{x}_i \hat{x}_{i'}$, where $V_{3,ii'}$ are the cubic anharmonicity interaction parameters, $\hat{Q}$ is the coordinate

operator of the mode, $\hat{x}_i = \sqrt{\hbar/2\omega_i}(\hat{a}_i + \hat{a}_i^+)$ are the coordinate operators of the phonons, $\hat{a}_i$ and $\hat{a}_i^+$ are the initial destruction and creation operators. The highly excited mode can be considered classically. In this approximation the phonon Hamiltonian takes the form

$$\hat{H} \approx \hbar \sum_i \omega_i (\hat{a}_i^+ \hat{a}_i + 1/2) + Q(t) \sum_{ii'} V_{3,ii'} \hat{x}_i \hat{x}_{i'}$$

where $Q(t)$ is the time-dependent classical coordinate of the mode. This Hamiltonian can be diagonalized by standard methods of the local dynamics. This is achieved by means of the new, time-dependent destruction and creation operators of phonons. The latter are determined by the time-dependent Bogolubov transformation

$$\hat{b}_j(t) = \sum_i (\mu_{ij}(t) \hat{a}_i + \nu_{ij}(t) \hat{a}_i^+)$$

(for the expressions for $\mu_{ij}(t)$ and $\nu_{ij}(t)$ see Ref. [14]). For a large time t as compared to the reciprocal frequency of the phonons ω_i^{-1} the transformation of phonon operators simplifies [13]:

$$\hat{b}_i(t) \approx \mu_i(t) \hat{a}_i + \nu_i(t) \hat{a}_i^+ \quad (1)$$

where $|\mu_i(t)|^2 = 1 + |\nu_i(t)|^2$. The initial zero-point state of phonons, $|0\rangle$, is not the zeroth state of the operators $\hat{b}_i(t)$. This means that phonons are generated in the lattice. The number of created phonons at temperature $T = 0$ equals

$$n_{i,t} = \sum_i |\nu_i(t)|^2$$

The energy of generated phonons is taken from the mode. This allows one to find the rate of the energy loss (relaxation) of the mode as follows:

$$\frac{dE(t)}{dt} = \frac{\hbar\omega_l}{k} \sum_i \frac{d|\nu_i(t)|^2}{dt} \quad (2)$$

(here $k = 2$ is the number of phonons emitted for each quantum $\hbar\omega_l$ of the mode). The effect of temperature can be included in a standard way by adding the stimulated transitions. The described approach to relaxation holds for an arbitrary interaction as far as the dependence of $|\nu_i(t)|^2$ on time is slow as compared to the characteristic phonon frequency.

From the given expression for dE/dt it follows that, in fact, one does not need the full knowledge of the operator transformation, i.e., one does not need to know the complex parameters $\mu_i(t)$ and $\nu_i(t)$. It is sufficient to know $|\nu_i(t)|^2$. To find the latter quantity, one does not necessarily need to diagonalize the Hamiltonian. It is much easier to obtain this parameter from the $\propto \exp(i\omega_l t)$ term of the large time asymptotic of the phonon correlation function $D_i(t, \tau) = \langle 0 | \hat{x}_i(t + \tau) \hat{x}_i(t) | 0 \rangle$ with t averaged over a vibrational period. Indeed, taking

$$\hat{x}_i(t) = (\hbar/2\omega_i)(\hat{b}_{it} e^{-i\omega_l t} + \hat{b}_{it}^+ e^{i\omega_l t})$$

where the operator b_{it} is given by equation (1), one gets

$$D_i(t, \tau) \approx (\hbar/2\omega_i)(|\mu_i(t)|^2 e^{-i\omega_i\tau} + |\nu_i(t)|^2 e^{i\omega_i\tau}) \quad (3)$$

the terms with $\exp(\pm i\omega_i(2t + \tau))$ drop out when averaging t over a vibrational period.

For what follows it is essential that equation (3) for the large-time asymptotic of the phonon correlation function holds rather generally, including cases if the interaction Hamiltonian contains more than two phonon operators and the Hamiltonian cannot be diagonalized [13,14]. This allows one to apply the method for the description of multiphonon relaxation processes caused by higher order anharmonicities.

2.1. Multiphonon relaxation

Let us consider first the decay of a strongly excited local mode due to simultaneous emission of $k > 2$ phonons. The Hamiltonian of the system under consideration is

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}, \quad \hat{H}_0 = \sum_i \hbar\omega_i(\hat{a}_i^\dagger \hat{a}_i + 1/2), \quad \hat{H}_{\text{int}} = \hat{Q} \sum_m V_{m,k} \hat{q}_m^k \quad (4)$$

Here H_{int} is the anharmonic interaction in the collinear-configurational approximation (see Refs. [5,7]), $V_{m,k} = \sqrt{n_l \hbar / 2\omega_l} U_m^{(k+1)}$. Here $U_m^{(k)}$ are the parameters of the k th order anharmonicity, $\hat{q}_m^k = \sum_i e_{imr} \hat{x}_i$ are the mutually orthogonal displacement operators of the host atoms with respect to the atom(s) of the mode ($\sum_i e_{im} e_{im'} = \delta_{mm'}$). We take into account that the strongly excited mode can be considered classically, and replace its coordinate operator by $Q(t) = A \cos(\omega_l t)$, where A is the initial amplitude of the mode. Then

$$\hat{H}_{\text{int}} \approx A \cos(\omega_l t) \sum_m V_{m,k} \hat{q}_m^k$$

This interaction Hamiltonian describes the k -phonon emission due to a periodical local field.

To calculate the rate of multiphonon emission, let us consider the phonon correlation function $D_i(t)$. We proceed from the equation of motion of a phonon

$$\ddot{\hat{x}}_i(t) + \omega_i^2 \hat{x}_i(t) + k e_i V_k Q(t) \hat{q}^{k-1}(t) = 0$$

(the subscript m is omitted); the integral form of it reads

$$\hat{x}_i(t) = \hat{x}_{0i}(t) - k e_i' A V_k \int_0^t dt_1 \sin(\omega_i(t - t_1)) \hat{q}^{k-1}(t_1) \cos(\omega_l t_1) \quad (5)$$

Here $e_i' = e_i/\omega_i$, and $\hat{x}_{0i}(t) = \hbar/2\omega_i(\hat{a}_i e^{-i\omega_i t} + \hat{a}_i^\dagger e^{i\omega_i t})$. Inserting equation (5) into equation (3) one gets

$$\begin{aligned} D_i(t, \tau) \approx & \frac{\hbar}{2\omega_i} e^{-i\omega_i \tau} + (k^2 e_i'^2 A^2 V_k^2 / 2) \int_0^{t+\tau} dt_1 \int_0^t dt_2 D_{k-1}(t_1, t_2) \\ & \times \cos(\omega_i(t_1 - t_2 - \tau)) \cos(\omega_l(t_1 - t_2)) \end{aligned} \quad (6)$$

Here $D_{k-1}(t_1, t_2) = \langle 0 | \hat{q}^{k-1}(t_1) \hat{q}^{k-1}(t_2) | 0 \rangle$ is the multi-particle displacement correlation function. Here the fast oscillating terms under the integrals are neglected as they drop out at large t when averaging over the vibrational period.

The function $D_{k-1}(t_1, t_2)$ under the integral (6) remarkably differs from zero only for $|t_1 - t_2| \leq ((k-1)\Gamma)^{-1} \ll t$, where Γ is the characteristic width of the phonon spectrum. This allows one to replace the upper integration limit $t + \tau$ by t . Then the residual τ dependence of the integral in equation (6) is given by the factor $\cos(\omega_l(t_1 - t_2 - \tau))$, i.e., the dependence of the phonon correlation function on τ indeed has the form (3). The factor of the $\propto \exp(i\omega_l\tau)$ term equals

$$|\nu_i(t)|^2 = \frac{e_i^2 A^2 V_k^2}{4\hbar\omega_i} \int \int_0^t dt_1 dt_2 e^{i\omega_l(t_2 - t_1)} D_{k-1}(t_1, t_2) \cos(\omega_l(t_1 - t_2)) \quad (7)$$

This relation holds only if the rate of the process is sufficiently small as compared to $(k-1)\Gamma$. The fact that in this case equation (3) holds also for $k > 2$, means that phonons remain almost harmonic. This allows one to use in equation (7) the pair correlation approximation: $D_{k-1}(t_1, t_2) \approx (k-1)! D^{k-1}(t_1, t_2)$, where $D(t, t') = \langle 0 | \hat{q}(t) \hat{q}(t') | 0 \rangle$ is the displacement pair correlation function. The same time pairings are neglected while they give contribution to $k-2, k-4, \dots$ -phonon transitions and, therefore, result in small change of the anharmonic constants V_k . Note also that the validity of equation (3) with a non-zero value of $|\nu_i(t)|$ means the existence of anomalous correlations $\langle \hat{b}_i^2(t) \rangle = \nu_{it} \mu_{it}$, these correlations depend on time.

To find the rate of energy loss of the mode, let us insert equation (7) into equation (2). After substitution of the integration variables $t' = (t_1 + t_2)/2$, $t'' = t_1 - t_2$, $D(t, t') = \langle 0 | \hat{q}(t) \hat{q}(t') | 0 \rangle$ is the displacement pair correlation function. The same time pairings are neglected while they contribute to $k-2, k-4$ -phonon transitions and, therefore, result in small change of the anharmonic constants V_k . Note also that the validity of equation (3) with a non-zero value of $|\nu_i(t)|$ means the existence of anomalous correlations $\langle \hat{b}_i^2(t) \rangle = \nu_{it} \mu_{it}$, these correlations depend on time.

To find the rate of energy loss of the mode, one should insert equation (7) into equation (2). After substitution of the integration variables $t' = (t_1 + t_2)/2$, $t'' = t_1 - t_2$ and replacing the integration limits $\pm t'$ by $\pm \infty$ (which can be done in the case under consideration as $t, t' \gg (k\Gamma)^{-1}$), one gets in the pair correlation approximation

$$\frac{dE(t)}{dt} = \frac{A^2 k! \omega_l}{4\hbar} \int_{-\infty}^{\infty} dt e^{i\omega_l t} Sp(V_k^2 d_0(t) D^{k-1}(t)) \quad (8)$$

where $d_0(t) = \sum_i (\hbar/2\omega_i) e_i^2 e^{i\omega_i t}$. Thus, to find the relaxation rate, one needs to calculate the displacement correlation function $D(t)$. If the anharmonic interaction is weak, then $D(t) \approx d_0(t)$. In this approximation result (8) coincides with the corresponding equation of the standard perturbation theory, which gives

$$\left(\frac{dE(t)}{dt} \right)_0 = \frac{A^2 k! V_k^2 \omega_l}{4\hbar} \int_{-\infty}^{\infty} dt e^{i\omega_l t} d_0^k(t)$$

If the anharmonic interaction is not weak, then $D(t)$ should be found from the equation of motion, which in case $k > 2$ turns out to be a non-linear integral equation. To get the corresponding equation, one should start from the equation of motion for the displacement operator(s) $\hat{q}$. From equation (5) it follows that

$$\hat{q}(t) = \hat{q}_0(t) - kAV_k \int_0^t dt_1 G(t - t_1) \hat{q}^{k-1}(t_1) \cos \omega_l t_1$$

where $\hat{q}_0(t) = \sum_i e_i \hat{x}_{0i}(t)$, $G(t) = \theta(t) \sum_i (e_i^2 / \omega_i) \sin \omega_i t$ is the Green function of the lattice dynamics [16–18] and $\theta(t)$ is the Heaviside step-function. By using this equation for the first operator $\hat{q}(t_1)$ under the integral, one gets:

$$\begin{aligned} \hat{q}(t) = & \hat{q}_0(t) - kAV_k \int_0^t dt_1 G(t - t_1) \\ & \times \left[\hat{q}_0(t_1) - kAV_k \int_0^{t_1} dt_2 G(t_1 - t_2) \hat{q}^{k-1}(t_2) \cos \omega_l t_2 \right] \hat{q}^{k-2}(t_1) \cos \omega_l t_1 \end{aligned}$$

Let us insert this equation into the displacement correlation function $D(t, t') = \langle 0 | \hat{q}(t) \hat{q}(t') | 0 \rangle$ and apply once again the pair correlation approximation

$$\langle 0 | \hat{q}^{k-1}(t_2) \hat{q}^{k-2}(t_1) \hat{q}(t') | 0 \rangle \approx (k-1)! D(t_2, t_1)^{k-2} D(t_2, t')$$

(the same time pairings are neglected). As a result, we obtain the following integral equation:

$$\begin{aligned} D(t, t') \approx & d^*(t, t') + \tilde{V}_k^2 \int_0^t dt_1 \int_0^{t_1} dt_2 e^{i\omega_l(t_2 - t_1)} G(t - t_1) \\ & \times G(t_1 - t_2) D^{k-2}(t_2, t_1) D(t_2, t') \end{aligned} \quad (9)$$

where $\tilde{V}_k = V_k A \sqrt{k k!} / 2$ and

$$d^*(t, t') = \langle 0 | \hat{q}_0(t) \hat{q}(t') | 0 \rangle = \langle 0 | \hat{q}(t') \hat{q}_0(t) | 0 \rangle^*$$

(the terms $\propto q^{(0)}(t_1)$ under the integrals lead to the same time pairing; they are small and, therefore, neglected; the terms $\sim e^{i\omega_l(t_1 + t_2)}$ are also neglected as they oscillate fast and give also very small contribution). Analogously, one finds

$$\begin{aligned} d(t, t') \approx & d_0(t - t') + \tilde{V}_k^2 \int_0^t dt_1 \int_0^{t_1} dt_2 e^{i\omega_l(t_2 - t_1)} G(t - t_1) \\ & \times G(t_1 - t_2) D^{k-2}(t_2, t_1) d(t_2, t') \end{aligned} \quad (10)$$

These equations in the spectral representation take the form

$$D(\omega) = d^*(\omega) + G(\omega) \tilde{V}_k g_k(\omega - \omega_l) \tilde{V}_k D(\omega)$$

$$d(\omega) = d_0(\omega) + G(\omega) \tilde{V}_k g_k(\omega - \omega_l) \tilde{V}_k d(\omega)$$

where $d_0(\omega)$ and $G(\omega)$ are the spectral representations of $d_0(t)$ and of $G(t)$, respectively, and

$$g_k(\omega - \omega_l) = \int_0^\infty dt e^{i(\omega - \omega_l)t} G(t) D^{k-2}(-t) \quad (11)$$

This gives

$$D(\omega) = d_0(\omega) |1 - G(\omega) \tilde{V}_k g_k(\omega - \omega_l) \tilde{V}_k|^{-2} \quad (12)$$

Within the given notations the rate of the energy loss in the spectral representation takes the form:

$$\dot{E} = \frac{\omega_l \tilde{V}_k^2}{k\hbar} \int \int \cdots \int d_0(\omega_l) \prod_{j=2}^k D(\omega_j) \frac{d\omega_j}{2\pi}, \quad \omega_l = \omega - \sum_{j=2}^k \omega_j$$

Here the expression under the integral gives a partial probability of the k -phonon transitions at $T = 0$.

Although the above-given expression for the rate of the energy loss was derived for a classical mode, it is also applicable for the description of the decay of energy levels. Indeed, taking into account that the decay is due to the k -phonon transitions between the adjoining levels n_l and $n_l - 1$, we get for the rate of the k -phonon transitions $\gamma_k = \dot{E}/\hbar\omega_l$ the following expression [19]:

$$\gamma_k \simeq (\tilde{V}_k^2/4k\hbar^2) \int_{-\infty}^\infty dt e^{i\omega_l t} d_0(t) D^{k-1}(t) \quad (13)$$

where $\tilde{V}_k = V_k \sqrt{n_l k k! \hbar / 2\omega_l}$ and $A = \sqrt{2n_l \hbar / \omega_l}$. Equations (11)–(13) allow to get a solution of the problem: by solving the non-linear integral equation (11), one finds $g_k(\omega)$ and $D(\omega)$, which allows one to calculate the rate γ_k .

In the case under consideration the rate of the generation of phonons is small as compared to the mean phonon frequency $\bar{\omega}$ and ω_l . This means that the account of all other levels, except n_l and $n_l - 1$, does not give any remarkable contribution to the transition rate. Therefore, the origin of the levels n_l and $n_l - 1$ is not essential, i.e., equation (13) is applicable not only for the description of the k -phonon decay of high levels but also of any excited level.

In the case of small $|\tilde{V}_k|$ one can take $D(t) \approx d_0(t)$. Then equation (14) coincides with the one given by the Fermi Golden Rule for arbitrary n_l .

The finite temperature effect can be described as usual: one should take into account the stimulated transitions. As a result, one gets an additional factor $(1 - \exp(-\hbar\omega_l/k_B T)) \prod_{j=1}^k (1 + \bar{n}_j)$ which takes into consideration phonon-induced transitions, where $\bar{n}_j = 1/(\exp(\hbar\omega_j/k_B T) - 1)$. In the case of multiphonon transitions in a two-level system, the first factor should be replaced by $(1 + \exp(-\hbar\omega_l/k_B T))$ [19–21].

In the weak coupling limit $D(\omega) = d_0(\omega)$ and $\gamma_k \sim |\tilde{V}_k|^2$ in accordance with the perturbation theory. In the opposite limit of a very strong coupling, as it follows from equation (12), $D \propto |\tilde{V}_k|^{-4/(2k-3)}$, which gives $\gamma_k \propto |\tilde{V}_k|^{-2/(2k-3)}$; i.e.,

$\gamma_k \rightarrow 0$ if $\tilde{V}_k \rightarrow \infty$ (see also Ref. [14] where an analogous conclusion was made on the basis of some qualitative arguments). This is the opposite behavior as compared to the perturbation theory. Yet the interpretation of this surprising result is straightforward – the multiphonon decay is of a purely quantum-mechanical origin and, therefore, it should disappear in the classical limit $n_l \propto A^2 \rightarrow \infty$. This is because in this limit the mean square velocity of the vibrations $\omega_l^2 A^2$ becomes so fast that the zero-point vibrations cannot react to so fast a motion.

Note that the Green function $G(\omega)$ is the sign-alternating complex function. Therefore, there may be some frequencies ω_{cr} for which the imaginary part of the denominator in equation (12) turns to zero. In these cases, for some specific value(s) of the interaction $\tilde{V}_{k,cr}$ the real part of the denominator also vanishes at ω_c . This means that γ_k has a sharp peak(s) at $\tilde{V}_{k,cr}$. To find out how γ_k depends on $\tilde{V}_k$ in the vicinity of $\tilde{V}_{k,cr}$ we expand the denominator $|R(\omega)|^2$ in equation (12) near ω_c : $|R(\omega)|^2 \approx |R + (\omega - \omega_{cr})R'|^2$; R is real and R' is imaginary. This gives $D(\omega) \sim [(\tilde{V}_k - \tilde{V}_{k,cr})^2 + (\omega - \omega_{cr})^2 |R'/R|^2]^{-1}$. Consequently, if $\tilde{V}_k \rightarrow \tilde{V}_{k,cr}$ then $D(\tau)$ diverges like $|\tilde{V}_k - \tilde{V}_{k,cr}|^{-1}$. This means that γ_k also diverges like $|\tilde{V}_k - \tilde{V}_{k,cr}|^{-k+1}$. Consequently, the behavior of the system in the vicinity of $\tilde{V}_{k,cr}$ is critical; i.e., it resembles a phase transition. The order parameter is connected with the mean field associated with the anomalous correlations, which is changed stepwise on the transition. The critical index equals $k - 1$.

2.2. Numerical example

As an example, we consider the multiphonon relaxation of a local mode caused by an anharmonic interaction with a narrow phonon band. We suppose that the mode is localized on an atom and take into account two diagonal elements of the Green function which stand for the contribution of two nearest atoms of the lattice to the interaction; the non-diagonal elements are usually much smaller [16] and approximate the density of states of the phonon band by the parabolic distribution

$$\rho(\omega) = (3/4\Gamma)[1 - (\omega - \omega_1)^2/\Gamma^2], \quad |\omega - \omega_1| < \Gamma < \omega_1 \quad (14)$$

$\rho(\omega) = 0$ if $|\omega - \omega_1| \geq \Gamma$. Here ω_1 is the mean frequency and Γ is the half-width of the band. By using the dimensionless frequency $\Omega = (\omega - \omega_1)/\Gamma$ and the dimensionless time $\tau = t\Gamma$, equation (14) takes the form

$$\gamma_k = \frac{2w_k^2\Gamma}{k} \int_0^\infty d\tau d_0(\tau) D^{k-1}(\tau)$$

where $w_k = (|\tilde{V}_k|/k\hbar\Gamma)(\hbar/2\omega_1)^{k/2}$ is the dimensionless interaction parameter and $D(\tau)$ is the Fourier transform of the function $D(\Omega)$. This function should be determined from the following non-linear equations:

$$g_k(\Omega) = \int_0^\infty d\tau e^{i\Omega\tau} G(\tau)^* D^{k-2}(\tau), \quad D(\Omega) = \frac{d_0(\Omega)}{|1 - w^2 G(\Omega) g_k(\Omega)|^2} \quad (15)$$

where $d_0(\Omega) = 2 \operatorname{Im} G(\Omega)$, $d_0(\tau) = iG(\tau) = (3/2\tau^3)(\sin \tau - \tau \cos \tau)$ and

$$G_0(\Omega) = \frac{3}{4} \left[(1 - \Omega^2) \ln \left| \frac{1 - \Omega}{1 + \Omega} \right| - 2\Omega + i\pi(1 - \Omega^2)\theta(1 - \Omega^2) \right] \quad (16)$$

For small dimensionless interaction parameter w_k (smaller than $w_{k,\text{cr}}$) equation (15) can be solved by using the standard iteration procedure. However, for large $w_k > w_{k,\text{cr}}$ this procedure diverges. In this case the solutions of these equations have been found by means of the approximation $D(\Omega) = A[1 - (\Omega^2 + c^2)^\beta / (1 + c^2)^\beta]$; parameters A , β and c have been obtained from the best fit of the input and the output functions. The results of calculations γ_k at $T = 0$ in dependence of the dimensionless interaction parameters w_k are given in Figs 1 and 2. For very small w_k ($w_k \ll 1$) the rates linearly increase with w_k^2 (in accordance with the Fermi golden rule). For larger w_k the rate superlinearity increases with k . The rates have sharp peaks at $w_{k,\text{cr}} \approx 1$. Thereby, as it should be, $\gamma_k \propto |w_k - w_{k,\text{cr}}|^{-k+1}$ if $w_k \rightarrow w_{k,\text{cr}}$.

We stress that only the rates satisfying the condition $\gamma_k \ll kT$ are consistent with the assumptions of the theory. In the case of a high-order multiphonon relaxation ($k \gg 1$) for large w_k (larger than $w_{k,\text{cr}}$) the rate very slowly decreases

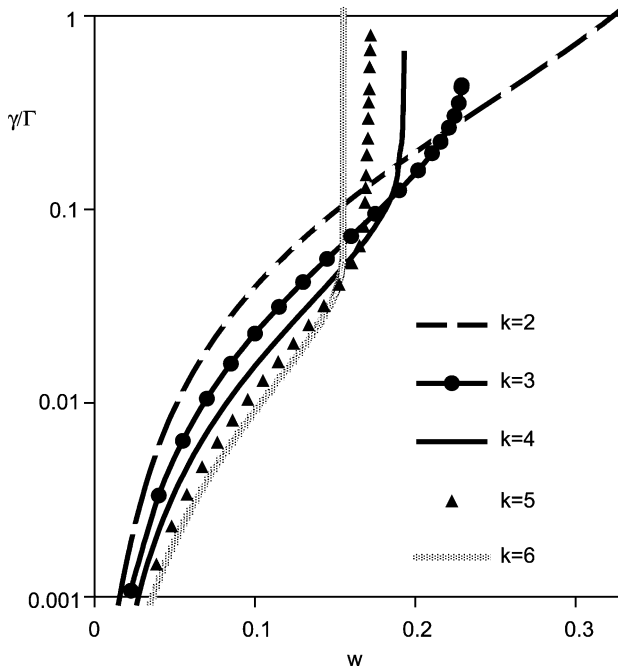


Fig. 1. The dependence of the transition rates γ_k (in Γ units) on the dimensionless interaction parameters w_k below $w_{k,\text{cr}}$.

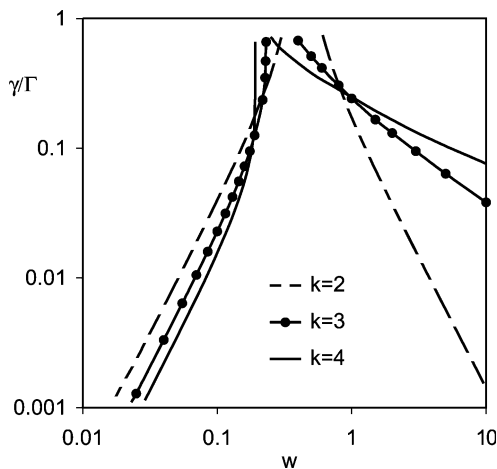


Fig. 2. The dependence of the rates γ_k (in Γ units) of two-phonon ($k = 2$), three-phonon ($k = 3$) and four-phonon ($k = 4$) transitions on the dimensionless interaction parameters w_k .

with the increasing of the interaction parameter (as $w_k^{2/2(k-3)}$) and is very high ($\approx \Gamma$) practically for all reasonable values of $w_k \geq w_{k,cr}$.

The temperature dependence of the rate in this model is given by the factor $(1 - \exp(-k\hbar\omega_1/k_B T))/(1 - \exp(-\hbar\omega_1/k_B T))^k$.

3. TEMPERATURE DEPENDENCE OF NON-RADIATIVE TRANSITIONS

Non-radiative transitions in molecular systems and in solids are usually considered in the framework of the time-dependent perturbation theory [1–10]. According to this theory, transition rate is described by the Fermi Golden Rule, and in most cases it increases with temperature T (only at low temperatures, when quantum tunneling regime is realized, the rate may decrease with T). According to Franck–Condon principle, at the electronic transition the nuclei remain in their previous equilibrium positions. But this configuration of nuclei is not the equilibrium configuration for the new configuration of electrons. So in the system excess vibrational energy is released. This energy will relax over the whole lattice. In the high temperature (i.e., classical) limit the process is described by an Arrhenius-like law with the activation energy being determined by the crossing of the adiabatic potentials of the initial and final electronic states. The theory is applicable if the non-diagonal vibronic interaction, which causes transitions, is weak.

3.1. Transition rate

Here we apply the method described above (see also Ref. [13]) for the investigation of the temperature dependence of non-radiative transitions between electronic levels in a center. The method [13] is based on the calculation of the large t asymptotic of the phonon correlation function $D_i(t, \tau) = \langle 1, 0 | \hat{x}_i(t + \tau) \hat{x}_i(t) | 1, 0 \rangle$ with t averaged over the vibrational period; here $|1, 0\rangle = |1\rangle|0\rangle$ is the product of the initial electronic state and the zero-point vibrational state.

We consider a non-radiative transition caused by linear diagonal and quadratic non-diagonal vibronic interactions. If the states belong to different representations of the point group of the center, then the Hamiltonian of the system reads:

$$\begin{aligned} H &= H_0 + H_{\text{int}}, \\ H_0 &= H_1 \times I + (V_0 \hat{q}_0 - \varepsilon)(I - \hat{\sigma}_3)/2, \\ H_1 &= \sum_i \hbar \omega_i (\hat{a}_{li}^\dagger \hat{a}_{li} + 1/2), \\ H_{\text{int}} &= \left(\sum_{l_1} V_{l_1} \hat{q}_{l_1} + \sum_{l'l'} W_{l'l'} \hat{q}_{l'} \hat{q}_{l'} / 2 \right) \hat{\sigma}_1 \end{aligned} \quad (17)$$

where H_1 is the phonon Hamiltonian of the initial electronic state, H_{int} is the Hamiltonian of the non-diagonal vibronic interaction, $\hat{\sigma}_1$ and $\hat{\sigma}_3$ are the Pauli matrices, ε is the energy difference of the electronic states, ω_i is phonon frequency and $\hat{a}_{li}$ and $\hat{a}_{li}^\dagger$ are the destruction and creation operators of the phonon i of the representation l , $\hat{q}_l$ are the symmetrized displacements of atoms of different representations ($l = 0$ corresponds to totally symmetric displacements, $l > 0$ to the non-totally symmetric ones); V_0 , V_{l_1} and $W_{l'l'}$ are the parameters of the vibronic interactions (V_{l_1} and $W_{l'l'}$ are equal to zero if $l, l', l_1 = 0$), l, l' may belong to different rows of the same representation. The $\hat{\sigma}_3$ -term in equation (4) stands for the dependence of the phonon Hamiltonian on the electronic level: the energy as well as the equilibrium values of the coordinates $\hat{q}_0$ of the first level differ from those of the second level. The symmetrized displacement operators can be expanded into the normal coordinate operators $\hat{x}_{li}$ as follows: $\hat{q}_l = \sum_i e_{li} \hat{x}_{li}$, where $\sum_i e_{li} e_{l'i} = \delta_{ll'}$. Here we focus on the reaction channels arising from the quadratic non-diagonal interaction.

Let us consider first the $T = 0$ case. If the non-diagonal interaction H_{int} is weak then the rate of the non-radiative transition is determined by the Fermi golden rule

$$\gamma^{(0)} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \langle 1, 0 | H_{\text{int}}(t) H_{\text{int}}(0) | 1, 0 \rangle \quad (18)$$

Here the time dependence of an operator is determined by the Hamiltonian H_0 ; e.g. $\hat{\sigma}_1(t_1) = e^{it_1 H_0 / \hbar} \hat{\sigma}_1 e^{-it_1 H_0 / \hbar}$. If one considers the contribution of the interaction

term $\sim \hat{q}_l \hat{q}_{l'}$ ($l, l' > 0$), then

$$\langle 1, 0 | H_{\text{int}}(t) H_{\text{int}}(0) | 1, 0 \rangle = W_{ll'}^2 d_{0l}(t) d_{0l'}(t) F(t) \quad (19)$$

Here and below $d_{0l}(t) = \hbar \sum_i e^{-i\omega_i t} e_{li}^2 / 2\omega_i$ and

$$F(t) = \langle 1, 0 | \hat{\sigma}_1(t) \hat{\sigma}_1(0) | 1, 0 \rangle = e^{i\epsilon t/\hbar} \langle 0 | e^{iH_1/\hbar} e^{-i\epsilon(H_1 + \hat{q}_0)/\hbar} | 0 \rangle$$

is the Fourier transform of the spectrum of multiphonon transitions. Using the shift operator e^∇ , where $\nabla = V_0 \sum_i (\bar{e}_{0i}/\omega_i^2) \partial/\partial x_i$, and applying the Wick theorem of pair correlations, the factor $F(t)$ can be presented in the form

$$F(t) = e^{i\omega_0 t} \langle 1, 0 | e^{\nabla(t)} e^{-\nabla} | 1, 0 \rangle = e^{i\omega_0 t + g(t)} \quad (20)$$

where $g(t) = \langle 1, 0 | (\nabla - \nabla(t)) \nabla | 1, 0 \rangle = (V_0^2/2\hbar) \sum_i (e_{0i}^2/\omega_i^3) (e^{-i\omega_i t} - 1)$, $\omega_0 = (\epsilon + S_1)/\hbar$ is the frequency of the zero-phonon transition and $S_1 = V_0^2 \bar{e}_{0i}^2 / 2\omega_i^2$. Thus, the Fermi Golden Rule yields

$$\gamma^{(0)} = \frac{1}{2\hbar^2} \sum_{ll'} W_{ll'}^2 \int_{-\infty}^{\infty} dt F(t) d_{0l}(t) d_{0l'}(t) \quad (21)$$

This is a standard equation for the non-radiative transitions caused by linear diagonal and quadratic non-diagonal vibronic interactions at $T = 0$ [3].

To apply described above non-perturbative method to the non-radiative transitions caused by the quadratic non-diagonal vibronic interaction $\sim q_l q_{l'}$, one needs to find the phonon correlation functions $D_{li}(t; \tau)$ in the initial (non-stationary) state $|1, 0\rangle$ for $l > 0$. To this end, we use the equation of motion $\hat{x}_{li} + \omega_i^2 \hat{x}_{li} + V e_{li} \hat{q}_{l'} \hat{\sigma}_1 = 0$ ($l, l' > 0$; $l \neq l'$); the integral form of it for $t > 0$ reads

$$\hat{x}_{li}(t) = \hat{x}_{li}^{(0)}(t) - \sum_{l'} W_{ll'} e_{li} \omega_i^{-1} \int_0^t dt_1 \sin(\omega_i(t - t_1)) \hat{q}_{l'}(t_1) \hat{\sigma}_1(t_1) \quad (22)$$

Here $\sin(\omega_i t)/\omega_i$ stands for the Green function of the harmonic oscillator at $t > 0$. Inserting equation (24) into equation (16), one obtains

$$\begin{aligned} D_{li}(t; \tau) = & d_{0li}(\tau) + \sum_{l'} W_{ll'}^2 e_{li}^2 \omega_i^{-2} \int_0^{t+\tau} dt_1 \sin(\omega_i(t + \tau - t_1)) \\ & \times \int_0^t dt_2 \sin(\omega_i(t - t_2)) \langle 1, 0 | \hat{q}_{l'}(t_1) \hat{\sigma}_1(t_1) \hat{q}_{l'}(t_2) \hat{\sigma}_1(t_2) | 1, 0 \rangle \end{aligned} \quad (23)$$

(We take into account that $\langle 1, 0 | \hat{\sigma}_1(t) | 1, 0 \rangle = 0$.) In systems with continuous phonon spectrum, the function under this integral differs essentially from zero only for $|t_1 - t_2| \leq \sigma^{-1} \leq \bar{\omega}^{-1}$. For such a small time difference, electronic and vibrational motions are only weakly correlated; this allows one to use the following decoupling of the electronic and the vibrational degrees of freedom:

$$\langle 1, 0 | \hat{q}_{l'}(t_1) \hat{\sigma}_1(t_1) \hat{q}_{l'}(t_2) \hat{\sigma}_1(t_2) | 1, 0 \rangle \approx F(t_1 - t_2) D_l(t_1, t_2) \quad (24)$$

where $D_I(t_1, t_2) = \langle 1, 0 | \hat{q}_I(t_1) \hat{q}_I(t_2) | 1, 0 \rangle$ is the pair correlation function of non-totally symmetrical displacements, $F(t)$ is the Fourier transform of the spectrum of the multiphonon transitions (see equation (22)).

The main contribution to the integral (23) comes from small $|t_1 - t_2| \leq \sigma^{-1}$. Therefore, in the large time $t \gg \tau$ limits this integral $\sim t$; this allows one to replace $t + \tau$ by t . Then, after the averaging over the vibrational period, the residual t -dependence consists of two terms: $\sim e^{i\omega_i \tau}$ and $\sim e^{-i\omega_i \tau}$. The factor of the $\sim e^{i\omega_i \tau}$ term equals

$$|\nu_{li}|^2 \approx \frac{1}{4} \sum_{l'} W_{ll'}^2 e_{li}^2 \omega_i^{-2} \int \int_0^t dt_1 dt_2 e^{-i\omega_i(t_1-t_2)} F(t_1 - t_2) D_{l'}(t_1, t_2) \quad (25)$$

Taking the derivative of $|\nu_{li}|^2$ with respect to t and summing up over i , one obtains for $t \geq \sigma^{-1} \gg \gamma^{-1}$.

$$\gamma \approx \frac{1}{2\hbar^2} \int_{-\infty}^{\infty} dt F(t) \sum_{l'} W_{ll'}^2 d_{0l'}(t) D_{l'}(t) \quad (26)$$

(here it is taken into account that in the considered time interval the $D_{l'}(t_1, t_2)$ -function depends only on the time difference). Thus, to find the rate of the non-radiative transitions, one needs to calculate the displacement correlation function $D_{l'}(t)$.

If $W_{ll'}^2$ is small then $D_{l'}(t) \approx d_{0l'}(t)$ and equation (27) coincides with the Fermi golden rule (see equation (23)). To get beyond the perturbation theory, one should find $D_I(t)$ more accurately. To this end, let us multiply the left- and the right-hand sides of equation (22) by e_i and sum over i ; we obtain an equation for $\hat{q}_I(t)$. Then, applying the latter equation once more (this time for $\hat{q}_I(t_1)$ under the integral in equation (22)), one obtains

$$\hat{q}_I(t) = \hat{q}_I^{(0)}(t) + V_I^2 \int_0^t dt_1 \int_0^{t_1} dt_2 G_I(t - t_1) G_I(t_1 - t_2) \hat{q}_I(t_2) \hat{\sigma}(t_2) \hat{\sigma}(t_1)$$

where $G_I(t) = \theta(t) \sum_i e_{li}^2 \sin(\omega_i t) / \omega_i$ is the phonon Green function [16,17], $G_I(t) = \sum_{l'} W_{ll'}^2 G_{l'}(t) / V_I^2$, $V_I^2 = \sum_{l'} W_{ll'}^2$. Inserting this equation into $D_I(t, t')$ and using once again the approximation of a small time difference, we get

$$\langle 1, 0 | \hat{q}_I(t_2) \hat{\sigma}(t_2) \hat{\sigma}(t_1) \hat{q}_I(t') | 1, 0 \rangle \approx F(t_2 - t_1) D_I(t_2, t') \quad (27)$$

$$D_I(t, t') = d_I(t, t') + V_I^2 \int_0^t dt_1 \int_0^{t_1} dt_2 G_I(t - t_1) \tilde{G}_I(t_1 - t_2) D_I(t_2, t') \quad (28)$$

where

$$d_I(t, t') = \langle 1, 0 | \hat{q}_I^{(0)}(t) \hat{q}_I(t') | 0 \rangle = \langle 1, 0 | \hat{q}_I(t') \hat{q}_I^{(0)}(t) | 0^* \rangle$$

and $\tilde{G}_I(t) = G_I(t)F(-t)$. The equation for $d_I(t, t')^*$ is analogous but with $d_{0l}(t - t')$ in place of $d_I(t, t')$. Let us again take into account that in case $\gamma^{-1} \gg t, t' \gg |t - t'| \approx \sigma^{-1}$, the functions $D_I(t, t')$ as well as $d_I(t, t')$ depend significantly only on

the time difference. Therefore, these equations can be easily solved in the spectral representation [13]. One gets

$$D_l(\omega) = d_{0l}(\omega) |1 - V_l^2 G_l(\omega) \tilde{G}_l(\omega - \omega_0)|^{-2} \quad (29)$$

Here $G_l(\omega)$ and $\tilde{G}_l(\omega)$ are the Fourier transforms of the functions $G_l(t)$ and $G_l(t) \times e^{g(-t)}$, respectively, $d_{0l}(\omega)$ is the Fourier transform of $d_{0l}(t)$. The equation for $d_l(\omega)$ is analogous.

To find the rate of the non-radiative transitions caused by the quadratic non-diagonal vibronic interaction, one needs to solve equation (27), where $D_l(t)$ in the spectral representation is given by equation (29),

$$\gamma = \frac{1}{4\pi\hbar^2} \sum_l V_l^2 \int_0^{\omega_M} \frac{d\omega d_{0l}(\omega) \tilde{d}_{0l}(\omega_0 - \omega)}{|1 - V_l^2 G_l(\omega) \tilde{G}_l(\omega - \omega_0)|} \quad (30)$$

where $\tilde{d}_{0l}(\omega)$ is the Fourier transform of $\sum_{l'} W_{ll'}^2 d_{0l'}(t) e^{g(t)}/V_l^2$ and ω_M is the top phonon frequency. This equation has a standard form for transitions caused by quadratic non-diagonal vibronic interactions. A non-perturbative description of the process involves an extra square resolvent under the integral.

When considering the effect of temperature on multiphonon processes, one should take into account stimulated phonon-assisted transitions ([20,21]) and include thermally activated reversed transitions. Account of these factors gives

$$\gamma = \frac{1 + e^{-\beta\omega_0}}{4\pi\hbar^2} \sum_l V_l^2 \int_0^{\omega_M} \frac{d\omega d_{lT}(\omega) \tilde{d}_{lT}(\omega_0 - \omega)}{|1 - V_l^2 G_l(\omega) \tilde{G}_{lT}(\omega - \omega_0)|^2} \quad (31)$$

Here $d_{lT}(\omega)$ is the Fourier transform of the function $d_{lT}(t)$, $\tilde{d}_{lT}(\omega)$ is the Fourier transform of the function $\tilde{d}_{lT}(t) = \sum_{l'} W_{ll'}^2 d_{l'T}(t) e^{g_T(t)}/V_l^2$ and $\tilde{G}_{lT}(\omega)$ is the Fourier transform of the function $\tilde{G}_{lT}(t) = \sum_{l'} W_{ll'}^2 G_{l'}(t) e^{g_T(-t)}/V_l^2$, $\beta = \hbar/k_B T$. The result holds not only for transitions down in energy but also for transitions up in energy, which may occur at $T > 0$. If the denominator here turns to zero or obtains a small value, there appears a peak in the transition rate.

3.2. Model calculations

To elucidate the effect of temperature, we performed calculations of the rate of multiphonon non-radiative transitions. We considered a case when l and l' belong to different rows of the same representation. The phonons, contributing to a non-diagonal vibronic interaction are considered in an Einstein-like model with the parabolic distribution function (14) (note that the results are not sensitive to the actual shape of the phonon bands); interaction is arbitrary. In this model the Green function is described by simple expression (16). In the case of a strong linear diagonal vibronic interaction one can expand the $g_T(t)$ -function into a series and take into account the terms up to the quadratic terms with respect to t : $g_T(-t) \approx iS_1 t - \sigma_T^2 t^2/2$. Here $S_1 = \sigma_0^2/\bar{\omega}_0$, $\bar{\omega}_0$ is the mean frequency of totally symmetric vibrations, $\sigma_0 = \sqrt{V_0^2 \langle 0|q_0^2|0 \rangle}/\hbar$, $\sigma_0/\bar{\omega}_0$ is the dimensionless parameter of

the diagonal linear vibronic interaction, $\sigma_T \approx \sigma_0 \sqrt{1 + 2\bar{n}_0}$ is the dispersion (width) of the spectrum of the phonon-assisted transitions, caused by the diagonal vibronic interaction, $\bar{n}_0 \approx 1/(e^{\beta\hbar\omega_0} - 1)$. In this approximation the spectral function of the phonon-assisted transitions equals $F(\omega) = \sqrt{\sigma_T^2/2\pi} \exp[-(\omega - S_1)^2/2\sigma_T^2]$. In this case

$$\tilde{G}_T(\omega - \omega_0) = \int_0^\infty dt \exp[i(\omega - \omega_0 + S_1)t - \sigma_T^2 t^2/2] G(t)$$

Using the dimensionless frequency $z = \omega/\omega_1$ we obtain

$$\gamma_T \approx \frac{\omega_1 w^2}{4\pi} (1 + e^{-\beta\omega_0}) \int_{-3}^3 \frac{dz d_T(z) \tilde{d}_T(\Omega_0 - z)}{|1 - w^2 G(z) \tilde{G}_T(z - \Omega_0)|^2} \quad (32)$$

where $w = V/\omega_1^2$ is dimensionless of non-diagonal quadratic interaction.

In our calculations we chose $\omega_0 = 2\omega_1$ (see Fig. 3, cases a and b) and $\omega_0 = 11.5\omega_1$ (case c). We chose $\Gamma = \omega_1/2$ and considered two zero-phonon frequencies: $\omega_0 = 11.5\omega_1$ (case a) and $\omega_0 = 2\omega_1$ (cases b and c). Besides we chose two diagonal interactions: $\sigma_0 = 2, 5$ (cases a and b) and $\sigma_0 = 0$ (case c). Results of numerical calculation of dependence of transition rate from temperature and interaction (as function of these two variables) are provided in Figs 4 and 5.

At high temperature in both weak and strong interaction limits, one observes a usual increase in the rate with temperature, well described by an Arrhenius-like law $\gamma \sim T^{3/2} e^{-E/k_B T}$. Activation energy in the case of a strong interaction is much larger than in the case of a weak interaction. This allows us to conclude that a strong quadratic non-diagonal interaction leads to a dynamic increase in activation energy;

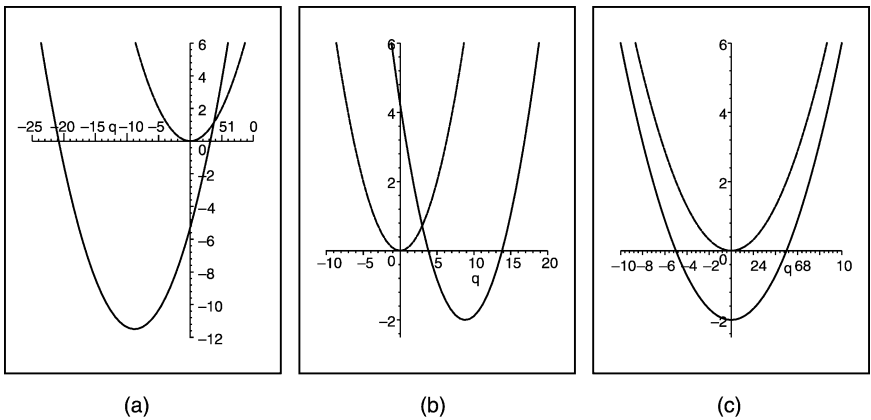


Fig. 3. Potential energies of the initial and final electronic states in the q_0 -space for $\bar{\omega}_0 = 0.4\omega_1$: (a) $\omega_0 = 20.875$, $\nu_0 = 6.25$; (b) $\omega_0 = 11.375$, $\nu_0 = 6.25$; (c) $\omega_0 = 2$, $\nu_0 = 0$ (all frequencies are in ω_1 units). ω_0 is the zero-phonon frequency, $\nu_0 = 2.5\sigma_0$.

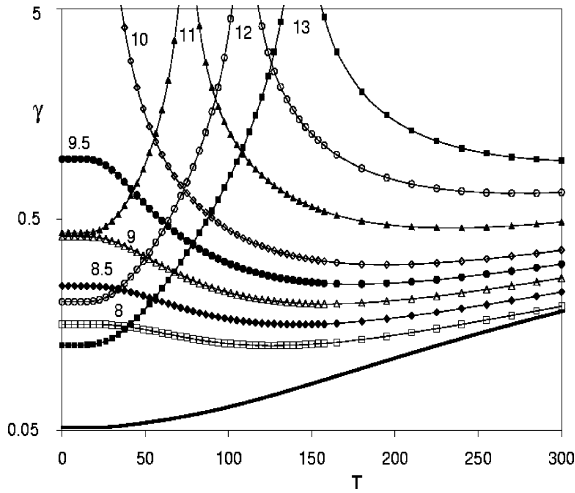


Fig. 4. The temperature dependence of the rate of non-radiative transitions γ for some (given) values of the interaction parameter w ; parameters ω_0 and σ_0 are the same as in Fig. 1(a). The sharp peaks result from the divergence of the resolvent in equation (31) for $w > 10$ at some positive $\omega > \omega_M$. For comparison, the golden rule result is also presented (the thick line below).

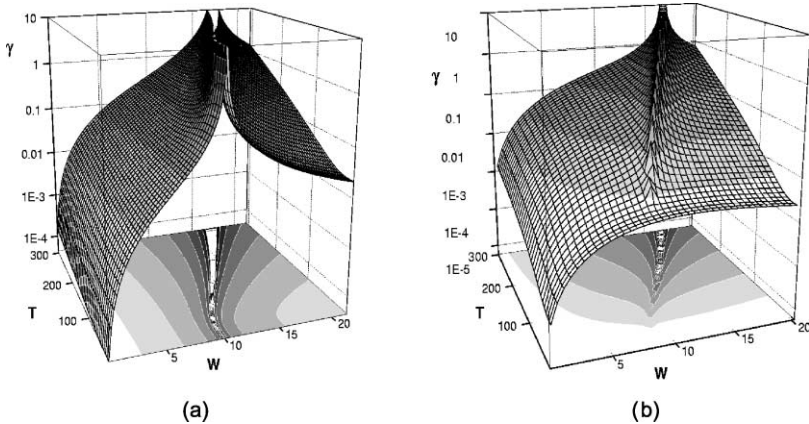


Fig. 5. (a) The dependence of the transition rate γ on temperature and the dimensionless interaction parameter w for the same ω_0 and σ_0 as in Fig. 3(a). The steep ridge is related to the divergence of the resolvent under the integral (31) for positive ω close to ω_M and for the critical values of w . (b) The dependence of the transition rate γ on temperature and the interaction w for the same ω_0 and σ_0 as in Fig. 3(b). The ridge at $T > 0$ is related to the divergence of the resolvent under the integral (31) for negative ω close to $-\omega_M$ and for the critical values of w .

the increase is especially significant (13 times), when the potential barrier below the crossing point of the potentials is thin (Fig. 3, case a). For some parameters there was found no critical behavior of the transition rate with interaction but just a smooth maximum (see also Ref. [22]). In the weak coupling limit the obtained results.

4. CONCLUSIONS

To sum up, we have developed a general non-perturbative method that allows one to calculate the rate of relaxation processes in conditions when perturbation theory is not applicable. Theories describing non-radiative electronic transitions and multiphonon relaxation of a local mode, caused by a high-order anharmonic interaction have been developed on the basis of this method. In the weak coupling limit the obtained results agree with the predictions of the standard perturbation theory.

The relaxation of a local mode is characterized by the time-dependent anomalous correlations; the rate of the relaxation is expressed through the non-stationary displacement correlation function. The non-linear integral equations for this function has been derived and solved numerically. In the physical meaning, the equation is the self-consistency condition of the time-dependent phonon subsystem. We found that the relaxation rate exhibits a critical behavior: it is sharply increased near a specific (critical) value(s) of the interaction; the corresponding dependence is characterized by the critical index $k - 1$, where k is the number of the created phonons. In the close vicinity of the critical point(s) the rate attains a very high value comparable to the frequency of phonons.

The method is also applied for the description of the non-radiative transitions between different electronic levels. It is found that the rate of these transitions is strongly enhanced near the critical value(s) V_{cr} of the non-diagonal vibronic interaction V and it is remarkably reduced if this interaction is strong (above V_{cr}). It was also found that the usual increase of the transition rate with temperature does not hold near some critical values of the non-diagonal interaction and temperature. At these critical values the rate is high (being comparable to the mean phonon frequency) and its temperature dependence is non-monotonous.

REFERENCES

- [1] R. Kubo and Y. Toyozawa, *Prog. Theor. Phys.*, 1955, **13**, 160.
- [2] G. W. Robinson, *J. Mol. Spectrosc.*, 1961, **6**, 58.
- [3] R. Englman, *Nonradiative Decay of Ions and Molecules in Solids*, North-Holland, Amsterdam, 1979 .
- [4] L. E. Brus and V. E. Bondybey, in *Radiationless Transitions* (ed. S. H. Lin), Academic Press, New York, 1980.

- [5] A. Nitzan and J. Jortner, *Mol. Phys.*, 1973, **25**, 713; A. Nitzan, S. Mukamel and J. Jortner, *J. Chem. Phys.*, 1975, **63**, 200.
- [6] V. P. Sakun, *Solid State Phys.*, 1976, **18**, 2517.
- [7] S. A. Egorov and J. L. Skinner, *J. Chem. Phys.*, 1997, **106**, 1034; S. A. Egorov and J. L. Skinner, *J. Chem. Phys.*, 1999, **112**, 275.
- [8] S. A. Egorov, E. Rabani and B. J. Berne, *J. Chem. Phys.*, 1999, **110**, 5238.
- [9] H. Dubost, *Low Temp. Phys.*, 1998, **111**, 615.
- [10] K. K. Pukhov, T. T. Basier, Y. V. Orlovskii and M. Glasbeek, *J. Luminescence*, 1998, **76–77**, 586.
- [11] P. Klemens, *Phys. Rev.*, 1961, **122**, 443.
- [12] R. Englman and J. Jortner, *Mol. Phys.*, 1970, **18**, 145.
- [13] V. Hizhnyakov, *Europhys. Lett.*, 1999, **45**, 508.
- [14] V. Hizhnyakov, *Phys. Rev. B*, 1996, **53**, 13981; V. Hizhnyakov and H. Kaasik, *J. Chem. Phys.*, 2001, **114**, 3127.
- [15] V. Hizhnyakov, M. Kink, M. Selg, R. Kink and J. Maksimov, *Physica B*, 1999, **263–264**, 683.
- [16] A. A. Maradudin, E. W. Montroll and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation*, Academic Press, New York, 1963.
- [17] E. N. Economou, *Green's Functions in Quantum Physics*, Springer, Berlin, 1983.
- [18] A. Maradudin, *Solid State Phys.*, 1966, **18**, 273.
- [19] V. Hizhnyakov and H. Kaasik, *J. Chem. Phys.*, 2002, **116** (21), 9485.
- [20] S. H. Lin, *J. Chem. Phys.*, 1974, **61**, 3810.
- [21] A. Nitzan and J. Silbey, *J. Chem. Phys.*, 1974, **60**, 4070.
- [22] V. Hizhnyakov, H. Kaasik and I. Tehver, *Eur. Phys. J. B*, 2002, **28**, 271.

Non-Condon Correction to Franck–Condon Values of Second-order Reduction Factors: The Cubic T Term

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Abstract

In the Franck–Condon approximation, the major contribution to the vibronic second-order Jahn–Teller (JT) reduction factors (RFs) originates from vertical virtual transitions between the Born–Oppenheimer electronic ground and excited states associated with the corresponding sheets of the adiabatic potential energy surfaces. However, an additional contribution to the polarizability arises from the vibrations of the nuclear frame of the system. To include such nuclear contributions, we must lift the restriction of the rigid-frame approximation by providing the electron wave functions an additional flexibility through allowing them to follow the nuclear vibrations. The transitions between the sheets are then no longer vertical. These non-Condon corrections to the RFs are calculated for the $T \otimes t$ JT system by perturbation theory. The new values obtained for the RFs are found to be much closer to those obtained earlier by numerical methods than the original analytical calculations. This means that calculations of second-order RFs are now available which are valid from very strong coupling to intermediate coupling.

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1. INTRODUCTION

Knowledge of the motion of electrons and nuclei and their interactions forms a major part in our understanding of many of the observed physical and chemical properties of condensed matter systems. This is particularly apparent for optical and infrared spectroscopic experiments, in EPR and in many of the cooperative phenomena seen in crystals. Much of our understanding is based on quantum mechanical principles involving Hamiltonians. Writing down an effective Hamiltonian can form one convenient bridge between experiment and theory. This very useful concept is often used to describe perturbations V present in electronic systems that are strongly coupled to vibrations of their surroundings by the Jahn–Teller (JT) effect. Typical examples of perturbations are spin–orbit coupling and strain. The JT effect can modify the size and character of such perturbations by introducing parameters into the effective Hamiltonian. These parameters multiply the orbital operators contained within the effective Hamiltonian. It is then possible to absorb the vibrations (phonons) into these factors so that the perturbations can be described in terms of a purely electronic Hamiltonian. These parameters were first introduced by Ham [1] in 1965, and used to show that a dynamic JT effect can cause large changes in the magnitudes of some of the matrix elements of electronic (orbital) operators. The parameters are known as vibronic reduction factors (RFs); when V occurs just once in the perturbation, the factors are termed first-order RFs. When V occurs twice, as in a second-order perturbation theory calculation, the corresponding factors are called second-order RFs.

It is well known that the terms involving second-order RFs can make very significant additions to the effective Hamiltonian when the vibronic coupling is large [2]. This is because new terms are introduced into the effective Hamiltonian and also because the first-order RFs in strong coupling can be significantly reduced in magnitude. As RFs in general implicitly result from combining phonons with the electronic terms, the electronic effective mass is increased. This reduces the energy gaps in the electron energy spectrum. Such spectra often provide the starting point for the modeling of experimental spectroscopic data. As the RFs involve the vibronic coupling, essential physics can be overlooked if the RFs are merely regarded as free parameters chosen to fit these data. It is important therefore to calculate the values for the second-order RFs in real systems in order to understand the underlying physics of the system.

Calculations of the second-order RFs are much more complicated than first-order RFs as they generally involve coupling to an infinite set of excited vibronic states for which details are often unknown. They can therefore only be calculated exactly in a pure adiabatic case, such as that found in the $T \otimes e$ system [1] in which the electronic states are not mixed. In other cases, approximations have to be made. Even so, as excited states with higher energies are included, the energy denominator increases whilst the overlaps between states located in different wells in the lowest adiabatic potential energy surface (APES) decrease. We note also that numerical approaches often mask the underlying physics whilst analytical methods such as

the shift transformation method [3] are not very accurate in very strongly coupled systems. An alternative method for very strong coupling is to use the Franck–Condon (FC) approximation in which virtual transitions between the ground and excited states (as present in the formula for second-order perturbation theory) take place so rapidly that the nuclei do not move during the transitions.

In a very recent paper [4], the FC approximation was developed in order to obtain values for second-order RFs in the limit of very strong coupling for the icosahedral $T_{1\mu} \otimes h_g$ JT system under the assumption of a rigid nuclear frame. Such an approach gives an accurate result with infinite vibronic coupling but, at weaker coupling strengths, the FC results deviate markedly from other analytical calculations (e.g. those in Ref. [5]). In order to extend the FC approximation to finite coupling strengths, we modify the basic theory by introducing non-Condon corrections into the theory. Our main interest is in icosahedral systems, which are of particular interest in the fullerenes. However, in order to use the present suggestions we need to test these new ideas on a system for which the answer is known by independent calculations. We thus apply them first to the much simpler and frequently discussed cubic $T \otimes t$ JT system [2,6–11] for which both analytical and numerical calculations of second-order RFs already exist [3,12–14].

2. GENERAL BACKGROUND TO CUBIC $T \otimes t$ JT SYSTEMS

Whereas orbital triplet states exist in many examples of substitutional impurity ions in octahedral coordination, they appear to involve a stronger coupling to the e vibrational modes of their surroundings rather than to the t_2 vibrational modes. This is not the case in tetrahedral coordination where the situation is reversed. A possible physical reason for these observations is that the t_2 -modes result in a trigonal distortion. In the octahedral case, this distortion is along the π bonds whereas in tetrahedral symmetry, the distortion is along the σ bonds. As the corresponding overlap integrals are known to be smaller for π bonds than σ bonds, the molecular bonds of t_2 -symmetry lie along the line joining the central ion and its nearest neighbours. Therefore vibronic coupling to the t_2 -modes in octahedral environments is expected to be weaker than to the e -modes. This is opposite to the tetrahedral case where the vibronic coupling t_2 -modes should be stronger. Thus the most likely place to find examples of such a system is in III–V and II–VI semiconductors (such as GaAs, GaP, and InP) doped with transition metal ions such as Cr^{2+} , Cr^{3+} , Fe^{2+} , and V^{3+} . Many of these impurities generate deep levels within the semiconductor band gap. They form the basis of semi-insulating device material which has been of significant importance during the last 15–20 years. Although the literature contains many examples of JT effects in such systems, there are relatively few cases in which the existence of a $T \otimes t$ JT system has been verified. Part of the problem stems from the difficulty of determining which properties of the system change according to whether the system is of a $T \otimes t$ or $T \otimes e$ type. This decision is made more difficult as it may be necessary then to involve terms containing the second-order RFs.

One example in which the $T \otimes t$ JT system was shown to be present arose from an analysis of the optical data [15] from the GaAs:V³⁺ system. It was shown that the structure of the accompanying zero-phonon line could be explained in terms of the RFs involving second-order spin–orbit coupling contributions [16]. We consider now a general development in the theory of second-order JT vibronic RFs with emphasis on the $T \otimes t$ system.

The Hamiltonian for the $T_1 \otimes t$ JT system can be written in the usual form:

$$\mathcal{H} = \sum_{i=4}^6 \left[\frac{1}{2} (\mu \omega_T^2 Q_i^2) T_0 + V_T(Q_i T_j) + P_j^2 / (2\mu) \right] \quad (1)$$

where the Q_i are the collective displacements of the t_2 mode, the P_j are the corresponding momenta, ω_T is the frequency of the mode and the T_j are T_2 orbital operators. In matrix form, these are

$$\begin{aligned} T_4 &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -\sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & 0 \end{pmatrix}, & T_5 &= \begin{pmatrix} 0 & 0 & -\sqrt{3}/2 \\ 0 & 0 & 0 \\ -\sqrt{3}/2 & 0 & 0 \end{pmatrix}, \\ T_6 &= \begin{pmatrix} 0 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (2)$$

in the x, y, z basis. T_0 is the 3×3 identity matrix. (Note a factor $\sqrt{3}/2$ that has been included in these definitions for convenience.) The first two terms in equation (1) represent the potential energies of the system. A four-dimensional adiabatic potential energy space is thus formed comprising the energy (along the vertical axis) and the three- t_2 displacement coordinates Q_4, Q_5 , and Q_6 . Within this space, the lowest adiabatic potential energy surface or sheet (APES) consists of four minima (or wells) labelled p ($= 1-4$) with their lowest energy points at $Q = Q_{0p}$, for example, as discussed in standard texts (e.g. Refs. [2,3,7]). Within each well, the vibrational states are equally spaced by $\hbar\omega_T$, to a first approximation.

3. DEFINITIONS OF SECOND-ORDER VIBRONIC RFs

A convenient definition of second-order vibronic RFs useful in the context of the FC approximation can be found in Ref. [4] based on earlier work [5]. The RFs will be expressed in the form $K_M^{(2)}(\Gamma_m \otimes \Gamma_l)$ for electronic perturbations V of symmetries Γ_l and Γ_m where the symmetry label $M \in \Gamma_l \otimes \Gamma_m$. The electronic perturbation Hamiltonian within an orbital triplet T_1 can be written as:

$$\mathcal{H}^{(1)}(\Gamma_l) = \sum_{\gamma} W_{\Gamma\gamma} C_{\Gamma\gamma} \quad (3)$$

where $W_{I\gamma}$ are coefficients and $C_{I\gamma}$ are the appropriate Clebsch–Gordan (CG) operators transforming like the row γ of the irrep. I given by:

$$C_{I\gamma} = \sum_{\sigma_1 \sigma_2} |T\sigma_1\rangle \langle T\sigma_2| \langle I\gamma T\sigma_1 | T\sigma_2 \rangle \quad (4)$$

where σ_1 and σ_2 are components. (The notation here is to use $|\cdot\rangle$ for an orbital state and $|\cdot\rangle$ for a vibronic state.) Second-order perturbation theory generates a Hamiltonian:

$$\mathcal{H}^{(2)}(I_l \otimes I_m) = \mathcal{H}^{(1)}(I_l) G(T_1) \mathcal{H}^{(1)}(I_m) \quad (5)$$

where $G(T_1)$ is the Green operator:

$$G(T_1) = \sum_{i,n} \frac{|i,n\rangle \langle i,n|}{\Delta E_{\text{vert}}} \quad (6)$$

involving the excited vibronic states $|i,n\rangle$. Here, i labels an excited state or sheet of the system and n gives the number of oscillator excitations. Thus the above sum (6) excludes the ground state for which $i = n = 0$.

The vibronic ground state can be recast in the form of a symmetry-adapted state:

$$|0, T_1 \sigma_i\rangle = \sum_p \alpha_i^p |\psi_p'; 0\rangle \quad (7)$$

involving the wells p . The ‘0’ indicates that the localized oscillators are in their ground states and α_i^p are coefficients following normalization. The second-order RF can then be defined as:

$$K_M^{(2)}(I_l \otimes I_m) = \frac{\sum_{p,q} \alpha_i^p \langle \psi_p' | \mathcal{L}_{M\mu}^{(2)p}(I_l \otimes I_m) | \psi_q' \rangle \alpha_j^q}{(T_1 x_i | L_{M\mu}^{(2)}(I_l \otimes I_m) | T_1 x_j)} \quad (8)$$

with

$$\mathcal{L}_{M\mu}^{(2)p}(I_l \otimes I_m) = \sum_{\gamma_1 \gamma_2} C_{I_l \gamma_1} G^p(T_1) C_{I_m \gamma_2} \langle I_l \gamma_1 I_m \gamma_2 | M\mu \rangle \quad (9)$$

and

$$L_{M\mu}^{(2)}(I_l \otimes I_m) = \sum_{\gamma_1 \gamma_2} C_{I_l \gamma_1} C_{I_m \gamma_2} \langle I_l \gamma_1 I_m \gamma_2 | M\mu \rangle \quad (10)$$

and $|T_1 \sigma_i\rangle$ are orbital states.

The general expression for the Green operator $G(T_1)$ in equation (9) is then replaced by the Green operator $G^p(T_1)$ for a general well p , for example, where

$$G^p(T) = \frac{1 - |\Psi'_p\rangle\langle\Psi'_q|}{\Delta E_{\text{vert}}} \delta_{pq}. \quad (11)$$

4. THE BASIS OF THE FC APPROXIMATION

The basis of the Franck–Condon approximation for the calculations of the second-order vibronic RFs is to simplify the summation over all the excited states of the system. We neglect first of all the well–well overlaps and consider therefore the contributions from individual wells. This is illustrated in Fig. 1 that shows a cross-section through the adiabatic potential energy space for the $T \otimes t$ JT system containing a trigonal well. The virtual FC transition is vertical in this diagram (shown by the solid arrow in the figure) and originates from the vibrational ground state in one of the wells on the lowest sheet of the APES. It ends at the turning point of the excited vibrational state of energy $n\hbar\omega_T$ associated with another well in an upper sheet that lies exactly above the bottom of the minimum on the lower sheet.

5. EVALUATION OF THE RFs $K_M^{(2)}(T_1 \otimes T_1)$ FOR THE $T \otimes t$ JT SYSTEM USING THE FC APPROXIMATION

In the FC approximation for the calculation of second-order vibronic RFs, we replace the sum over the excited states by a sum over just the excited sheets [4].

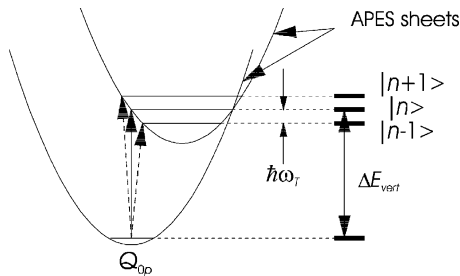


Fig. 1. A cross-section in the adiabatic potential energy space through one of the trigonal wells centred on $Q = Q_{0p}$ in the lower sheet.

It follows that the energy denominator in equation (11) is then the energy gap

$$\Delta E_{\text{vert}} = 3E_{\text{JT}} = \frac{4K_T^2}{\hbar\omega_T} \quad (12)$$

with $-E_{\text{JT}}$ the JT energy and with $K_T^2 = (3V_T^2\hbar)/8\mu\omega_T$. We follow Ref. [4] and begin by replacing the vibronic well states $|\Psi'_p\rangle$ by a product $|\varphi_p(r, Q)\rangle|\phi_p(Q)\rangle$ of electronic and nuclear wave functions. $|\varphi_p(r, Q)\rangle$ is the orbital ground state in well p and $|\phi_p(Q)\rangle$ is the associated three-dimensional oscillator wave function centred about $Q = Q_{0p}$. The nuclear wave function is given by:

$$|\phi_p(Q)\rangle = (\pi/\tau)^{3/2} \exp[-\tau(Q - Q_{0p})^2] = (\pi/\tau)^{3/2} \exp[-\tau q_p^2] \quad (13)$$

where $\tau = m\omega_T/(2\hbar)$ where q_p is the displacement from the minimum point in well p .

As interwell transitions can be neglected, the calculation of the RFs reduces to the consideration of each well separately as in Ref. [4]. We consider the spin–orbit coupling as our perturbation. It is then convenient to use CG coefficients for the T_1 -type of perturbation this introduces. Within the T_1 orbital states, the CG coefficients are

$$\begin{aligned} C_{T_1x} &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{2} \\ 0 & -1/\sqrt{2} & 0 \end{pmatrix}, & C_{T_1y} &= \begin{pmatrix} 0 & 0 & -1/\sqrt{2} \\ 0 & 0 & 0 \\ 1/\sqrt{2} & 0 & 0 \end{pmatrix}, \\ C_{T_1z} &= \begin{pmatrix} 0 & 1/\sqrt{2} & 0 \\ -1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (14)$$

In principle, there are four second-order RFs as the label $M \in T_1 \otimes T_1 = A_1 \oplus E \oplus T_1 \oplus T_2$. From this, the FC Green function G_{FC} which replaces $G^p(T_1)$ in equation (9) can be obtained with the results:

$$\begin{aligned} K_A^{(2)}(T_1 \otimes T_1) &= -\frac{1}{3E_{\text{JT}}}, & K_{T_2}^{(2)}(T_1 \otimes T_1) &= -\frac{2}{9E_{\text{JT}}}, \\ K_E^{(2)}(T_1 \otimes T_1) &= K_{T_1}^{(2)}(T_1 \otimes T_1) = 0 \end{aligned} \quad (15)$$

These results agree with those obtained previously by analytical methods for the same problem [3]. It should be noted that all the contributions to the above RFs come from the identity operator in equation (11) only as the matrix elements arising from the electronic ground state functions are zero for the T_1 orbital operator involved.

6. NON-CONDON CORRECTIONS OF THE FC VALUES

6.1. Basic theory of the non-Condon corrections

The above analysis is based on the Born–Openheimer approximation in which the adiabatic electron wave functions are frozen at the bottom of the corresponding minimum. An important advantage of this approach is that we work with the limited size for the electron basis functions and not with the infinite basis of the vibrational states. This makes the problem solvable in simple terms.

Now we want to introduce the non-Condon corrections to the electron wave functions by lifting the restriction of the rigid-frame approximation and provide the electronic wave functions with an additional flexibility, namely the ability to follow the nuclear vibrations. We return to the expression (8) for the second-order RF. The numerator of this expression consists of three factors namely the bra $\langle \Psi'_p |$, the operator $\mathcal{L}_{M\mu}^{(2)p}(\Gamma_l \otimes \Gamma_m)$, and the ket $|\Psi'_q\rangle$. In order to find the second-order correction to the RF itself, it is necessary to find such corrections to all three factors separately and multiply them together. Each factor takes the form of a quadratic trinomial of the vibrational coordinates Q_j . However, some simplifications are possible as only terms involving even powers of K_T , and hence also of Q_j , remain. One term is of zero-degree (i.e., the term used already in the FC calculation), but there are six terms of second-degree that remain. The most important of these corrections is that from applying perturbation theory to the bra and ket wave functions.

As we are interested in the low energy states close to the bottom of the wells, the amplitude of nuclear motion is small compared to the overall average value of the nuclear displacement. Thus the criterion for smallness comes from the small deviation q_p of the displacement from the bottom of the minimum point. Ultimately, we should include nuclear motion as a part of the dynamic problem so that the parameter q_p will become a dynamic variable associated with the ground harmonic oscillator state $|0\rangle$ in well p . However, this will not be considered further here.

It is necessary next to relate these small displacements to the collective coordinates Q_j from a Taylor expansion of the general potential energy $U(Q)$. In the adiabatic approximation, the nuclear coordinates Q are free parameters and can be used as a basis for the Taylor expansion. Thus we write $U(Q)$ in the general form (Ref. [2], Chapter 3):

$$\begin{aligned}
 U(Q) &= U(Q^{(0)}) + \sum_{\Gamma_\gamma} \left[\frac{\partial U(Q^{(0)})}{\partial Q_{\Gamma_\gamma}} \right]_0 q_{\Gamma_\gamma} + \frac{1}{2} \sum_{\Gamma_1\gamma_1} \sum_{\Gamma_2\gamma_2} \\
 &\quad \times \left[\frac{\partial^2 U(Q^{(0)})}{\partial Q_{\Gamma_1\gamma_1} \partial Q_{\Gamma_2\gamma_2}} \right]_0 q_{\Gamma_1\gamma_1} q_{\Gamma_2\gamma_2} + \cdots \\
 &= U(Q^{(0)}) + U_1 + U_2 + \cdots
 \end{aligned} \tag{16}$$

where $U(Q)$ is the vibronic Hamiltonian given in equation (1) but expressed as a function of Q . $Q^{(0)}$ is the equilibrium value of Q replacing Q_{0p} , for example. Also, we have $q_{T\gamma} [= Q_{T\gamma} - Q_{T\gamma}^{(0)}]$ as the small displacement in the coordinate $Q_{T\gamma}$ ($\equiv Q_j$ here) from the equilibrium value $Q_{T\gamma}^{(0)}$. U_1 and U_2 are first- and second-order perturbation terms in the potential. On acting with equation (16) on the bra and ket, an effective perturbation correction to the potential energy of the system can be written as:

$$U_1 = \sum_j (\mu\omega_T^2 Q_j T_0 + V_T T_j) q_j \quad (17)$$

in which the sum over j replaces the sum over γ . This term mixes the ground electronic state Ψ'_p in a well p with the excited states e_{pi} in that well. Such corrections can be calculated using standard perturbation theory up to the first order in each well. Other higher order perturbations such as U_2 may be neglected, as they involve only diagonal operators which cannot admix the excited states. Thus $|\Psi'_p\rangle$ becomes $|\Psi'_p\rangle + |e_{pi}\rangle$ where

$$|e_{pi}\rangle = \sum_{i=1,2} \langle \Psi'_p | U_1 | e_{pi} \rangle | e_{pi} \rangle q_p / \Delta E_{\text{vert}} \quad (18)$$

The ground and excited states in the wells for the $T \otimes t$ JT system are well known (e.g. Refs. [2,6,17]) and are reproduced in Table 1.

Before completing these calculations, it is necessary first of all to introduce anisotropy into the problem. This arises because the wells in the ground APES are not symmetric, leading to different vibrational frequencies in different directions. More specifically, the wells have trigonal symmetry so that the cubic coordinates in a well should be reclassified in terms of a trigonal singlet mode and

Table 1. The ground and excited states in the wells

Well p	Ground state $ \Psi'_p\rangle$	Excited state $ e_{p1}\rangle$	Excited state $ e_{p2}\rangle$
a	$\frac{1}{\sqrt{3}}(-1, -1, 1)$	$\frac{1}{\sqrt{2}}(1, 0, 1)$	$\frac{1}{\sqrt{6}}(-1, 2, 1)$
b	$\frac{1}{\sqrt{3}}(1, -1, 1)$	$\frac{1}{\sqrt{2}}(-1, 0, 1)$	$\frac{1}{\sqrt{6}}(1, 2, 1)$
c	$\frac{1}{\sqrt{3}}(-1, 1, 1)$	$\frac{1}{\sqrt{2}}(1, 0, 1)$	$\frac{1}{\sqrt{6}}(1, 2, -1)$
d	$\frac{1}{\sqrt{3}}(1, 1, 1)$	$\frac{1}{\sqrt{2}}(-1, 0, 1)$	$\frac{1}{\sqrt{6}}(-1, 2, -1)$

After Ref. [17].

a trigonal doublet mode with associated oscillator frequencies ω_A and ω_E , respectively [17,18]. Previous calculations [12] involving anisotropy in the $T \otimes t_2$ JT system have shown that ω_A does not appear in the second-order RFs of A and T_2 symmetry and thus only ω_E is needed. The calculations also showed that in the infinite coupling limit used here $\omega_E = \sqrt{2/3}\omega_T$.

From Table 1 and equations (17) and (18), the corrections to the well ground states are readily found. These corrections then change the values of the second-order RFs because of the consequential corrections to the symmetry-adapted states given by equation (5). From these calculations and also additionally including the anisotropy as given above, the total second-order RFs for two perturbations each of T_1 -type are

$$\begin{aligned}
 K_A^{(2)\text{corr}}(T_1 \otimes T_1) &= -\frac{1}{3E_{JT}} - \frac{(\hbar\omega_T)^4}{162K_T^4} \langle 0 | (q_4^2 + q_5^2 + q_6^2) | 0 \rangle \\
 &= -\frac{1}{3E_{JT}} - \frac{(\hbar\omega_T)^3}{72\sqrt{6}K_T^4} \\
 K_{T_2}^{(2)\text{corr}}(T_1 \otimes T_1) &= -\frac{2}{9E_{JT}} - \frac{(\hbar\omega_T)^4}{114K_T^4} \langle 0 | \left(q_4^2 + q_5^2 - \frac{1}{2}q_6^2 \right) | 0 \rangle \\
 &= -\frac{2}{9E_{JT}} + \frac{(\hbar\omega_T)^3}{216\sqrt{6}K_T^4} \\
 K_E^{(2)\text{corr}}(T_1 \otimes T_1) &= \frac{(\hbar\omega_T)^4}{648K_T^4} \langle 0 | (q_4^2 + q_5^2 - 2q_6^2) | 0 \rangle = 0 \quad K_{T_1}^{(2)\text{corr}}(T_1 \otimes T_1) = 0
 \end{aligned} \tag{19}$$

Figure 1 provides a physical explanation of the first-order non-Condon corrections to the second-order RFs. Due to the coupling between the ground and excited states in the wells *via* the perturbation U_1 given in equation (17), the transitions between the ground and upper sheets are no longer vertical in this diagram as phonon excitations are involved. Thus the non-vertical transitions corresponding to first-order non-Condon corrections are represented by the broken arrows in the figure. These transitions are to levels $\hbar\omega_T$ above and $\hbar\omega_T$ below the vibrational state of energy $n\hbar\omega_T$ that is active in the vertical transition. The insert to the right shows the corresponding upper vibrational energy levels within the excited well and the energy gap ΔE_{vert} used in all calculations. The presence of terms in q_i^2 in equation (19) implies a participation of the excited states that differ by one phonon excitation from the ground state.

In the above expressions, the displacement coordinates q_j are directly related to the well displacements q_p as defined by equation (18). Thus a further

simplification has been made in the final expressions above by taking the expectation values of q_j^2 over the oscillator ground states such that $q_j^2 = 1/(2\hbar\omega_T)$. We see that therefore $K_E^{(2)\text{corr}}(T_1 \otimes T_1) \rightarrow 0$ whereas $K_{T_1}^{(2)\text{corr}}(T_1 \otimes T_1) = 0$ on symmetry grounds alone so that only two of the second-order RFs are finite. It can be seen that the non-Condon corrections are proportional to $1/K_T^4$, which results in a significant modification to the original FC results. It should be noted that there are other corrections that can be made to the original FC results, although they are unlikely to be larger than the corrections just described.

6.2. Results including the non-Condon corrections

Figures 2 and 3 contain plots of the two non-zero RFs for $M \equiv A$ and T_2 , respectively, as a function of the coupling strength K_T . Also included in each figure are the original analytical calculations of Bates *et al.* [3] (who also included corrections due to anisotropy) and the numerical results of O'Brien [9] (The key is shown as an insert in each figure.) It should be emphasized that, even though the results shown cover the range $K_T = 0$ –2.5, all but the numerical results of O'Brien [9] are only strictly valid in the strong coupling limit (K_T larger than unity).

As ΔE_{vert} is directly proportional to K_T^2 , the product $K_T^2 K_M^{(2)}(T_l \otimes T_l)$ is a constant in the standard FC approximation [4]. It is therefore convenient to plot

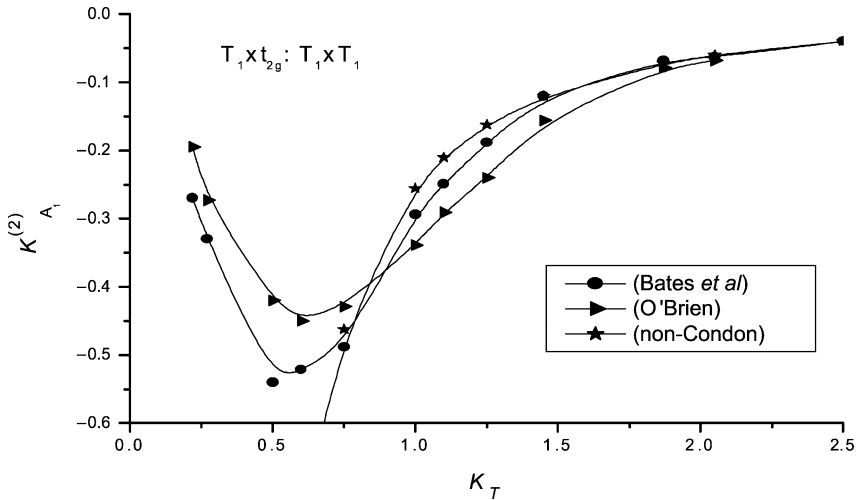


Fig. 2. A plot of the second-order RF $K_A^{(2)}(T_1 \otimes T_1)$ as a function of the vibronic coupling constant K_T . The new results (non-Condon) as well as the analytical calculations of Bates *et al.* [3] and the numerical results of O'Brien [9] are shown.

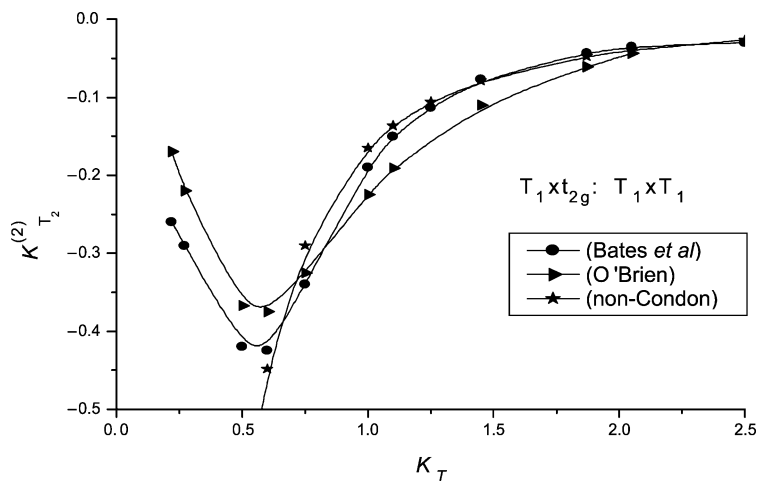


Fig. 3. A plot of the second-order RF $K_T^{(2)}(T_1 \otimes T_1)$ as a function of the vibronic coupling constant K_T . The new results (non-Condon) as well as the analytical calculations of Bates *et al.* [3] and the numerical results of O'Brien [9] are shown.

this product as a function of K_T . Figures 4 and 5 show the results. These figures also contain the standard FC limiting values as deduced here and the non-Condon corrections to the FC values deduced from equations (19).

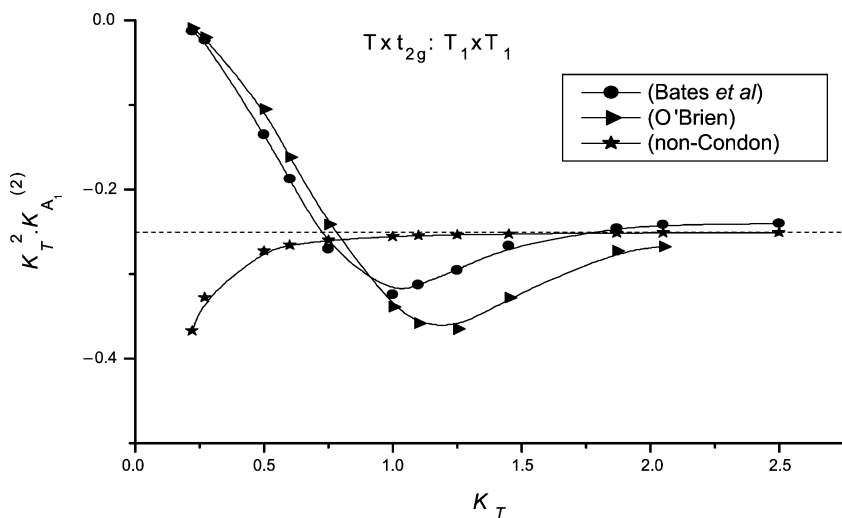


Fig. 4. A plot of the second-order RF $K_T^2 K_{A_1}^{(2)}(T_1 \otimes T_1)$ as a function of the vibronic coupling constant K_T . The new results (non-Condon) as well as the analytical calculations of Bates *et al.* [3] and the numerical results of O'Brien [9] are shown.

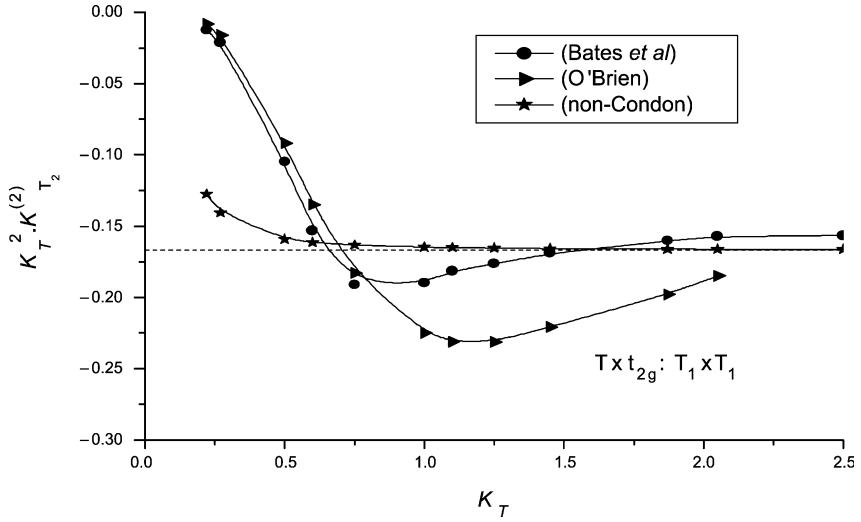


Fig. 5. A plot of the second-order RF $K_T^2 K_{T_2}^{(2)}(T_1 \otimes T_1)$ as a function of the vibronic coupling constant K_T . The new results (non-Condon) as well as the analytical calculations of Bates *et al.* [3] and the numerical results of O'Brien [9] are shown.

7. DISCUSSION

The aim of this work was to take the simplest of the possible non-Condon corrections to the standard FC calculations to see if the gap between the numerical calculations of O'Brien [9], the analytical calculations of Bates *et al.* [3], and the FC limiting values could be reduced. The results obtained in Figs 2 and 3 show that the non-Condon corrections indeed give final results closer to the numerical work of O'Brien [9]. Thus the non-Condon corrections are a valid improvement on the standard FC results and provide an accurate estimate of the second-order RFs in the case of strong vibronic coupling for $K_T > 1$ in the $T \otimes t$ JT system. The non-Condon corrections lift the assumption of rigid electronic wave functions that are assumed in the standard FC approximation. They provide a way for the vibronic wave functions to adjust to the effects of electronic perturbations up to and including those of second order. This concept is based on ideas that are similar to those involved in Raman scattering in optical spectra.

It is therefore worthwhile to use the non-Condon correction in other systems in which the second-order RFs is an important parameter especially in icosahedral systems. This will be the subject of future work.

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REFERENCES

- [1] F. S. Ham, *Phys. Rev.*, 1965, **138**, 1727.
- [2] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, Berlin, 1989.
- [3] C. A. Bates, J. L. Dunn, L. D. Hallam, P. J. Kirk and V. Z. Polinger, *J. Phys.: Condens. Matter*, 1991, **3**, 3441.
- [4] M. Abou-Ghantous, V. Z. Polinger, J. L. Dunn and C. A. Bates, *J. Phys.: Condens. Matter*, 2002, **14**, 3115.
- [5] Q. C. Qiu, J. L. Dunn, C. A. Bates, M. Abou-Ghantous and V. Z. Polinger, *Phys. Rev. B*, 2000, **62**, 16155.
- [6] J. L. Dunn, *J. Phys. C: Solid State Phys.*, 1988, **21**, 383.
- [7] J. L. Dunn, *J. Phys.: Condens. Matter*, 1989, **1**, 7861.
- [8] C. A. Bates and J. L. Dunn, *J. Phys.: Condens. Matter*, 1989, **1**, 2605.
- [9] M. C. M. O'Brien, *J. Phys.: Condens. Matter*, 1990, **2**, 5539.
- [10] F. S. Ham, *J. Phys.: Condens. Matter*, 1990, **2**, 1163.
- [11] I. B. Bersuker, *Chem. Rev.*, 2001, **101**, 1067.
- [12] J. L. Dunn, C. A. Bates and J. Kirk, *J. Phys.: Condens. Matter*, 1990, **2**, 10379.
- [13] S. Jamila, J. L. Dunn and C. A. Bates, *J. Phys.: Condens. Matter*, 1992, **4**, 4945.
- [14] C. A. Bates, J. L. Dunn, V. Z. Polinger, L. D. Hallam, P. J. Kirk and S. Jamila, *Mater. Sci. Forum*, 1992, **83–87**, 487.
- [15] W. Ulrici, L. Eaves, K. Friedland and D. P. Halliday, *Phys. Status Solidi b*, 1987, **141**, 191.
- [16] C. A. Bates, J. L. Dunn and W. Ulrici, *J. Phys.: Condens. Matter*, 1990, **2**, 607.
- [17] U. Öpik and M. H. L. Pryce, *Proc. R. Soc. (Lond.) Series A*, 1957, **238**, 425.
- [18] J. L. Dunn and C. A. Bates, *J. Phys.: Condens. Matter*, 1989, **1**, 375.

Embedding of the K_{10} Graph on a Surface with Seven Cross-caps and the Icosahedral $H \otimes 2h$ Jahn–Teller Surface

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Abstract

Chemical processes are associated with paths between minima on a multidimensional potential hypersurface. Graph theory is frequently applied to represent the essential structure of this surface. In spite of the apparent complexity of some of these representations, they are entirely based on only two descriptors: *vertices* for the chemical structures, and *edges* for the connecting paths. To understand the spatial relationships and dimensionality of the pathways, it is necessary to add to the graph the concept of *faces*. In this way, one obtains a polyhedral representation of the reaction hypersurface on a two-dimensional (2D) surface of a higher genus. The use of this method to study chemical interconversion processes is explored. As an illustration we apply this technique to obtain 2D representations of the 5D hypersurface, which describes the Jahn–Teller distortions of an icosahedral fivefold degeneracy, such as is present in the cationic ground state of C_{60} . The starting point is the complete graph K_{10} , which can be represented on a surface with seven crosscaps. The warping of this surface under different coupling conditions is described by subgroup relations on this parent surface. Symmetries and contraction schemes of the substructures are also analyzed. It is found that cycles which exhibit a Berry phase of π correspond to non-contractible cycles on the parent K_{10} polyhedron.

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1. INTRODUCTION

Chemical reactions are identified as trajectories between minima on an adiabatic potential energy surface. Already in 1968 Muetterties [1] realized that the essential features of this surface could be represented by a graph. Its vertices correspond to the stable chemical structures, and its edges represent elementary reaction processes connecting reagents and products. Graph-theoretical concepts thus became relevant for the description of dynamic aspects of molecular science, much in the same way, as atom-bond graphs had been identified previously as the basic descriptors for the static molecular structure. The current literature offers many illustrations of graphtheoretical approaches to a multitude of chemical problems [2]. In spite of the apparent complexity of some of these approaches, one should realize that the underlying concept of a graph has only two ingredients: points and lines. In a *polyhedral* [3] representation the concept is enriched by adding the notion of a face. This introduces into graph theory aspects of dimensionality and spatial relationships [4]. In this way, the topological nature of many chemical and physical phenomena can be expressed more clearly. This is especially important for the study of surface crossings, such as conical intersections, which are described both in the context of Jahn–Teller (JT) effect [5] and of photochemical reaction processes [6]. In the present contribution, we illustrate the polyhedral representation for a highly symmetrical case of an interconversion graph, corresponding to the icosahedral $H \otimes 2h$ JT problem. First the concept of a polyhedral surface is explained and then it is shown how to construct the polyhedral surface in this case.

2. THE POLYHEDRAL REPRESENTATION

In its simplest form, molecules or reactions can be represented by the mathematical concept of a graph, consisting only of a set of points (vertices) and lines (edges) connecting some of these points. In this very crude approach, all the geometrical information contained in the system is thrown overboard. It is therefore no longer possible to talk about distances or the dimensionality of the system; the only aspects a graph recognizes are the constituent elements (vertices) and a set of binary relations between them (edges). Maybe the best way to see a graph is as a collection of beads held together by a set of elastics. Although many problems can be described surprisingly well by means of graphs [7], there is clearly a need for a more

elaborated representation that also includes spatial relationships to some extent. One way to achieve this is by projecting the graph onto a surface, which encloses a finite region of space to form what is called a polyhedron. In this way, the surface is divided into polygons, which we shall call faces and which form a new entity that was not apparent in the graph-like representation. As an example of a polyhedral representation, think of the five platonic solids, which are polyhedra formed by putting their corresponding graphs on a sphere. So in contrast to the graph, a polyhedron contains not only points and lines, but also faces.

In a recent paper [8] we have explored the use of this representation for the description of molecular structure.

The main properties of a polyhedral surface are undoubtedly related to the topology of the underlying manifold that it decorates. This topology can be completely described by two properties: the Euler characteristic and the orientability of the surface. The former can easily be calculated from the celebrated Euler theorem [9] which states that the number of vertices, edges, and faces, denoted as V , E , and F respectively, obey the following rule:

$$V - E + F = \chi \quad (1)$$

Here χ is a fixed integer, the Euler characteristic that marks the particular topology of the surface on which the polyhedron is embedded. However, in order to describe the topology completely, one also has to specify the orientability of the surface [3]. A surface is orientable if there is no walk on the surface that would take you from the outside to the inside. Such is the case of a sphere with handles. Otherwise, it is non-orientable. This is the case of a sphere with crosscaps. Based on this orientability, the infinite class of surfaces can be divided into two subclasses:

1. Take the sphere and attach p handles to form the orientable surface S_p . The corresponding Euler characteristic is given by $\chi(S_p) = 2 - 2p$. For example, the torus is homeomorphic to a sphere with one handle and has $\chi = 0$.
2. Take the sphere and attach q crosscaps to form the non-orientable surface N_q which has the Euler characteristic $\chi(N_q) = 2 - q$. For example the projective plane is homeomorphic to the sphere with one crosscap and has $\chi = -1$.

By a theorem of Brahana [10], any two-dimensional closed surface falls into one of these two classes. In particular, the surface obtained by adding p handles and q crosscaps ($q \geq 1$) is homeomorphic to N_{2p+q} . Connected with every surface is its Euler genus, defined as: $\bar{\gamma} = 2p$ if the surface is orientable or $\bar{\gamma} = q$ if the surface is non-orientable. Because $\bar{\gamma} = 2 - \chi$, this Euler genus can easily be calculated using the Euler equation (1). As stated before, this Euler genus is not sufficient to uniquely classify all surfaces because it contains no information about the orientability of the surface. The missing information can only be obtained by reducing the surface to its standard form [3].

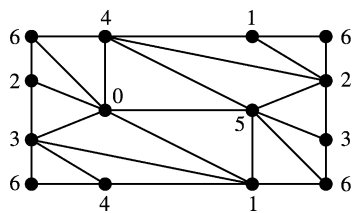


Fig. 1. Embedding of K_7 on the torus. The surface is obtained by gluing together opposite edges so that corresponding points coincide.

From the definition of a polyhedron as described above, we can now turn to a problem that is crucial for the present discussion:

Given a certain graph: what is the surface with the lowest Euler genus on which this graph can be embedded without edges crossing each other?

Take for example the complete graph K_7 on seven vertices, which obviously can not be embedded on the sphere. In fact the torus is as Fig. 1 illustrates the surface with lowest genus on which a polyhedral embedding is possible. In general the problem of finding the genus of a random graph is NP-complete (there exists no algorithm that runs in polynomial time), except for some special types of graphs. Among these are the complete graphs for which in the orientable case:

$$\gamma(K_n) = 2 \left\lceil \frac{(n-3)(n-4)}{12} \right\rceil \quad \text{for } n \geq 3 \quad (2)$$

or in the non-orientable case:

$$\gamma(K_n) = \left\lceil \frac{(n-3)(n-4)}{6} \right\rceil \quad \text{for } n \neq 7 \quad \text{and} \quad n \geq 3, \quad (3)$$

$$\gamma(K_7) = 3$$

where the notation $\{x\}$ is the ceiling function, i.e., it corresponds to the smallest integer not less than x . This result is related to the long standing map coloring problem and was successfully solved by Gerhard Ringel in 1968 [11]. When we talk about the genus of a graph in the following sections, we mean the minimal Euler genus (orientable or non-orientable) of that graph. As we can see, $\gamma(K_{10})$ will be equal to seven (a surface with seven crosscaps), a result that will be of great importance in the following sections.

3. WHY A POLYHEDRAL REPRESENTATION IS USEFUL

By associating the reaction graph with a surface we obtain a minimal crosssection of the actual multidimensional potential energy hypersurface, which still has

a geometric meaning. It is therefore the simplest way to depict a complex reaction scheme in a spatial map, which can be drawn on a sheet of paper. This map should still represent the adjacency relations that exist in hyperspace. It also may offer topological means to distinguish closed reaction paths, describing a looping on the hypersurface. This is especially relevant in the study of JT processes and conical intersections, where special dynamical features are associated with closed loops that encircle an intersection point [12]. Notice that by mapping the graph on a surface, the original cycles of the graph are divided into two classes: the contractible cycles which are homotopic to a point on the surface (this means that they can be contracted until they eventually become a point on the surface) and the non-contractible cycles which cannot be contracted to a point because they encircle a point which does not belong to the surface itself. Take as a simple example the torus: cycles that go around the ‘rim’ or ‘waist’ of the torus are indeed cycles of the graph imposed on the surface, but are not faces of the embedding. They encircle the ‘central hole’ or the ‘inside’ of the torus, neither of which belongs to the topological surface. The faces of a polyhedron obviously are in the first class of cycles, and furthermore, we can state that all contractible cycles can be formed by gluing some faces together. In the following, we will apply this polyhedral mapping technique to elucidate the structure of a complicated JT surface associated with a fivefold degenerate electronic instability in molecules with icosahedral symmetry. Graph-like representations of JT distortions have been introduced before in the discussion of the Epikernel Principle [13] and were recently discussed by King [14].

4. THE INTERCONVERSION PATHS ON THE LINEAR $H \otimes (g \oplus 2h)$ JT SURFACE

The linear $H \otimes (g \oplus 2h)$ JT problem describes the instability of icosahedral molecules in fivefold degenerate states. Previous studies have revealed that this problem may have two kinds of solution, depending on the relative strengths of the coupling parameters [15]. In one regime one finds six equivalent pentagonal minima of D_{5d} symmetry, while in the other there are ten equivalent trigonal minima of D_{3d} symmetry. Both these coupling regimes can be studied in the restricted $H \otimes 2h$ surface, where the fivefold degenerate instability is coupled to a space of five effective components of a mode with h -type symmetry with two symmetry independent coupling parameters. The ‘natural habitat’ of the interconversion graph is thus a hyperspace in a 5D coordinate space. Several attempts have been made in the literature to represent the essential geometric structure of this surface. These studies were motivated by the observation of a ground state crossover under certain coupling conditions [16–20]. While phase tracking along the interconversion paths has yielded an explanation of the crossover, the general structure of the surface remains unknown. In the following we will investigate this problem using the polyhedral representation.

4.1. The D_5 minima

The six pentagonal minima are equidistant in coordinate space, so it is clear that the corresponding interconversion graph is nothing else than the complete graph on six vertices. Following equations (2) and (3) we find that the genus of this graph will equal one. Therefore, there must exist an embedding on the surface with one crosscap, also known as the projective plane. Using the Euler equation (1), we can deduce that this embedding needs ten faces.

$$V - E + F = 2 - \bar{\gamma} \Rightarrow 6 - 15 + F = 2 - 1 \Rightarrow F = 10 \quad (4)$$

Because in a polyhedral embedding every edge occurs in exactly two faces, we also know that the sum of the ‘lengths of the faces’ (the number of edges in the face) must be equal to twice the number of edges, being thirty. The embedding therefore has to be a triangulation of the projective plane and is illustrated in Fig. 2. Notice that to form the original surface from this planar representation, sides labeled with the same index must be identified and in such a way that their orientation is preserved. A closer look at the embedding reveals that the original symmetry group of K_6 (S_6 with 720 elements), is reduced by the embedding to the icosahedral group I with 60 elements. Although in a graph it was sufficient for the symmetry-elements to map vertices to vertices and edges to edges, in the case of a polyhedral embedding these symmetry-elements have to satisfy a supplementary condition, namely that they also take faces to faces. The symmetry-group of a polyhedral embedding will therefore always be a subgroup of the original symmetry-group of the graph, as in our case: $I \subset S_6$. In the representation of Fig. 2, the lowest-energy closed paths (in this case triangles), are realized as faces of the embedding. In fact, all ten faces of the embedding are triangles.

4.2. The D_3 minima

As already indicated, under a different coupling regime an alternative solution is possible with ten D_{3d} minima. Although we find that all ten trigonal minima are

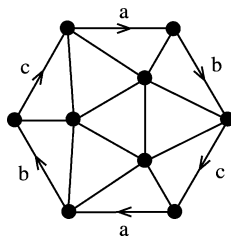


Fig. 2. The embedding of K_6 in the projective plane. The Euler equation reads: $V - E + F = 6 - 15 + 10 = 1$. The surface is obtained by gluing together opposite edges so that arrows match.

equivalent, they are no longer equidistant in coordinate space. Each trigonal minimum is surrounded by three minima at distance r_A and six minima at another distance r_B .

$$\begin{aligned} r_A^2 &= \frac{20}{27} \frac{F_G^2}{K_G^2} + \frac{32}{27} \frac{F_{Ha}^2}{K_H^2} \\ r_B^2 &= \frac{40}{27} \frac{F_G^2}{K_G^2} + \frac{16}{27} \frac{F_{Ha}^2}{K_H^2} \end{aligned} \quad (5)$$

Here the K s are elastic force constants associated with the vibrational modes of G and H symmetry, and F_G and F_{Ha} are linear JT coupling constants to the respective modes. There is another JT constant, F_{Hb} , which is however active along the pentagonal distortions. Depending on the magnitude of the coupling parameters, these distances will change and give rise to three possible cases [15]:

1. $r_A < r_B$: The corresponding interconversion graph is the ten-vertex Petersen graph, with each vertex only connected to its three nearest neighbors.
2. $r_B < r_A$: The corresponding interconversion graph is the complement of the Petersen graph, with each vertex connected to its six closest neighbors. By the complement we mean the graph with connections only between vertices that were not connected in the original graph.
3. The special case $r_A = r_B$ where all vertices are equidistant. The problem is therefore depicted by the complete graph K_{10} on ten vertices. This graph has genus seven and can therefore be embedded on the non-orientable surface with seven crosscaps.

In the following section we will consider the polyhedral representation of these three cases in further detail. Our strategy will be to start from the high-symmetry case $r_A = r_B$ where the polyhedral solution is known. The other cases are derived from there.

5. POLYHEDRAL EMBEDDING OF THE INTERCONVERSION GRAPHS FOR THE TRIGONAL MINIMA

5.1. Minimal embedding of K_{10}

Figure 3 gives a minimal polyhedral embedding of K_{10} on the non-orientable surface with seven crosscaps. Before explaining how this figure was derived, some preliminary concepts have to be introduced.

As an external observer, this means not positioned on the surface itself, we can have two positions relative to the surface; we can be on the ‘inside’ or the ‘outside’. Suppose we are on the outside and look at a graph on the surface, then for every vertex, we can write down a cyclic sequence (clockwise or counterclockwise) of

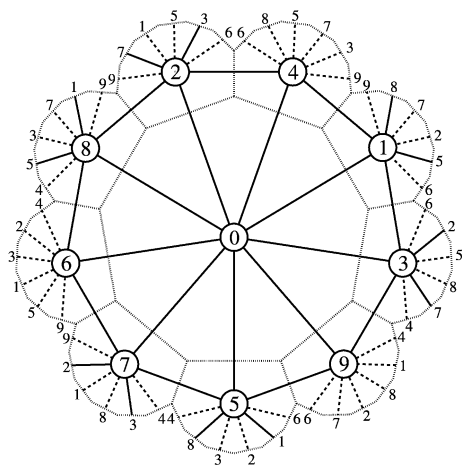


Fig. 3. The embedding of K_{10} in the surface with seven crosscaps. When one leaves, e.g. vertex 2 by exit 3 one should connect to vertex 3 *via* entrance 2, etc. Dashed lines represent connections via crosscaps.

the edges incident on that vertex. We shall call this a *rotation* of the vertex [21,22]. It is well known in topological graph theory that a polyhedral embedding is completely described by giving rotations to all vertices, which together form a rotation scheme. The problem of finding a minimal embedding can therefore be reformulated as finding a ‘minimal’ rotation scheme. This problem was solved by Ringel for all complete graphs. From equations (2) and (3), we see that the surface with the lowest genus on which K_{10} can be embedded, is the non-orientable surface with seven crosscaps.

Table 1 gives the rotation scheme of this embedding, deduced from the proof of Ringel [11], with all rotations defined in a clockwise order. This table completely

Table 1. Combinatorial description of the embedding of K_{10} . The first column gives the vertices around which we describe the cyclic rotation. The following columns give the endpoints of the edges, radiating from the given vertex, in a clockwise order

0.	6	8	2	4	1	3	9	5	7
1.	0	4	9	8	7	2	5	6	3
2.	0	8	9	7	1	5	3	6	4
3.	0	1	6	2	5	8	7	4	9
4.	0	2	6	8	5	7	3	9	1
5.	0	9	6	1	2	3	8	4	7
6.	0	7	9	5	1	3	2	4	8
7.	0	5	4	3	8	1	2	9	6
8.	0	6	4	5	3	7	1	9	2
9.	0	3	4	1	8	2	7	6	5

describes the embedding. To obtain a pictorial representation we start by drawing vertex 0 (we could have chosen any vertex) and its incident edges, in the order given by the rotation scheme. In a second step, we draw connections between the endpoints of neighboring edges, which gives rise to the central vertex 0 surrounded by nine triangles. The remaining edges also follow the order imposed by Table 1, but it is not possible to draw them in the plane without intersections. Therefore, we only draw them in the proximity of the vertices they connect, and denote by the number at their ends to which other vertex they must be linked. A closer look at Fig. 3 shows that there are two kind of edges (full lines and dashed lines). Full lines correspond to normal edges and dashed lines to edges that run over a crosscap. Before determining which edges run over crosscaps, we have to explain what happens when they do so. The physical meaning of a crosscap is that the relative position to the surface changes when we go over it, so we go from the ‘outside’ to the ‘inside’ of the surface or vice versa. This implies that if we had seen a clockwise rotation of edges from the outside, they will be turned into a counterclockwise rotation when we look at them from the inside and otherwise. Take for instance the edge (ik) and we want to know if it runs over a crosscap or not. If the cyclic permutation of edges around i contains the sequence (jkl) we expect that the cyclic permutation around k contains the sequence (lij) (Fig. 4). This will indeed be so if edge (ik) is a normal edge. However, when the cyclic permutation around k is not (lij) but (jil) , the rotation is changed from clockwise to anticlockwise, unless we ran over a crosscap and thereby changed our relative position. It is now easy to investigate if an edge runs over a crosscap or not. Take for example the edge (89) . Looking at Table 1, we find the sequence (192) in the rotation of vertex 8 and sequence (182) in that of vertex 9, which implies that we ran over a crosscap. Applying this algorithm to all edges makes it possible to divide them into normal and dashed ones.

With all this in mind, we can now find the faces of the polyhedral embedding. Therefore, we start out at one end of an edge in a plus state (clockwise orientation). We walk along that edge and if the edge is normal (a full line), we keep the current state; if it runs over a crosscap (dashed line) we toggle the current state. We now reach the other end of the edge and if our current state is plus, we use the local rotation (clockwise) to search for the next edge. If however our current state is minus, our relative position to the surface is changed and we have to use the

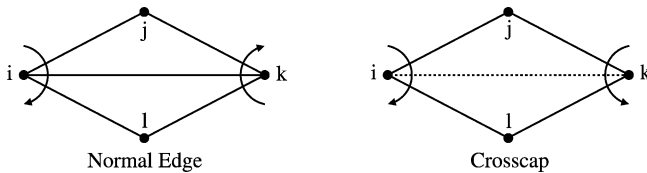


Fig. 4. The rotation around vertex i contains the sequence (jkl) , so we expect that (lij) will be part of the rotation around k . This is so when edge (ik) is normal. If however this edge is a crosscap, we find the opposite sequence (jil) around k .

inverse of the local rotation (counterclockwise) to search for the next edge. The same procedure must be followed repeatedly until we reach our original edge-end in the same state as we started from. When we apply this algorithm in the appropriate way, all faces will be found and every edge will occur in exactly two of those faces.

Table 2 lists all thirty faces of the embedding in Fig. 3. Once the number of faces is known, the Euler genus can easily be verified using the Euler equation. In this case, we find an Euler genus of seven, which means that the surface is indeed homeomorphic to a sphere with seven crosscaps.

$$V - E + F = 10 - 45 + 30 = 2 - \bar{\gamma} \Rightarrow \bar{\gamma} = 7 \tag{6}$$

As in the case of the embedding of K_6 , the lowest-energy closed paths (cycles of length three) are realized as faces of the embedding. The fact that we only find 30 of the 120 possible cycles of length three does not mean that they are absent in the embedding, but only that they are not realized as faces. In other words, these remaining 90 cycles are non-contractible and enclose some point that does not belong to the topological surface.

5.2. Embedding of the Petersen graph and its complement

Because the case of $K_{10}(r_A = r_B)$ is intermediate to that of the Petersen graph ($r_A < r_B$) and its complement ($r_A > r_B$), we expect that both graphs are in some way coexisting in the minimal embedding of K_{10} . Indeed, when we look at one vertex in the embedding of K_{10} (take for instance the central vertex 0), we see that it is contained in exactly nine faces. Putting these nine faces together all the edges starting at 0 are contained exactly twice in these nine faces. There are however nine edges remaining that are only contained once and therefore need to be part of another face. These nine missing faces are formed by combining the remaining edges with only three different vertices, in this case the vertices 4, 6 and 9. Consequently, these three vertices have a different relationship to 0 than the other six vertices. By applying the same procedure to all vertices of K_{10} , the neighbors of each vertex can be divided into two adjacency classes, one with three and one with six elements. Therefore, the 45 edges of K_{10} are also divided into two classes, those that connect a vertex with the vertices of the class with three elements (giving rise to

Table 2. List of faces of the embedding of K_{10} in Fig. 3

1.	013	7.	059	13.	149	19.	246	25.	378
2.	014	8.	067	14.	156	20.	279	26.	457
3.	024	9.	068	15.	178	21.	289	27.	458
4.	028	10.	125	16.	189	22.	347	28.	468
5.	039	11.	127	17.	235	23.	349	29.	569
6.	057	12.	136	18.	236	24.	358	30.	679

Table 3. Three-six adjacency classes of the neighbors for all ten vertices

0.	4	6	9	1	2	3	5	7	8
1.	2	3	9	0	4	5	6	7	8
2.	1	6	8	0	3	4	5	7	9
3.	1	4	5	0	2	6	7	8	9
4.	0	3	8	1	2	5	6	7	9
5.	3	6	7	0	1	2	4	8	9
6.	0	2	5	1	3	4	7	8	9
7.	5	8	9	0	1	2	3	4	6
8.	2	4	7	0	1	3	5	6	9
9.	0	1	7	2	3	4	5	6	8

the Petersen-graph with 15 edges) and those that connect a vertex with the vertices of its class with six elements (forming the complement of the Petersen-graph with 30 edges). The embedding of K_{10} can thus be seen as formed from the superposition of two graphs: the Petersen graph and its complement.

Table 3 gives the three–six division of the neighbors for all ten vertices. The desired pictorial representations of the Petersen-graph and its complement can be found in Fig. 5. These polyhedra are induced, meaning that the embedding was obtained, starting from K_{10} and leaving out the edges that do not belong to the graph. Notice however that in the general case an induced embedding is not necessarily a minimal one. In the following sections, we take a closer look at both induced embeddings and investigate if they are indeed minimal.

5.2.1. The Petersen graph

When we examine the Petersen-graph [23], we will discover 12 shortest cycles of length five (Table 4). Six of these cycles will be realized as faces in the embedding

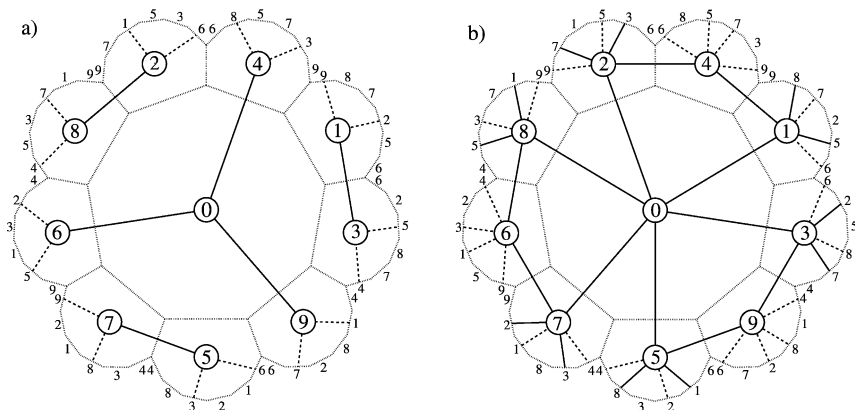


Fig. 5. Induced embedding of the Petersen graph (left) and its complement (right).

Table 4. List of the twelve 5-cycles of the Petersen graph

1.	04826*	4.	82197*	7.	04356	10.	13579
2.	09134*	5.	13562*	8.	04879	11.	28756
3.	06579*	6.	57843*	9.	06219	12.	82134

Cycles marked with an asterisk are also faces of the embedding in Fig. 5a.

shown in Fig. 5a. Indeed, when we apply the previously mentioned algorithm to search for the faces, we will find exactly six faces, all of length five. Using the Euler equation we can therefore easily calculate the genus $\bar{\gamma}$ of our induced embedding:

$$V - E + F = 10 - 15 + 6 = 2 - \bar{\gamma} \Rightarrow \bar{\gamma} = 1 \tag{7}$$

Figure 5a is thus an embedding of the Petersen-graph in the non-orientable projective plane. It is a well-known fact that this is the simplest surface on which the Petersen-graph is embeddable. The symmetry group corresponding to this embedding can be shown to be the icosahedral point group I with 60 elements. So, by mapping the Petersen-graph on the projective plane, its symmetry is reduced from the completely symmetrical group on five elements S_5 to I . In other words, the embedding has removed all odd permutations of S_5 therefore giving rise to two non-equivalent sets of six 5-cycles: those that are realized as faces and those that are non-contractible.

5.2.2. *The complement of the Petersen graph*

The complement of the Petersen graph has 30 shortest cycles of length three. However, when we look at the induced embedding of this graph (Fig. 5b), we find no faces with this length. Instead all fifteen faces have length four (Table 5), which verifies that the genus of the embedding is seven, just like that of K_{10} .

$$V - E + F = 10 - 30 + 15 = 2 - \bar{\gamma} \Rightarrow \bar{\gamma} = 7 \tag{8}$$

None of the 30 cycles of length three existing in the complement are faces in the embedding of K_{10} . They are thus part of the 90 non-contractible 3-cycles. Symmetry investigation showed the embedding to be of S_5 symmetry. There is however, no reason to believe that this embedding is indeed minimal. Therefore we shall investigate if there exist an embedding on a surface with lower genus.

Table 5. List of the fifteen faces of the complement of the Petersen graph given in Fig. 5b

1.	0142	6.	8029	11.	7692
2.	0593	7.	2463	12.	6854
3.	0867	8.	4189	13.	2385
4.	1036	9.	3947	14.	3718
5.	5074	10.	9516	15.	7251

To this end we use a formula in topological graph theory which fixes an upper bound on the Euler characteristic and thus a lower bound on the genus of a graph [22]:

$$3\chi \leq 3V - E \quad \text{or} \quad \bar{\gamma} \geq E/3 - V + 2 \tag{9}$$

The Euler genus of the complement of the Petersen-graph therefore has to be greater than or equal to two:

$$\bar{\gamma} \geq 30/3 - 10 + 2 = 2 \tag{10}$$

We now have found a lower bound of two (a complete triangulation of the graph) and an upper bound of seven (corresponding to the quadrangulation of the induced embedding) on the genus of the graph. Therefore, for the moment the only necessary conditions for a minimal embedding will be

- 1. The embedding must have 15 to 20 faces. This follows directly from the Euler equation (1) in combination with the limits on the genus.
- 2. The sum of the lengths of the faces must be equal to 60, being twice the number of edges.

This still gives rise to many possibilities. In our case, however, we are only interested in embeddings that are a faithful representation of our 5D coordinate space. Therefore, we state that all ten vertices have to be equivalent in the embedding. This implies that all vertices must be surrounded by the same number of cycles of a given length. Using these arguments, we are only left with seven possible embeddings in the range of allowed genera (see Appendix A). Their genera and the length of their faces are given in Table 6. Notice that these solutions are only hypothetical so there is no certainty that they do indeed yield feasible embeddings.

Two of these solutions, namely the total triangulation with genus two and the first solution with genus six, are of great importance, because they are the only ones that can exhibit the same icosahedral symmetry as our problem in 5D coordinate space and in the same time have a genus smaller than seven. It can however be shown that the triangulation of genus two does not exist [24], which leaves us only with the embedding of genus six, consisting of ten triangular and six pentagonal faces. This

Table 6. Possible embeddings with ten equivalent vertices and genus between 2 and 7

Genus $\bar{\gamma}$	Faces	3-Cycles	4-Cycles	5-Cycles	6-Cycles	10-Cycles
2	20	20	–	–	–	–
5	17	10	5	2	–	–
6	16	10	–	6	–	–
6	16	10	5	–	–	1
7	15	10	–	–	5	–
7	15	–	15	–	–	–
7	15	10	5	–	–	–

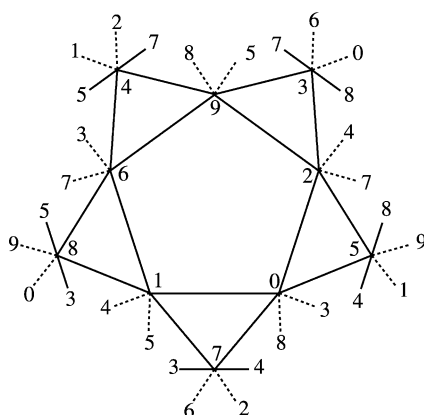


Fig. 6. Embedding of the complement on the surface with genus six.

embedding does indeed exist as is demonstrated in Fig. 6. The list of faces is given in Table 7. In this embedding, every vertex is surrounded by six faces with alternating lengths of five and three. Symmetry considerations show that the embedding is indeed of icosahedral symmetry. Notice that because all these faces travel over an odd number of crosscaps in the embedding of K_{10} , they can never be completely positioned on the surface of that embedding. So in the embedding of K_{10} they are all non-contractible cycles!

6. DISCUSSION AND CONCLUSIONS

In this paper, we have introduced the polyhedral representation of reaction surfaces for chemical interconversion processes, and applied it to the interconversion of JT distortions of icosahedral molecules. In this case, the minimal hypersurface is 5D. Two types of distortions are investigated: pentagonal and trigonal. Interconversions between pentagonal distortions can simply be represented by a triangulation of the projective plane. This is the prototype of a JT surface in a

Table 7. List of faces of the embedding of the complement on a surface with genus 6

3-Cycles				5-Cycles	
1.	017	6.	239	1.	02961
2.	025	7.	247	2.	03645
3.	038	8.	367	3.	07498
4.	145	9.	469	4.	15937
5.	168	10.	589	5.	25867
				6.	38142

centrosymmetric molecule, where the active distortions conserve the center of symmetry. Trigonal distortions and their interconversions present a much richer topology. As we have shown the polyhedron in this case can be derived from the complete graph K_{10} , in which all ten trigonal minima are adjacent. Following the method of Ringel [11], this graph can be embedded on a surface with seven crosscaps. On this surface, every distortion has nine equidistant neighbors. Nonetheless, the symmetry of this polyhedron is only icosahedral. This implies that the nine neighbors fall into two adjacency classes of three and six vertices. Unlike the K_{10} graph, the polyhedron thus incorporates the true icosahedral spatial relationships with distinct adjacencies. On this basis, we then proceeded to identify the interconversion substructures when the neighbors are not equidistant. For the case of three close neighbors we obtain the Petersen graph which can be represented on a projective plane and appears as the dual of the pentagonal distortion polyhedron. For the case of six close neighbors, the graph corresponds to the complement of the Petersen graph. We show that this graph can be represented on a polyhedron with six crosscaps, and that this corresponds to the minimal solution. The topological representation of the K_{10} surface reduces the problem of localization of the flux-lines [25] generating the Berry phase of π to two dimensions. A discussion of the physical significance of this connection will be deferred to a forthcoming publication.

ACKNOWLEDGEMENTS

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APPENDIX A: EMBEDDINGS OF THE COMPLEMENT THAT KEEP THE EQUIVALENCE OF THE TEN VERTICES

In view of the condition that vertices remain equivalent after the embedding, every vertex must be surrounded by an equal number of faces of the same length. This directly implies that the number of faces n_i of length i has to satisfy the following equation:

$$n_i \times i \equiv 0 \pmod{10} \quad (11)$$

A second condition states that the sum of the lengths of all faces must be equal to 60, being two times the number of edges in the complement.

$$\sum_{3 \leq i \leq 10} n_i \times i = 60 \quad (12)$$

As a result, there is no possibility for the faces to be of length 7, 8 or 9. For the odd sizes this is evident, because their number must be a multiple of 10 in order to satisfy equation (11) and

this will automatically lead to an inequality in equation (12). In the case of length 8, there must be at least five cycles of that length. With the remaining $60 - 40 = 20$ edges it is not possible to form the remaining ten to fifteen faces, that are needed to form an embedding of genus two to seven. Using the same arguments, we can show that there are only seven combinations of face-lengths that simultaneously satisfy equations (11) and (12). These are given in Table 6.

REFERENCES

- [1] E. L. Muetterties, *J. Am. Chem. Soc.*, 1968, **90**, 5097.
- [2] J. Brocas, M. Gielen and R. Willem, *The Permutational Approach to Dynamic Stereochemistry*, McGraw-Hill, New York, 1983.
- [3] P. J. Giblin, *Graphs, Surfaces and Homology*, Chapman & Hall, London, 1977.
- [4] M. Deza, P. W. Fowler, A. Rassat and K. M. Rogers, *J. Chem. Inf. Comp. Sci.*, 2000, **40**, 550.
- [5] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, Berlin, 1989.
- [6] M. A. Robb and M. Olivucci, *J. Photoch. Photobio. A: Chem.*, 2001, **144**, 237–243.
- [7] A. T. Balaban, *Chemical Applications of Graph Theory*, Academic Press, London, 1976.
- [8] A. Ceulemans and E. Lijnen, *Eur. J. Inorg. Chem.*, 2002, **7**, 1571.
- [9] H. S. M. Coxeter, *Convex Polytopes*, 3rd edn, Dover, New York, 1973.
- [10] H. R. Brahana, *Ann. of Math.*, 1923, **30**, 234.
- [11] G. Ringel, *Map Color Theorem*, Springer, Berlin, 1974.
- [12] M. V. Berry, in *Geometric Phases in Physics*, *Adv. Series in Math. Phys.* (eds A. Shapere and F. Wilczek), World Scientific, Singapore, 1989, Vol. 5.
- [13] A. Ceulemans and L. G. Vanquickenborne, *Structure and Bonding*, 1989, **71**, 125.
- [14] R. B. King, *Mol. Phys.*, 2002, **100**, 1567.
- [15] A. Ceulemans and P. W. Fowler, *J. Chem. Phys.*, 1990, **93**, 1221, The drawings labeled as Fig. 3 in this paper are erroneous. Fig. 3a should be replaced by the drawing of the Petersen graph, and Fig. 3b by its complement.
- [16] C. P. Moate, M. C. M. O'Brien, J. L. Dunn, C. A. Bates, Y. M. Liu and V. Z. Polinger, *Phys. Rev. Lett.*, 1996, **77**, 4362.
- [17] P. De Los Rios, N. Manini and E. Tosatti, *Phys. Rev.*, 1996, **B54**, 7157.
- [18] N. Manini and P. De Los Rios, *J. Phys.: Condens. Matter*, 1998, **10**, 8485.
- [19] N. Manini and P. De Los Rios, *Phys. Rev.*, 2000, **B62**, 29.
- [20] H. Koizumi and I. B. Bersuker, *Phys. Rev. Lett.*, 1996, **83**, 3009.
- [21] J. L. Gross and T. W. Tucker, *Topological Graph Theory*, Dover, New York, 2001.
- [22] For a brief introduction into the field of Topological Graph Theory, see the survey by Dan Archdeacon on the webpage <http://www.emba.uvm.edu/~archdeac/papers/papers.html>
- [23] D. A. Holton and J. Sheehan, *The Petersen Graph*, Cambridge University Press, Cambridge, 1993.
- [24] M. Conder and P. Dobcsanyi, *J. Comb. Theory B*, 2001, **81**, 224.
- [25] B. R. Judd, in *Vibronic Processes in Inorganic Chemistry* (ed. C. D. Flint), NATO Advanced Study Institute Series, Kluwer, Dordrecht, 1989, Vol. C288, pp. 79–101.

Combined Jahn–Teller and Pseudo-Jahn–Teller Effects in the Benzene Radical Cation

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Abstract

The multi-state vibronic interactions in the benzene radical cation are investigated by an *ab initio* quantum dynamical approach, based on, and extending the work of J. Chem. Phys. 117 (2002) 2645. The $\tilde{X}^2E_{1g}$ ground state and several excited electronic states are included in the calculations, which focus on the vibronic structure of the photoelectron (PE) spectrum and on the internal conversion dynamics. Good agreement with the experimental PE spectrum of Baltzer *et al.* is achieved. New *ab initio* data are provided on the pseudo-rotational barrier in the ground state. The $\tilde{D} - \tilde{E}$ state pseudo Jahn–Teller interaction is shown to lead to a femtosecond population decay of the $\tilde{E}$ state. The importance of stepwise internal conversion processes, involving more than two strongly coupled potential energy surfaces, in this and other medium-sized molecular systems is pointed out.

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1. INTRODUCTION

Among the organic molecules and cations, benzene and its radical cation (Bz^+) are prototype aromatic systems and also showcases for a variety of vibronic effects. For example, Herzberg–Teller intensity borrowing and Jahn–Teller (JT) coupling effects have been well established in the literature for valence and Rydberg excited states of neutral benzene. Similarly, already for the earliest published photoelectron (PE) spectra of benzene, the JT effect in various electronic states of the radical cation played a major role in the analysis [1–5], and has been elaborated upon in later experimental [6] and theoretical [7–12] work. The limited PE spectroscopic resolution has been overcome in extensive studies of emission spectra of several halogenated Bz^+ derivatives, and a wealth of information on intermolecular couplings and structural aspects of the JT distortion could be derived by different groups (see, for example, Refs. [13–15] and references therein). In the parent system Bz^+ , however, there is no detectable emission [16,17] and higher-resolution data emerged only through advances in zero-kinetic-energy photoelectron (ZEKE) spectroscopy and other modern techniques [18–20].

Theoretical investigations have focused on *ab initio*-based characterization of the static [9] and dynamic [10,12,21] JT effect in Bz^+ , both in the ground [9,21] and excited [10,12] electronic states. Pseudo-Jahn–Teller (PJT) interactions between different, energetically close electronic states have also been included in some of these studies [10,12]. A detailed investigation of the multi-mode dynamic JT effect in the $\tilde{X}^2E_{1g}$ state of Bz^+ has been presented in Ref. [21]. A nearly quantitative characterization, including, in particular, a detailed consideration of the pseudo-rotational barrier in the ground state of Bz^+ , has been put forward recently by Applegate and Miller [22].

In the present contribution we aim to study the simultaneous JT and PJT interactions in Bz^+ . This study is based on our recent, rather extensive work on *multi-state vibronic interactions* in this species [23,24]. The latter relied on state-of-the-art *ab initio* calculations of the underlying potential energy surfaces and vibronic coupling constants, and extensive wave-packet dynamical simulations of the resulting vibronic motion. The five lowest, i.e., the $\tilde{X}^2E_{1g} - \tilde{E}^2B_{2u}$ states of Bz^+ , were included in this study. Most important, a series of conical intersections between potential energy surfaces of *different* electronic states has been identified, which complement the well-known JT intersections occurring *within* a degenerate electronic manifold. They lead to an intricate interplay between JT and PJT vibronic interactions in this prototypical system.

Apart from reviewing part of this earlier work, we wish to extend it here in several ways. First, new results on the JT effect in the $\tilde{X}^2E_{1g}$ ground state will be presented and compared with the recent work of Applegate and Miller [22]. Second, the influence of a $\tilde{X}^2E_{1g} - \tilde{B}^2E_{2g}$ conical intersection on the ground state vibronic motion will be investigated explicitly, and demonstrated to be small (previously, only its influence on the $\tilde{B}^2E_{2g}$ and $\tilde{C}^2A_{2u}$ electronic states was considered [11]).

Third, the energetically close-lying higher-energy $\tilde{D}^2E_{1u}$ and $\tilde{E}^2B_{2u}$ electronic states will be analysed, and a ‘propensity’ rule for the JT and PJT couplings [12] be tested numerically by suitable companion calculations. As a consequence, also the relatively small (JT and PJT) coupling terms, neglected earlier [12] are found to have a significant influence on the vibronic dynamics. The results on the lower-energy (i.e., $\tilde{X}^2E_{1g}$ and $\tilde{B}^2E_{2g}$) and on the higher energy (i.e., $\tilde{D}^2E_{1u}$ and $\tilde{E}^2B_{2u}$) electronic states will be collected in two separate sections (Sections 3 and 4, respectively). Before, we briefly review the pertinent theoretical methods in Section 2. The paper concludes with a short summary in Section 5.

2. THEORETICAL FRAMEWORK

2.1. The linear vibronic coupling approach

The lowest electronic states of Bz^+ are of the following symmetry species (at the D_{6h} nuclear configuration, vertical ionisation potentials (IPs) from Ref. [23] given in parentheses):

$\tilde{X}^2E_{1g}$	(9.47 eV)
$\tilde{B}^2E_{2g}$	(11.84 eV)
$\tilde{C}^2A_{2u}$	(12.44 eV)
$\tilde{D}^2E_{1u}$	(14.21 eV)
$\tilde{E}^2B_{2u}$	(14.61 eV)

These states are all single-hole states, differing from the ground state of neutral benzene by the occupancy of a single electron (satellite states are predicted to occur only above 14.7 eV ionisation energy [6,25], i.e., beyond the energy range of interest here). The numbering adopted – without the letter $\tilde{A}$ – is frequently used in the literature to account for the splitting of the $\tilde{X}$ state upon asymmetric substitution.

The JT and PJT vibronic interactions in the electronic manifold are described within the framework of linear vibronic coupling (LVC) theory [26,27]. To this end a diabatic electronic basis is adopted where the pertinent coupling terms arise from the potential energy part while the nuclear kinetic energy is approximately diagonal [26,27]. (The residual derivative couplings are neglected, which constitutes part of the LVC model.) Contrary to the adiabatic basis, the potential energy couplings are smooth functions of the nuclear coordinate also at conical intersections of potential energy surfaces [26], and can be expanded into a Taylor series in the nuclear displacements. Truncation of this series after the linear term, for the off-diagonal matrix elements, and a harmonic approximation for the diagonal elements, are the basic ingredients of the LVC approach. A systematic exposition of the resulting

Hamiltonian for the $\tilde{X}^2E_{1g} - \tilde{E}^2B_{2u}$ electronic manifold of Bz^+ , involving extended group theoretical considerations, is given in Ref. [23]. The relevant submatrices for the cases treated below will be quoted in subsequent sections. Here we only note a general symmetry selection rule for the mode l in order to linearly couple the states i and j :

$$\Gamma_i \otimes \Gamma_j \supset \Gamma_l \quad (1)$$

In other words, the irreducible representation Γ_l of the vibrational mode has to be contained in the direct product of those (Γ_i and Γ_j) of the electronic states [26]. For the intra-state, or JT, couplings, the selection rule (1) involves the symmetrised direct product $(\Gamma_i)^2$ for the degenerate electronic state and leads to the well-known result:

$$(E_{1g})^2 = (E_{2g})^2 = (E_{1u})^2 = (E_{2u})^2 = A_{1g} + E_{2g} \quad (2)$$

The JT active modes are thus always of E_{2g} symmetry, of which benzene has four modes. Adopting Herzberg numbering throughout, these are the modes $\nu_{15} - \nu_{18}$ [28]. The PJT active modes will be specified below.

2.2. *Ab initio* computations

In order to determine the parameters entering the vibronic coupling matrix Hamiltonian, a series of different *ab initio* computations has been performed [23]. The ground state harmonic force field of neutral benzene has been determined by the MP2 and CCSD electronic structure methods. Based upon the resulting normal coordinates, cuts and gradients of the ionic potential energy surfaces have been obtained by the so-called outer-valence Green's functions (OVGF) method [29,30], by an IP variant of the equation-of-motion coupled-cluster (EOMIP-CCSD) method [31,32] and by the second-order approximation of the latter [EOMIP-CCSD(2)] [33]. Basis sets of double-zeta and triple-zeta quality have been employed in these studies. For all further details we refer to the original literature [23]. Figure 1 depicts a representative set of EOMIP-CCSD results, namely cuts along the two cartesian displacement components of the JT-active mode ν_{18} . The higher (lower) symmetry component carries the system to the D_{2h} (C_{2h}) molecular point group. Both these point groups and all electronic states of Bz^+ in question are included in the figure. While the full lines represent results deriving from (analytical) gradients at the origin $Q_{18} = 0$, the filled circles (interconnected by dashed lines to guide the eye) denote single-point calculations performed for various displacements. The agreement between the two data gives an idea of the quality of the LVC approach underlying the full lines. It is generally somewhat better for the C_{2h} component than for the D_{2h} component, because in the former case the actual potential energy curves are symmetric under the reflection $Q \rightarrow -Q$ whereas in the latter case, comprising the stationary points of the system, they are not (remember that for the LVC approach the surfaces are always symmetric, corresponding to the rotational symmetry of the $E \otimes e$ Mexican hat potential surfaces [34]). Similar results have

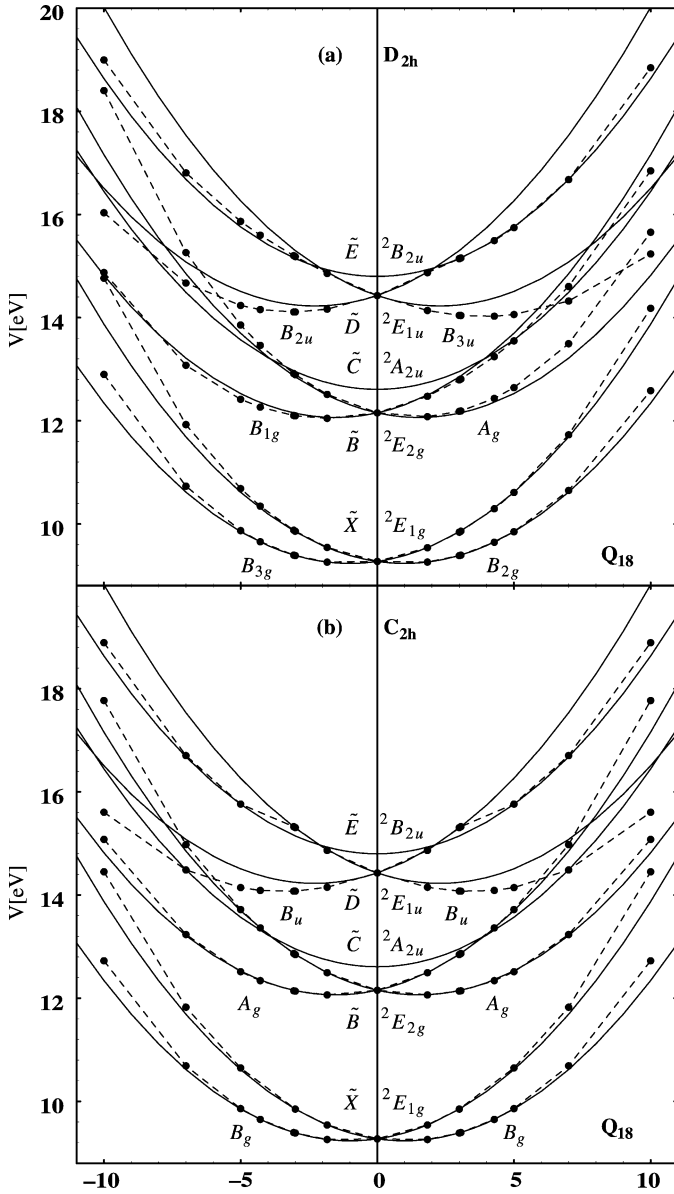


Fig. 1. Comparison of LVC model potential energy curves (full lines) and individual single-point energies (dots, interconnected by dashed lines to guide the eye) for the normal coordinate Q_{18} of one of the JT-active vibrational modes. All data derive from the EOMIP-CCSD calculation. The upper panel displays results for the D_{2h} symmetry-preserving component of Q_{18} , the lower panel for the C_{2h} symmetry-preserving component.

been reported in Ref. [23] for the mode ν_{16} and for linear combinations of the normal coordinates of ν_{16} and ν_{18} . The significance of these results, and the set of corresponding coupling constants, will be detailed below.

2.3. Quantum dynamical simulations

The consequences of the multi-state vibronic interactions are revealed, among others, in the vibrational (also termed ‘vibronic’) structure of PE spectra and in the electronic population dynamics (internal conversion processes) of the interacting manifold. To study the former, we utilize Fermi’s golden rule and express the final states (taken to be eigenstates of the vibronic Hamiltonian) as linear combinations of direct products of suitable harmonic oscillator wavefunctions [26]. The resulting algebraic eigenvalue problem is solved efficiently with the aid of the Lanczos algorithm [35,36], especially when choosing the initial Lanczos vector to be the transition operator $\hat{T}$ acting on the initial wavefunction Ψ_0^i [27]. For all further details we refer to the earlier literature.

Despite the efficiency of the Lanczos algorithm, the exponential increase of the basis set size with the number of vibrational modes renders the above expansion impracticable for systems with more than ~ 5 – 8 nuclear degrees of freedom and moderate-to-large vibrational excitation energies. Therefore, we have resorted to the multi-configurational time-dependent Hartree (MCTDH) method as a powerful wave-packet propagation technique [37,38]. The basis of the MCTDH method is to use a multi-configurational ansatz for the wavefunction, with each configuration being expressed as a Hartree product of time-dependent single-particle basis functions. Equations of motions for the expansion coefficients as well as single-particle functions are derived using a variational principle. This ensures an optimal description of the wave-packet by keeping the basis set small and rendering the expansion of the state vector compact. For many cases of interest the size of the configurational basis is reduced by orders of magnitude, thus making the calculation feasible at all.

In the calculations reported below, the MCTDH method has been employed for all calculations involving more than a single ^2E electronic state, i.e., involving PJT interactions. As a drawback, vibronic line spectra are not directly obtained from this (as with any wave-packet propagation) method. The spectral envelope is, however, easily obtained as a Fourier transform according to Ref. [26]:

$$P(E) \sim \text{Re} \int_0^\infty dt \exp(iEt) \langle \Psi_0^i | \hat{T}^\dagger \exp(-i\mathbf{H}t) \hat{T} | \Psi_0^i \rangle \quad (3)$$

With increasing resolution, vibronic line spectra can at least be approximately mimicked by the calculations. Finally, also electronic populations are directly extracted from the time-dependent wave-packet [27].

3. THE MULTI-MODE JT EFFECT IN THE $\tilde{X}^2E_{1g}$ STATE

3.1. General

We start from the well-known Hamiltonian of the linear $E \otimes e$ JT effect, comprising the four e_{2g} modes $\nu_{15} - \nu_{18}$. For later purposes this is written immediately for both the $\tilde{X}^2E_{1g}$ and $\tilde{B}^2E_{2g}$ states of Bz^+ , and including the linear inter-state coupling term between them. From our earlier work (see Fig. 2 of Ref. [23] and equation (7) of Ref. [24]) this is adopted to be

$$\mathbf{H} = (T_N + V_0)\mathbf{1} + \begin{pmatrix} E_X + \sum_{i=1}^2 \kappa_i^{(X)} Q_{ig} & \sum_{m=15}^{18} \lambda_m^{(X)} Q_{my} & 0 & \sum_{j=7}^8 \lambda_j^{(XB)} Q_j \\ + \sum_{m=15}^{18} \lambda_m^{(X)} Q_{mx} & E_X + \sum_{i=1}^2 \kappa_i^{(X)} Q_{ig} & -\sum_{j=7}^8 \lambda_j^{(XB)} Q_j & 0 \\ \sum_{m=15}^{18} \lambda_m^{(X)} Q_{my} & -\sum_{m=15}^{18} \lambda_m^{(X)} Q_{mx} & E_B + \sum_{i=1}^2 \kappa_i^{(B)} Q_{ig} & \sum_{m=15}^{18} \lambda_m^{(B)} Q_{my} \\ 0 & -\sum_{j=7}^8 \lambda_j^{(XB)} Q_j & + \sum_{m=15}^{18} \lambda_m^{(B)} Q_{mx} & E_B + \sum_{i=1}^2 \kappa_i^{(B)} Q_{ig} \\ \sum_{j=7}^8 \lambda_j^{(XB)} Q_j & 0 & \sum_{m=15}^{18} \lambda_m^{(B)} Q_{my} & -\sum_{m=15}^{18} \lambda_m^{(B)} Q_{mx} \end{pmatrix} \quad (4)$$

Here the nuclear coordinates Q are taken to be dimensionless normal coordinates of the neutral ground state characterized by subscripts x and y in case of the doubly degenerate modes (where cartesian displacement components are meant). The vertical IPs are denoted by E_X and E_B , with an obvious labelling. T_N and V_0 collect the nuclear kinetic energy and unperturbed harmonic potential, with frequency ω_i for the i -th mode. The quantities λ_i^X and λ_i^B are the usual linear JT coupling constants.

The new feature in equation (4) are the inter-state $\tilde{X} - \tilde{B}$ coupling terms which have been derived in Ref. [23] from group-theoretical arguments. From symmetry alone, also the e_{2g} -mode ν_{11} can lead to a linear $\tilde{X} - \tilde{B}$ coupling, according to the decomposition [see equation (1)]

$$E_{1g} \otimes E_{2g} = B_{1g} + B_{2g} + E_{1g} \quad (5)$$

However, the *ab initio* results indicate that the latter coupling is negligibly small and only the b_{2g} modes ν_7 and ν_8 contribute significantly. The relevant set of parameters entering equation (4) and determined from the earlier *ab initio* MP2/OVGF calculations [23] is collected in Table 1.

Table 1. *Ab initio* calculated coupling constants, frequencies and vertical ionisation potentials (IPs) for the coupled $\tilde{X} - \tilde{B}$ states of Bz^+ ; frequencies are from an MP2 force field calculation for the neutral ground state, coupling constants and IPs from *ab initio* Green’s function results

		ω	$\tilde{X}^2E_{1g}$	$\tilde{B}^2E_{2g}$
A_{1g}	ν_1	0.4081	0.0271	−0.1163
	ν_2	0.1257	0.0467	0.0467
E_{2g}	ν_{16}	0.2055	0.1643	0.3276
	ν_{17}	0.1497	0.0764	
	ν_{18}	0.0757	0.0744	
B_{2g}	ν_{eff}	0.0954		0.1498
IP	—	—	9.48	11.57 ^a

All quantities are in eV.
^aAdjusted value to facilitate convergence.

3.2. Analysis of the JT effect

The data of Ref. [23] reveal, in agreement with all other literature [7,8,21,22], that the JT activity of the asymmetric C–H stretching mode ν_{15} is negligibly small in $\text{Bz}^+(\tilde{X}^2E_{1g})$. We have therefore neglected it in Table 1. Accordingly, three-mode calculations of the JT effect in this state have been performed, utilizing the Lanczos algorithm as indicated above [39]. The resulting PE line spectrum is depicted in Fig. 2 and compared there with the experimental recording of Ref. [6]. The theoretical line spectra are fully *ab initio* and are presented without (Fig. 2(a)) and with inclusion (Fig. 2(b)) of the symmetric C–C stretching mode ν_2 . They have been convoluted with Lorentzians of width FWHM = 20 meV to yield the smooth envelope and to better compare with experiment.

The agreement between panels (b) and (c) can be considered semi-quantitative, when discarding the low-energy hot bands observed experimentally (they are not included in the simulation which has been performed for $T = 0$). The vibronic lines at a computed/observed energy of 86/83 and 123/120 meV are assigned to the modes ν_{18} and ν_2 , respectively. At higher energies mode-mixing effects become increasingly important [26] and the next spectral features are attributed to excitation of ν_{17} , ν_{16} , and their combinations with multiple quanta of ν_{18} , rendering simple assignments difficult. Similarly, good agreement with the PE spectroscopic data of Karlsson *et al.* [4] has been obtained before [21], and the conclusions of that work are generally confirmed by the present study. Apparently, the data of Table 1 yield a reliable description of the JT effect in $\text{Bz}^+(\tilde{X}^2E_{1g})$.

When this work has been completed, results of a careful theoretical study by Applegate and Miller on the JT effect in the $\tilde{X}^2E_{1g}$ state appeared in the literature [22]. These relied on a variety of different *ab initio* calculations and on the analysis of high-resolution ZEKE and IR spectra. Table 2 collects some key results on the JT parameters of this work in comparison to those underlying

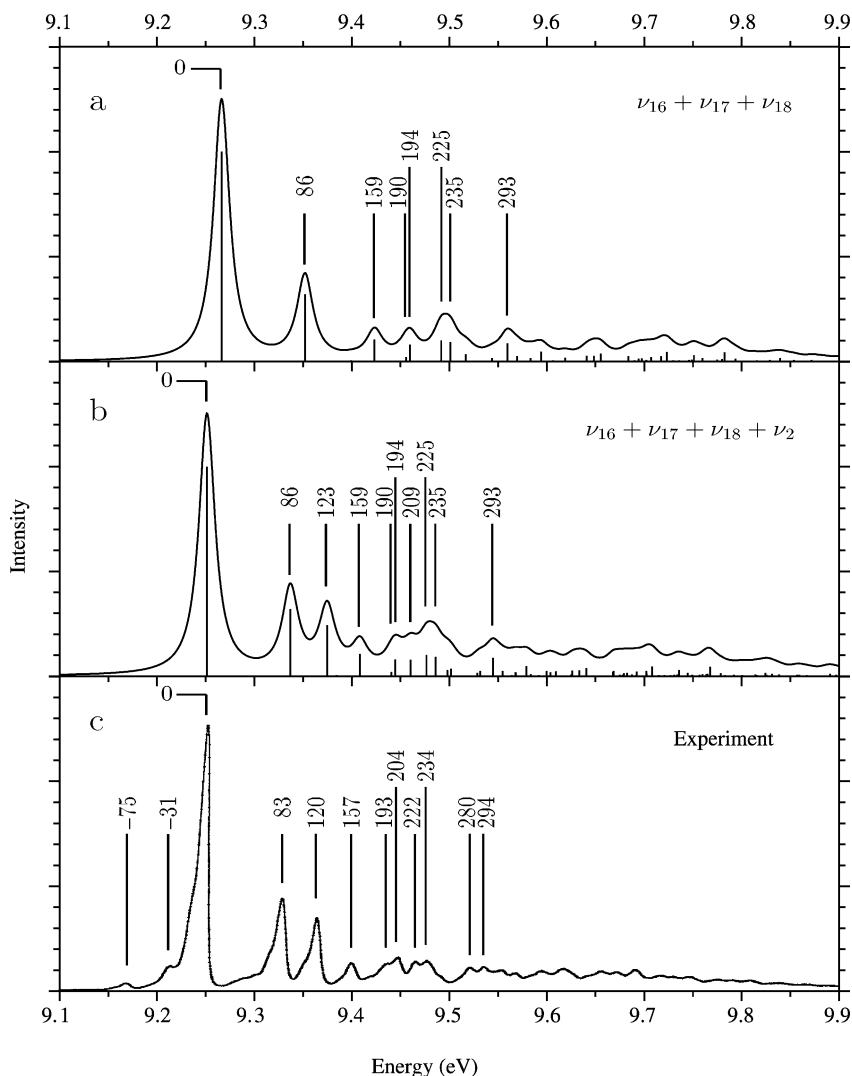


Fig. 2. Comparison of the theoretical (a,b) and experimental (c) results for the first PE band of benzene, corresponding to the $\tilde{X}^2E_{1g}$ ground state of Bz^+ . In the calculation, the line spectra, obtained from the Lanczos algorithm, were convoluted with Lorentzians of width $FWHM = 20$ meV to yield the smooth envelope. For the parameter values, see Table 1. (a) Pure three-mode JT spectrum without mode ν_2 . (b) Convolution of JT spectrum of (a) with a Poisson distribution corresponding to ν_2 . (c) Experimental recording of Ref. [6].

Fig. 2 (second column) and to other theoretical data. By and large, the agreement between the various sets is satisfactory, at least in a qualitative sense. A more detailed comparison shows that the more recent *ab initio* calculations generally lead to a reduction of the JT coupling parameters $D_i = (\lambda_i/\omega_i)^2/2$.

Table 2. Comparison of JT stabilization energies E^{JT} and barriers for pseudo-rotation E^{B} for $\text{Bz}^+(\tilde{X}^2E_{1g})$ from present and earlier (theoretical) work

	OVGF [21]	OVGF [23]	EOMIP-CCSD [23]	CASSCF [22]	EOMIP-CCSD(2) (Present)
E_{16}^{JT}	562	530	456	364	439
E_{17}^{JT}	170	157	170	138	163
E_{18}^{JT}	352	295	308	246	330
E_{16}^{B}	—	—	—	−9 ^a	−5 ^a
E_{17}^{B}	—	—	—	−6 ^a	1 ^a
E_{18}^{B}	—	—	—	6 ^a	−5 ^a

All quantities are in cm^{-1} .
^a $E^{\text{B}} = E(B_{3g}) - E(B_{2g})$, see also Ref. [22].

This holds, in particular, for the asymmetric C—C stretching mode ν_{16} , also when determining D_{16} from ZEKE spectra [22], and leads to a reduced total JT stabilization energy when comparing with earlier work.

A particularly interesting feature is the low barrier for pseudo-rotation in the $\tilde{X}^2E_{1g}$ state. This has been determined to be as low as 8 cm^{-1} by Lindner *et al.* [40], and would lead to an essentially free pseudo-rotation in view of the large zero-point energy of $\sim 400\text{ cm}^{-1}$ for the mode ν_{18} alone [40]. In Ref. [22] this question has been addressed further, and similar contributions from the other e_{2g} modes, though with different signs, been found. (These might lead to an overall barrier as small as $\sim 1\text{ cm}^{-1}$ [22].) We have therefore conducted similar calculations at the EOMIP-CCSD(2) level for $\text{Bz}^+(\tilde{X}^2E_{1g})$, by optimising both JT components separately. The results are included in the last column of Table 2 and seen to be of similar magnitude, i.e., a few wavenumbers only. There is general agreement with the results of Applegate and Miller [22], the only exception being the sign of the barrier for mode ν_{18} . In view of the small absolute numbers we do not try to resolve this minor discrepancy in the present work. However, we have performed full geometry optimisations for both JT components of the $\tilde{X}^2E_{1g}$ state and obtained a barrier of -18 cm^{-1} , to be compared with the result of -14 cm^{-1} from the full EOMIP-CCSD calculations. The full geometry optimisation also gives a total JT stabilization energy of 943 cm^{-1} at the EOMIP-CCSD(2) level (930 cm^{-1} at the EOMIP-CCSD level), close to the sum of the single-mode quantities in Table 2, last column.

3.3. Influence of the coupling with the $\tilde{B}^2E_{2g}$ state

A major point of the current study is, similar to Refs. [23,24], the *simultaneous* consideration of the JT and PJT interactions. Indeed, in an earlier work, a significant $\tilde{X}^2E_{1g} - \tilde{B}^2E_{2g}$ interaction has been established and shown to crucially affect the

excited state population dynamics of Bz^+ [24]. We therefore extend the present work on the $\tilde{X}^2E_{1g}$ state to take that interaction into account.

The pertinent parameter values for the $\tilde{X} - \tilde{B}$ vibronic interaction and the $\tilde{B}$ state JT system are included in Table 1. To facilitate the numerical computations, an effective b_{2g} mode has been introduced which is obtained from the two actual b_{2g} modes ν_7 and ν_8 through the relations [41,42]

$$\lambda_{\text{eff}} = \sqrt{\lambda_7^2 + \lambda_8^2} \quad (6)$$

and

$$\omega_{\text{eff}} = (\lambda_7^2 \omega_7 + \lambda_8^2 \omega_8) / (\lambda_7^2 + \lambda_8^2) \quad (7)$$

for its coupling constant and frequency, respectively. (Such a procedure has been shown in Ref. [10] to give good results for the $\tilde{B} - \tilde{C}$ vibronic dynamics.) Still, the vibrational basis needed to achieve convergence is large, and comprises $\sim 10^{10}$ basis functions. This is reduced to $\sim 10^6$ single-particle functions by the MCTDH contraction effect, which renders the calculation feasible at all. The result, utilizing equation (3) for the spectral envelope, is depicted in Fig. 3.

Figure 3 displays in comparison the spectral profile including (full line) and excluding (dashed line) the $\tilde{X} - \tilde{B}$ interaction. The latter result differs from the envelope of Fig. 2(b) only by the smaller linewidth of $\text{FWHM} = 7 \text{ meV}$, chosen in Fig. 3 to allow for a more detailed comparison between the two curves. The similarity of the two curves of the figure is evident. They differ only by a small shift

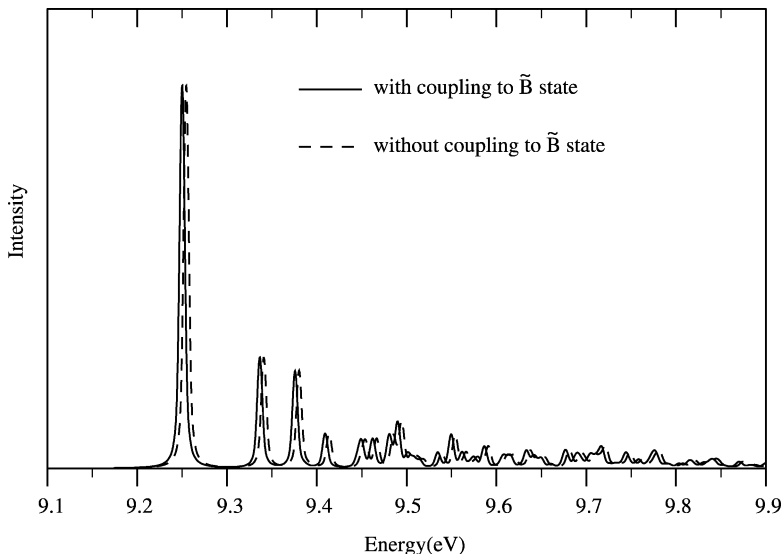


Fig. 3. Comparison of spectral envelopes for the first PE band, computed with (full line) and without (dashed line) coupling to the $\tilde{B}$ state. For more details see text.

of 4.3 meV; applying this shift to one of the curves, they become virtually indistinguishable. The effect of the $\tilde{X} - \tilde{B}$ coupling can thus be ‘absorbed’ by an adjusted vertical IP for the $\tilde{X}$ state. This has been chosen to be 9.475 eV in the full calculation of Fig. 3 which can thus be considered an accurate, experimentally derived datum for this quantity.

The minor influence of the $\tilde{X} - \tilde{B}$ coupling on the ground state dynamics is not surprising when considering the large $\tilde{X} - \tilde{B}$ energy gap *and* the relatively high energy of the $\tilde{X} - \tilde{B}$ conical intersection, which has been established in earlier work [23]. This conical intersection is represented in Fig. 1 by the curve crossing between the lower JT component of the $\tilde{B}$ state and the upper JT component of the $\tilde{X}$ state. It occurs at an energy ≥ 11.6 eV according to the extended analysis of Ref. [23] and is thus not accessible energetically for the $\tilde{X}$ -state vibronic motion (neither can it be encircled in a closed loop which would render the geometric phase effect important [43]). We nevertheless found it instructive to reveal explicitly the influence of the $\tilde{X} - \tilde{B}$ coupling on the $\tilde{X}$ -state PE band in Fig. 3.

Let us emphasize that the $\tilde{X} - \tilde{B}$ conical intersection is of major importance for the $\tilde{B}$ (and, indirectly, also higher) electronic state(s) of Bz^+ . It is well accessible energetically for this state and leads to a $\tilde{B} - \tilde{X}$ internal conversion process at a time-scale of ~ 200 fs [24]. It also affects the population dynamics of the $\tilde{C}$ state (and higher states) which are in turn strongly coupled to the $\tilde{B}$ state [10,24]. Ultimately this conical intersection is responsible for the lack of detectable emission corresponding to the dipole-allowed $\tilde{C}^2A_{2u} - \tilde{X}^2E_{1g}$ transition in Bz^+ [16,17]. The analysis shows that the $\tilde{B}^2E_{2g}$ state is needed to mediate the stepwise $\tilde{C} - \tilde{B} - \tilde{X}$ non-radiative decay processes. As an intriguing feature, the $\tilde{C} - \tilde{X}$ transition is indeed observed in fluorinated Bz^+ derivatives where the $^2E_{2g}$ state is higher in energy than the $^2A_{2u}$ state [14]. Preliminary analysis suggested indeed that the present $\tilde{B} - \tilde{X}$ conical intersection lies too high in energy in these cases to affect the $\tilde{C}^2A_{2u}$ state significantly [11]. A more detailed investigation is left to future work.

4. SIMULTANEOUS JT AND PJT INTERACTIONS IN THE $\tilde{D}^2E_{1u} - \tilde{E}^2B_{2u}$ SYSTEM

4.1. General

The higher-energy $\tilde{D}$ and $\tilde{E}$ states of Bz^+ represent an example of simultaneous JT and PJT interactions between *close-lying* electronic states. From the energetic proximity (difference of vertical IPs of only ~ 0.4 eV) the PJT interaction can be expected to affect *both* states significantly. According to the symmetry selection

rule, equation (1), we have

$$E_{1u} \otimes B_{2u} = E_{2g} \quad (8)$$

and, hence, the JT-active e_{2g} modes $\nu_{15} - \nu_{18}$ are also PJT active in this system. This differs from the lower pair of $\tilde{B}^2E_{2g}$ and $\tilde{C}^2A_{2u}$ states, which are also subject to simultaneous JT and PJT interactions, but where the JT and PJT modes are different by symmetry [10].

The form of the pertinent matrix Hamiltonian in the LVC scheme has already been given in Refs. [23,24] and is reproduced here for convenience:

$$\mathbf{H} = (T_N + V_0)\mathbf{1} + \begin{pmatrix} E_D + \sum_{i=1}^2 \kappa_i^{(D)} Q_{ig} & \sum_{m=15}^{18} \lambda_m^{(D)} Q_{my} & \sum_{m=15}^{18} \lambda_j^{(DE)} Q_{my} \\ + \sum_{m=15}^{18} \lambda_m^{(D)} Q_{mx} & E_D + \sum_{i=1}^2 \kappa_i^{(D)} Q_{ig} & \sum_{m=15}^{18} \lambda_j^{(DE)} Q_{mx} \\ \sum_{m=15}^{18} \lambda_m^{(D)} Q_{my} & -\sum_{m=15}^{18} \lambda_m^{(D)} Q_{mx} & \\ \sum_{m=15}^{18} \lambda_m^{(DE)} Q_{my} & \sum_{m=15}^{18} \lambda_m^{(DE)} Q_{mx} & E_E + \sum_{i=1}^2 \kappa_i^{(E)} Q_{ig} \end{pmatrix} \quad (9)$$

The relative phases of the JT and PJT coupling terms require careful group-theoretical consideration and have been worked out in Ref. [23]. There, also *ab initio* results for the whole set of coupling parameters have been reported, following the lines indicated in Section 2. The relevant frequencies and coupling constants are reproduced in Table 3. Few earlier comparison data exist in the literature for the JT

Table 3. *Ab initio* calculated coupling constants, frequencies and vertical ionisation potentials (IPs) for the coupled $\tilde{D} - \tilde{E}$ states of Bz^+ ; frequencies are from an MP2 force field calculation for the neutral ground state, coupling constants and IPs from *ab initio* Green's function results. For the e_{2g} modes, the entries below the heading $\tilde{D}^2E_{1u}$ denote the JT coupling constants, while those *between* the headings $\tilde{D}^2E_{1u}$ and $\tilde{E}^2B_{2u}$ stand for the PJT coupling constants

		ω	$\tilde{D}^2E_{1u}$		$\tilde{E}^2B_{2u}$
A_{1g}	ν_2	0.1257	0.0705		0.1846
E_{2g}	ν_{16}	0.2055	0.1032	0.1701	
	ν_{17}	0.1497	0.0579	0.1288	
	ν_{18}	0.0757	0.1755	0.0417	
IP	—	—	14.31		14.61

All quantities are in eV.

coupling constants [8], which have been reconsidered in the very recent work of Johnson [44]. They will be compared to the data of Table 3 below.

4.2. Analysis of the PE spectral bands

The mode ν_{15} , again, turns out to be negligible in the $\tilde{D} - \tilde{E}$ system [23]. The data of Table 3 give evidence of a rather strong JT activity of the C—C—C bending mode ν_{18} . It should be mentioned that generally the mode ν_{16} (asymmetric C—C stretching mode) and ν_{18} dominate the JT effect in the various electronic states of Bz^+ [21,22,44]. However, the mode ν_{18} has clearly the largest JT coupling strength $D = \lambda^2/(2\omega^2)$ occurring in all electronic states in question here ($D_{18} \approx 2.7$ according to Table 3 and ≥ 4 according to Ref. [44]). This by far exceeds that of the modes ν_{16} and ν_{17} in the $\tilde{D}$ state. Conversely, these latter two modes are characterized by large PJT couplings whereas for mode ν_{18} this is quite small. This propensity of the coupling strengths has been utilized in Ref. [12] to arrive at a simplified model description, where each of the modes $\nu_{16} - \nu_{18}$ is treated as *either* JT or PJT active only [12].

In the present work we aim at a more accurate description and treat the Hamiltonian, equation (9), fully, with all JT and PJT couplings of Table 3 included. Only the inherently low-resolution experimental PE spectra of Refs. [4,6] are available for comparison which is thus confined to the gross overall features of the composite $\tilde{D} - \tilde{E}$ PE band. Nevertheless, it proved necessary to adjust the vertical IPs, since their difference affects the computed vibronic structure [26]. Being a small difference of large numbers, we increased it from the *ab initio* value of 0.3 eV to a value of 0.45 eV. The PE spectral profile thus obtained with the MCTDH algorithm is depicted in Fig. 4, and compared there with the experimental recording of Ref. [6].

The overall agreement between theory and experiment in Fig. 4(a) and (b), is rather satisfactory: there are three broad overlapping ‘humps’, forming a plateau-like structure and showing a modulation with a spacing of ~ 0.07 eV at lower energy. The latter is attributed to the strong excitation of the JT-active mode ν_{18} , thus confirming earlier more tentative assignments [6,12]. However, almost no line structure is resolved experimentally for higher energies, because of the high density and large number of individual lines. This earlier conclusion [12] is confirmed by the present calculation when performed for higher resolution (FWHM = 14.5 meV), as presented in Fig. 5. Here, the different vibronic symmetries are shown separately and, for comparison, also the spectral profiles obtained without the PJT couplings are included. Apparently, the higher-resolution envelopes and the underlying line spectra are severely affected by the PJT interaction. This holds already for low energies, where the PJT couplings lead to additional anharmonicities of the adiabatic potential energy surfaces [12]. For higher energies, these couplings lead to strong $\tilde{D}^2E_{1u} - \tilde{E}^2B_{2u}$ nonadiabatic effects and a profound change of the $\tilde{E}$ state vibronic line structure (see also Ref. [12]). Clearly, higher-resolution experimental

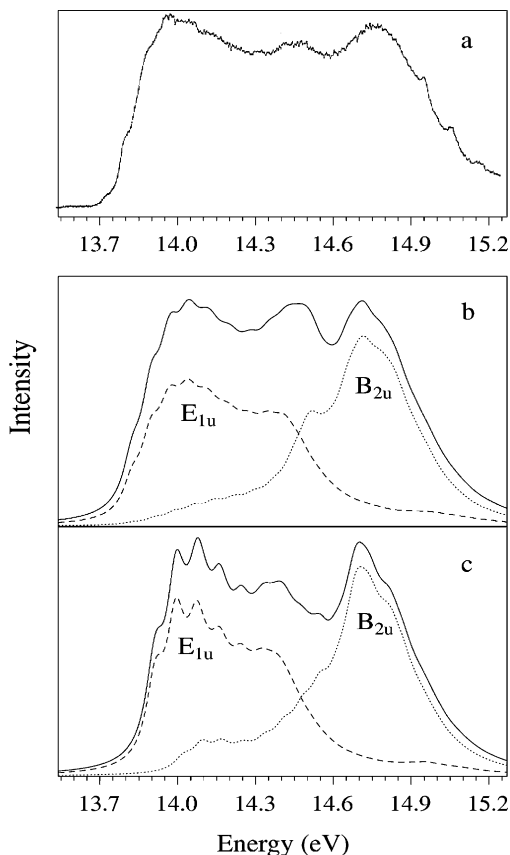


Fig. 4. Comparison of lower-resolution spectral profiles for the composite $\tilde{D} - \tilde{E}$ PE band. (a) Experimental recording of Ref. [6]. (b) Result of the present calculation utilizing the parameter values of Table 3 and including the modes ν_2 and $\nu_{16} - \nu_{18}$ with all couplings. The E_{1u} and B_{2u} vibronic symmetries are drawn separately as dashed lines, their 1.4:1 weighted sum is given by the full line (FWHM = 88 meV). (c) Same as (b), but employing the ‘propensity rule’ $\lambda_{16}^D = \lambda_{17}^D = \lambda_{18}^{DE} = 0$. For more details see text.

recordings would be highly desirable to confirm the present general predictions and to give more quantitative information on these interesting effects.

4.3. The $\tilde{E} - \tilde{D}$ internal conversion process

The aforementioned $\tilde{E} - \tilde{D}$ nonadiabatic interactions also lead to efficient, i.e., femtosecond internal conversion processes which we now briefly address. The presence of such processes is indicated indirectly by experimental studies, where Bz^+ has been prepared initially in the $\tilde{E}$ state, but fragmentation been found to occur via lower (even the $\tilde{X}$) electronic states [45,46]. To describe this non-radiative decay

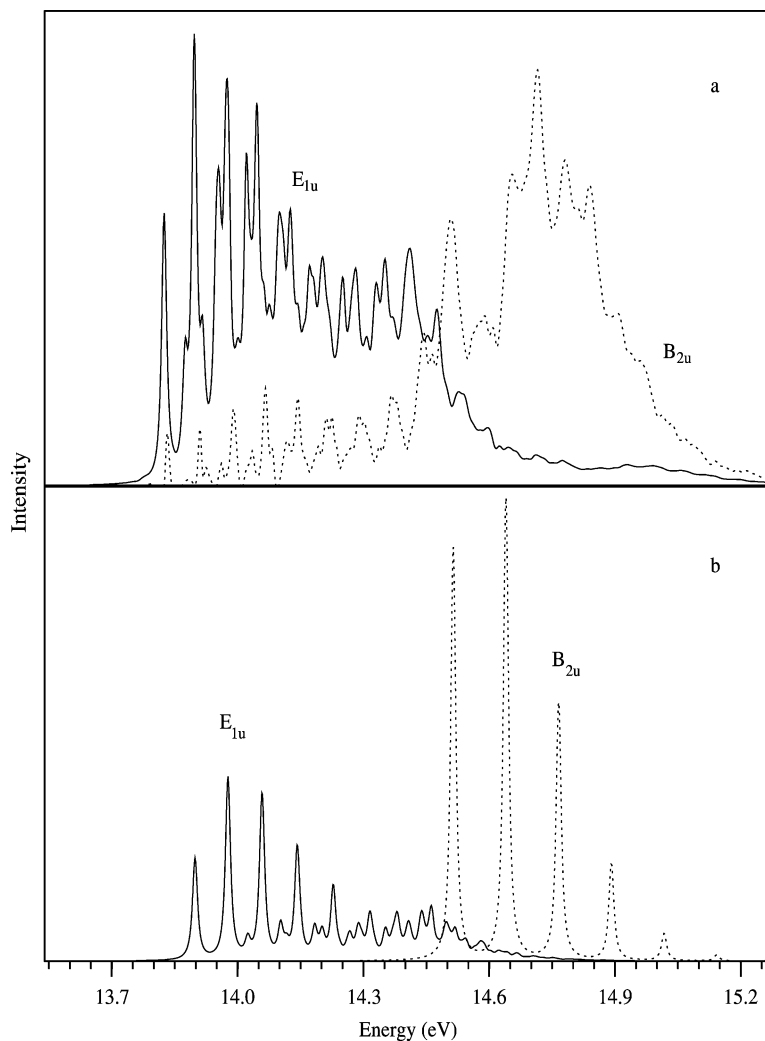


Fig. 5. Comparison of higher-resolution calculated spectral profiles for the $\tilde{D}$ and $\tilde{E}$ PE bands. For more details see text.

theoretically, an initial wave-packet, generated by an optical transition in the center of the FC zone, is propagated with the Hamiltonian, equation (9), utilizing the MCTDH algorithm. The electronic populations are extracted directly as expectation values of suitable projection operators [26,27].

The result for the $\tilde{E}$ state population thus obtained is depicted in Fig. 6. It should be pointed out that *diabatic* populations are given here for simplicity (for two-state problems, also *adiabatic* populations have been computed [47]). In agreement with

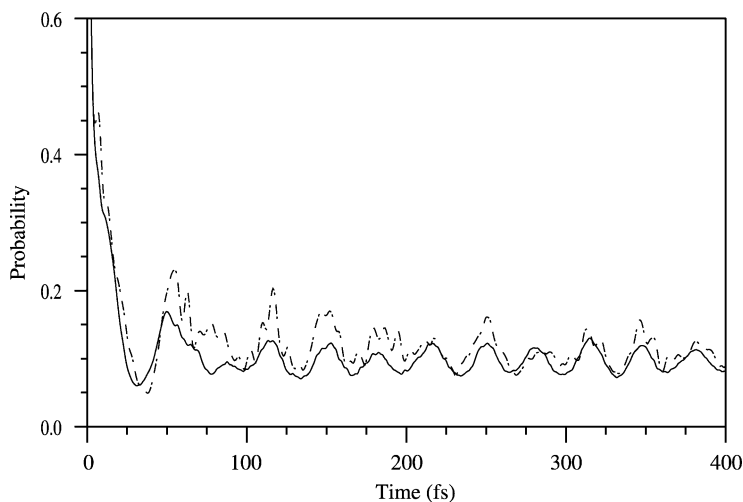


Fig. 6. Time-dependent electronic population of the $\tilde{E}^2B_{2u}$ state of Bz^+ for a vertical transition. The wave-packet is located initially at the $\tilde{E}$ state surface and seen to undergo an efficient radiationless transition at a time scale of ~ 10 – 20 fs. The results of the full calculation (solid line) and of the propensity rule (dashed line) are compared.

earlier, more simplified calculations [12], we indeed find an ultrafast initial decay occurring at a time scale of ~ 15 fs. This is followed by small oscillations around a long-time limit of ~ 0.1 . The initial decay relates to half the period of the symmetric C–C stretching mode ν_2 , and is caused by a conical intersection between the $\tilde{E}$ and $\tilde{D}$ state potential energy surfaces, that occurs upon a symmetric stretching of the C–C bond (see Fig. 3 of Ref. [12]). The importance of conical intersections in triggering such ultrafast internal conversion processes is well established nowadays in the literature [48]. The present results extend the general findings to more complicated three-state problems such as described by the Hamiltonian, equation (9).

We emphasize here that the present calculation is from first principles, without any phenomenological broadening. Since we are considering a bound state problem, the finite long-time limit of Fig. 6 necessarily follows.

For comparison, the figure also contains the result of a calculation using the propensity rule of Ref. [12]. In this calculation the weaker coupling (either JT or PJT) for each of the modes $\nu_{16} - \nu_{18}$ has been suppressed, that is, $\lambda_{16}^D = \lambda_{17}^D = \lambda_{18}^{DE} = 0$ been assumed. The result, represented by the dashed line in the figure, reproduces the overall behaviour of the full calculation rather well. Finer details differ considerably in the two curves. This holds more for the PE spectral envelope which has been included as panel (c) in Fig. 4. It underlines the need to include all coupling terms in order to arrive at an accurate description of the simultaneous JT and PJT interactions in this system.

5. CONCLUDING REMARKS

The benzene radical cation is a prototype organic species with a rich variety of vibronic interactions, and intriguing combinations of JT and PJT coupling effects. Often, the focus in the literature is on the JT effect in a given degenerate electronic state alone. Here, we have given new data and results characterizing the multi-mode dynamical JT effect in the $\tilde{X}$ and $\tilde{D}$ electronic states. In addition, we focused on the impact of the PJT couplings on the $\tilde{X}^2E_{1g}$ and $\tilde{D}^2E_{1u}$ state vibronic dynamics. Whereas this influence is quite small in the former case, it is rather strong for the $\tilde{D}$ and $\tilde{E}$ electronic states. This relates to the different energetic locations of the respective inter-state conical intersections. We emphasize that the $\tilde{X}^2E_{1g} - \tilde{B}^2E_{2g}$ interaction has a profound impact on the $\tilde{B}$ -state population dynamics [24].

The present analysis relies on – and extends – the comprehensive theoretical study of Refs. [23,24] on the multi-state interactions in the manifold of the $\tilde{X} - \tilde{E}$ states of Bz^+ . Like this recent work, it utilizes an *ab initio* quantum-dynamical approach. In Refs. [23,24] we have, in addition, identified strong coupling effects between the $\tilde{B} - \tilde{C}$ and $\tilde{B} - \tilde{D}$ electronic states, caused by additional conical intersections between their potential energy surfaces. A whole sequence of stepwise femtosecond internal conversion processes results [24]. Such sequential internal conversion processes are of general importance as is evidenced indirectly by the fluorescence and fragmentation dynamics of organic closed-shell molecules and radical cations [49,50]. It is therefore to be expected that the present approach and results may be of relevance for many other medium-sized molecular systems.

ACKNOWLEDGEMENTS

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REFERENCES

- [1] L. Asbrink, E. Lindholm and O. Edquist, *Chem. Phys. Lett.*, 1970, **5**, 609.
- [2] L. Asbrink, O. Edquist, E. Lindholm and L. E. Selin, *Chem. Phys. Lett.*, 1970, **5**, 192.
- [3] A. W. Potts, W. C. Price, D. G. Streets and T. A. Williams, *Faraday Discuss. Chem. Soc.*, 1972, **54**, 168.
- [4] L. Karlsson, L. Mattsson, R. Jadrny, T. Bergmark and K. Siegbahn, *Phys. Scr.*, 1976, **14**, 230.
- [5] L. Mattsson, L. Karlsson, R. Jadrny and K. Siegbahn, *Phys. Scr.*, 1977, **16**, 221.
- [6] P. Baltzer, L. Karlsson, B. Wannberg, G. Öhrwall, D. M. P. Holland, M. A. MacDonald, M. A. Hayes and W. von Niessen, *Chem. Phys.*, 1997, **224**, 95.
- [7] N. O. Lipari, C. B. Duke and L. Pietronero, *J. Chem. Phys.*, 1976, **65**, 1165.

- [8] P. Pulay, G. Fogarasi and J. E. Boggs, *J. Chem. Phys.*, 1981, **74**, 3999.
- [9] K. Raghavachari, R. C. Haddon, T. A. Miller and V. M. Bondybey, *J. Chem. Phys.*, 1983, **79**, 1387.
- [10] H. Köppel, L. S. Cederbaum and W. Domcke, *J. Chem. Phys.*, 1988, **89**, 2023.
- [11] H. Köppel, *Chem. Phys. Lett.*, 1993, **205**, 361.
- [12] M. Döscher and H. Köppel, *Chem. Phys.*, 1997, **225**, 93.
- [13] C. Cossart-Magos and S. Leach, *Chem. Phys.*, 1980, **48**, 349.
- [14] T. A. Miller and V. E. Bondybey, in *Molecular Ions: Spectroscopy, Structure and Chemistry* (eds T. A. Miller and V. E. Bondybey), North Holland, Amsterdam, 1983, p. 201.
- [15] D. Klapstein, *et al*, *Mol. Phys.*, 1984, **51**, 413.
- [16] J. P. Maier, *Kinetics of Ion–Molecule Reactions*, Plenum Press, New York, 1979, p. 437.
- [17] O. Braitbart, E. Castellucci, G. Dujardin and S. Leach, *J. Phys. Chem.*, 1983, **87**, 4799.
- [18] K. Walter, R. Weinkauff, U. Boesl and E. W. Schlag, *Chem. Phys. Lett.*, 1989, **155**, 8.
- [19] R. Lindner, H. Sekiya and K. Müller-Dethlefs, *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 603.
- [20] J. G. Goode, J. Hofstein and P. M. Johnson, *J. Chem. Phys.*, 1997, **107**, 1703.
- [21] J. Eiding, R. Schneider, W. Domcke, H. Köppel and W. von Niessen, *Chem. Phys. Lett.*, 1991, **177**, 345.
- [22] B. E. Applegate and T. A. Miller, *J. Chem. Phys.*, 2002, **117**, 10654.
- [23] M. Döscher, H. Köppel and P. G. Szalay, *J. Chem. Phys.*, 2002, **117**, 2645.
- [24] H. Köppel, M. Döscher, I. Bâldea, H.-D. Meyer and P. G. Szalay, *J. Chem. Phys.*, 2002, **117**, 2657.
- [25] H.-G. Weikert and L. S. Cederbaum, *Chem. Phys. Lett.*, 1995, **237**, 1.
- [26] H. Köppel, W. Domcke and L. S. Cederbaum, *Adv. Chem. Phys.*, 1984, **57**, 59.
- [27] H. Köppel and W. Domcke, in *Encyclopedia in Computational Chemistry* (ed. P. v. R. Schleyer), Wiley, New York, 1998, p. 3166.
- [28] G. Herzberg, *Molecular spectra and molecular structure, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, New York, 1945, Vol. 2.
- [29] L. S. Cederbaum and W. Domcke, *Adv. Chem. Phys.*, 1977, **36**, 205.
- [30] W. von Niessen, J. Schirmer and L. S. Cederbaum, *Comp. Phys. Rep.*, 1984, **1**, 57.
- [31] M. Nooijen and G. Snijders, *Int. J. Quant. Chem.*, 1992, **S26**, 55.
- [32] J. F. Stanton and J. Gauss, *J. Chem. Phys.*, 1994, **101**, 8938.
- [33] J. F. Stanton and J. Gauss, *J. Chem. Phys.*, 1995, **103**, 1064.
- [34] I. B. Bersuker, V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, Heidelberg, 1989.
- [35] C. Lanczos, *J. Res. Nat. Bur. Stand.*, 1950, **45**, 255.
- [36] J. C. Cullum, B. Willoughby, *Lanczos Algorithms for Large Symmetric Eigenvalue Computations*, Birkhäuser, Boston, 1985.
- [37] M. H. Beck, A. Jäckle, G. A. Worth and H.-D. Meyer, *Phys. Rep.*, 2000, **324**, 1.
- [38] G. A. Worth, M. H. Beck, A. Jäckle and H.-D. Meyer, *The Heidelberg MCTDH Package: A Set of Programs for Multi-dimensional Quantum Dynamics*. User's Guide, version 8.2, 2000, (see <http://www.pci.uniheidelberg.de/tc/usr/mctdh/>)
- [39] M. Döscher, PhD Thesis, Universität Heidelberg, 2000.
- [40] R. Lindner, K. Müller-Dethlefs, E. Wedum, K. Haber and E. R. Grant, *Science*, 1996, **271**, 1698.
- [41] E. Haller, L. S. Cederbaum and W. Domcke, *J. Chem. Phys.*, 1980, **64**, 603.
- [42] J. R. Fletcher, M. C. M. O'Brien and S. N. Evangelou, *J. Phys. A*, 1980, **13**, 2035.
- [43] C. A. Mead, *Rev. Mod. Phys.*, 1992, **64**, 51.
- [44] P. M. Johnson, *J. Chem. Phys.*, 2002, **117**, 9991.
- [45] T. Baer, G. D. Willet, D. Smith and J. S. Phillips, *J. Chem. Phys.*, 1979, **70**, 4076.
- [46] H. Kühlewind, A. Kiermeier and H. J. Neusser, *J. Chem. Phys.*, 1986, **85**, 4427.
- [47] U. Manthe and H. Köppel, *J. Chem. Phys.*, 1990, **93**, 1658.
- [48] Special issue on conical intersections, *Chem. Phys.* (eds Y. Haas, M. Klessinger and S. Zilberg), 2000, **259**, pp. 121–327
- [49] M. Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.
- [50] M. Allan, E. Kloster-Jensen and J. P. Maier, *J. Chem. Soc. Faraday Trans. II*, 1977, **73**, 1406.

Symmetry Aspects of Distortivity in π Systems

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Abstract

The distortive effect of π electrons in conjugated systems can be modelled, following Heilbronner, by varying the Hückel bond integrals subject to retention of a constant sum at each (non-pendant) unsaturated atom. In this simplified graph theoretical model, symmetry theorems give the numbers and types of constrained distortion modes leading away from the σ -optimal geometry. For the class of systems without pendant edges, these *Heilbronner* modes correspond to specific eigenvectors of the edge-incidence matrix. They also model directly the most efficient distortive modes as predicted from the eigenvectors of the bond-polarisability matrix, and add specificity to the symmetry rules for non-alternants that are based on the second-order Jahn–Teller effect. An orbital model for induced ring currents in π systems shows that π currents are resilient to σ framework changes, indicating a survival of π delocalisation and mobility, in systems such as pentalene even after distortion has taken place, and under significant bond alternation in (σ) ‘clamped’ benzenes.

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1. INTRODUCTION

It is a truism that many of the most useful concepts in chemistry draw their strength from a certain amount of fuzziness of definition. Aromaticity is perhaps the most celebrated example. Used to predict and rationalise reactivity and properties of cyclic π systems, this concept is associated with a loose cluster of geometric, energetic, magnetic and reactivity-based criteria, and debate still rumbles on about the extent to which these logically distinct criteria can or do give consistent measures of a single, identifiable characteristic [1]. Probably all chemists would

agree that benzene is the archetypal aromatic π system, though, if a much-quoted exchange at the 1970 Jerusalem conference [2] is to be taken seriously, some would also say that it is the only such system.

Benzene has a number of properties that might be taken as the basis of a definition of aromaticity. For one, to revive a term from a paper presented at the same conference, the π system of benzene has the ability to sustain a ring-current circulation—the property of *strobilism* (from *ξνλινα αλογα στροβιλιζομενα*, Greek for a children's merry-go-round, according to Ref. [3]). In recent years attention has focused on this particular magnetic response property as *the* defining characteristic of an aromatic molecule: an aromatic molecule is taken to be one that sustains a diamagnetic (diatropic) ring current [4a,b]. From the points of view of physical detection, through the effect of the ring current on ^1H NMR shifts [5], and of quantum mechanical calculation, either indirectly through chemical shifts at nuclei and at ring centres [6], or directly through visualisation of the induced current density [7a,b], this concentration on induced mobility of the π electrons has the definite advantage of providing a simple yes/no answer for any given system.

Another striking aspect of benzene is its regular hexagonal structure, which raises the question of the connection between geometry, electron delocalisation, ring current and aromaticity. After vigorous debate, it now seems to be generally accepted that the geometric structures of many conjugated π systems result from a compromise between the tendency of a σ framework to produce symmetrical arrangements with equal or near-equal bondlengths, and the opposing tendency of π electrons to favour bond alternation, bond fixation and, typically, broken symmetry. The history, defence, computational exploration and experimental verification of this concept is detailed in recent comprehensive review articles by Shaik and co-workers [8a,b].

Simple considerations suggest that all π systems are inherently distortive, whether or not this tendency is realised in observable geometric changes. Again the paradigm is benzene, where π stabilisation would be greater in a D_{3h} geometry that resembles a single Kekulé structure with three fully realized double bonds, but distortion in this direction is prevented by the stiffness of the σ framework which prefers the regular equilateral hexagon with longer bonds and smaller β integrals [9]. The opposite case is exemplified by pentalene, where the π -favoured C_{2h} localised Kekulé structure is lower in total energy than the σ -favoured D_{2h} delocalised transition-state [10], and the structure distorts. Various criteria for predicting whether it is the σ or the π electrons that win the energy–geometry competition in any particular case have been developed [11,12].

Once the possibility of distortion is raised, an immediate next question is the *direction* of this distortion, considered as a vibrational mode of the undistorted system. A simple model for the directional aspect of π -distortivity was proposed in a tutorial context for benzene itself by Heilbronner [9]. It has an easy generalisation, which turns out to predict the most likely pattern of distortion of many systems by pencil-and-paper construction of the *Heilbronner vectors* or *Heilbronner modes* [13]. The present paper reviews some symmetry- and graph-theoretical aspects

of this model, their connection with more formal treatments and with the pseudo-Jahn–Teller effect, and in view of recent calculations of ring-current maps [14], discusses the connection between π -distortivity and π ring currents.

2. THE HEILBRONNER MODEL

In his classic paper in the *Journal of Chemical Education* entitled ‘Why do some molecules have symmetry different from that expected?’ [9], Heilbronner pointed out that the notion of π -distortivity is already implicit in the Hückel treatment of benzene.

The standard treatment employs equal Coulomb parameters α for all six carbon atoms, and equal resonance parameters β for all six CC bonds. In effect, α is the origin and β the unit in a scaled representation of the Hückel hamiltonian matrix as

$$\mathbf{H} = \alpha \mathbf{1} + \beta \mathbf{A} \quad (1)$$

where, for a conjugated system, $\mathbf{1}$ is the $n(v) \times n(v)$ unit matrix and $\mathbf{A}$ is the adjacency matrix ($A_{ij} = 1$ for vertices i, j on σ -bonded neighbouring atoms, and $A_{ij} = 0$ otherwise, $i, j = 1, \dots, n(v)$). The unsaturated carbon atoms are the $n(v)$ vertices and the σ -bond CC links are the $n(e)$ edges of the molecular graph of the π system. The weights of p_π atomic orbitals in the π molecular orbitals ψ_i are defined by eigenvectors of $\mathbf{A}$. The π orbital energies ϵ_i are defined by the eigenvalues of $\mathbf{A}$, $\{\lambda_i^A\}$, $i = 1, \dots, n(v)$, with $\epsilon_i = \alpha + \beta \lambda_i^A$.

In Heilbronner’s model, the π -Hamiltonian for benzene is modified by replacing the constant entries of the scaled adjacency matrix with entries $(1 \pm \delta)\beta$ which alternate around the edges of the ring (Fig. 1). The sum of integrals around each vertex thus remains constant at 2β . The modified eigenvalues $\{\lambda_i^A\}$ are

$$\lambda_1^A = +2, \quad \lambda_2^A = \lambda_3^A = +\sqrt{1 + 3\delta^2}, \quad \lambda_4^A = \lambda_5^A = -\sqrt{1 + 3\delta^2}, \quad \lambda_6^A = -2 \quad (2)$$

giving a total, distortion-dependent, energy for the π configuration $\psi_1^2 \psi_2^2 \psi_3^2$ of

$$E_\pi = 6\alpha + 4\beta(1 + \sqrt{1 + 3\delta^2}) \quad (3)$$

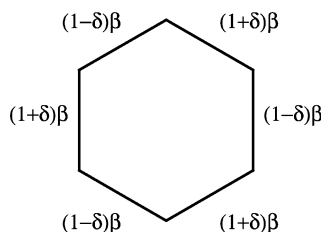


Fig. 1. Heilbronner model for the distortive mode of benzene.

In this simplified model, the π stabilisation energy is at its lowest in the regular hexagonal structure is at a minimum, with curvature $(\partial^2 E / \partial [\delta\beta]^2) = 12\beta^{-1}$. Hence the prediction is that distortion along the b_{2u} Kekulé mode, in which three disjoint bonds strengthen at the expense of the other three, will produce a quadratic stabilisation of the π system.

As the energy depends on δ , the implication is that it will also depend on bond length, and so the prediction is that, if π electronic effects are given free rein, the equilibrium structure of the molecular framework will be one in which there has been distortion towards a short–long bond-alternated Kekulé structure. That benzene does not in fact distort in this way is then explained by the relative strengths and force constants of σ and π bonds – the σ framework of benzene is simply too stiff to be distorted by the relatively weak π forces [9,12].

The precise form of the model has clearly a limited range in that the constancy of the sum of bond integrals around a given vertex will not persist indefinitely: the limit $\delta \rightarrow 1$ would give bond integrals 0β and 2β , which probably exaggerates the increase in magnitude of the integrals in the localized form of the molecule, but does give a basis for prediction of the initial direction of any distortive behaviour. The generalisation to other π systems is [13] that the d CC bonds around a given d -valent vertex of the carbon framework graph should be allowed to change by $\delta_i\beta$ ($i = 1, \dots, d$) subject to the constraint that $\sum_i \delta_i = 0$.

In his tutorial paper [9], Heilbronner considers two examples: benzene, in which $d = 2$ for every vertex, and the allyl radical, in which $d = 1$ for end vertices, and $d = 2$ for the central vertex. In the latter case, he allows the two bonds to change by $\pm\delta$, preserving the sum at the central vertex but not at the terminal vertices. For systems that include some vertices of degree 1, the most natural generalisation seems to be that the constant-sum constraint should be applied only at vertices of degree d greater than 1. We can define any such set of changes to the β integrals, with the implied changes in the bond lengths, as a *Heilbronner mode*, and term it more precisely a *Heilbronner distortion* if these changes would lead to loss of symmetry.

An obvious first question for a given carbon skeleton is: how many distinct Heilbronner modes and distortions are possible? Given the form of the model, where the freedoms involve the values of β on the edges of the graph of the carbon framework, and the constraints are imposed at the (multivalent) vertices, it is reasonable to expect $n(\delta)$, the number of independent Heilbronner modes, to depend on a difference function of edges and vertices. The next section deals with this connection.

3. COUNTING HEILBRONNER MODES

Given a particular graph representing a π system, construction of sets of distortions that obey the Heilbronner condition is not difficult. A solution can be propagated from an initial vertex, bringing in new parameters for each edge as needed, subject

to the constant-sum constraint, and making a final sweep to remove any redundancies introduced by cycles in the graph. The procedure is reminiscent of the well known construction for non-bonding eigenvectors of a Hückel framework [15], and it can be used in any individual case to obtain the number of independent Heilbronner distortions. The number of free parameters left at the end of the procedure is equal to $n(\delta)$.

An example of the construction is given in Fig. 2 for the $[n]$ -polyacene. Parameters $a_1, \dots$ are used to describe the departure of a bond β integral from its original value: $\beta \rightarrow (1 + a_i)\beta$. Beginning at one end of the chain, a parameter a_1 is attached to the starting ring. Propagation along the top half of the perimeter leads to introduction of one new parameter for each hexagon encountered, $a_2, a_3, \dots$ until the final ring is reached, taking parameter $\pm a_{n-1}$ on the five of its edges that lie in the boundary. Consideration of the sum rule at the vertices on internal edges, starting from the ends of the molecule and working into the centre, then shows that the assignment of parameters to the lower perimeter follows that of the top as an exact mirror image, requiring no new independent parameters.

In this case there are exactly as many independent Heilbronner vectors as there are rings in the molecule, although as Fig. 2 also shows, the number of parameters can be less than the number of rings, as in pentacene, or more, as in butadiene.

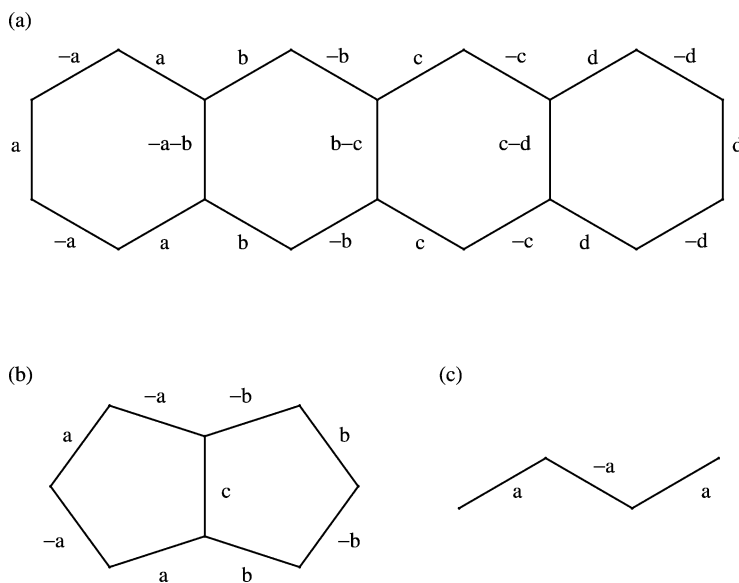


Fig. 2. Construction of Heilbronner modes: (a) in [4]polyacene, attachment of parameters to the perimeter clockwise from a to d determines all remaining parameters; (b) in pentacene, propagation outwards from one vertex of the central bond leads to a mode with $a = -b$ and $c = 0$; (c) in butadiene, specification of a single parameter on any one edge of the graph determines the whole mode.

These three examples cover all the possible cases. The relation between $n(\delta)$, $n(e)$ and $n(v)$ depends on two factors: the presence/absence of pendant vertices, and the presence/absence of odd cycles in the graph. The set of independent parameters is determined by solution of a set of linear equations, one for each vertex at which the sum constraint is to be applied, and with every edge appearing in two such equations. The distinct cases are as follows [13]. If the graph has no pendant vertices, then *either*

- (a) the graph contains at least one odd cycle, and each edge introduces a freedom and each vertex contributes an independent constraint, i.e.,

$$n(\delta) = n(e) - n(v) \quad (4)$$

or

- (b) all cycles in the graph are even, and

$$n(\delta) = n(e) - n(v) + 1 \quad (5)$$

where the term $+1$ on the LHS arises from the fact that in such a graph it is possible to find (exactly) one combination of vertex constraints such that each edge parameter appears with a weight of zero, and hence to find one vertex constraint that is no constraint at all (see below).

If the graph has pendant vertices, then

- (c) the number of constraints is now equal to the number of non-pendant vertices and the number of Heilbronner modes is

$$n(\delta) = n(e) - n(v) + n(v_1) \quad (6)$$

where $n(v_1)$ is the number of pendant vertices. This formula is independent of the parity of any cycles that may be present, as for $n(v_1) \neq 0$ it is no longer possible, even for bipartite graphs, to construct the special combination of vertex constraints in which every edge has zero weight: a pendant *edge* is constrained only at one end, so that its parameter appears in only one linear equation.

Thus, case (a) tells us, for example, that odd monocycles have no Heilbronner modes, odd–odd bicycles have 1 mode, and all-odd trivalent polyhedra on $n(v)$ vertices, such as the tetrahedon and the dodecahedron, have $3n(v)/2 - n(v) = n(v)/2$ modes, as do the fullerenes.

Case (b) tells us that even monocycles have one Heilbronner mode and indeed, since $n(e) - n(v) + 1$ is the number of rings in a polycyclic molecule, that any all-even polycyclic has as many Heilbronner modes as it has rings. Any all-even trivalent polyhedron such as the cube or $2n$ -gonal prism has as many Heilbronner modes as it has rings in its Schlegel diagram, i.e., one fewer than the number of faces of the polyhedron itself.

Case (c) tells us that all unbranched polyene chains have one Heilbronner mode, and more generally, all trees (acyclic connected graphs) have $n(v_1) - 1$ Heilbronner

modes, since $n(e) = n(v) + 1$ for any tree. (The unbranched tree is the *path*, with $n(v_1) = 2$ terminal vertices.)

The three relations connect the raw counts of structural components with the numbers of Heilbronner modes, without considering the equivalences introduced by symmetry, which reduce the number of independent distortions that need to be considered. Section 4 introduces this aspect.

4. SYMMETRY AND HEILBRONNER MODES

Scalar counting relations for sets of structural components can be seen as expressions for characters under the identity operation of more general relations between representations of those sets. For example, the Euler relation in topology can be generalised to connect not only the *numbers* of *edges*, vertices and faces of a polyhedron, but also various symmetries associated with the structural features. The well-known Euler theorem

$$n(v) + n(f) = n(e) + 2 \quad (7)$$

for a spherical polyhedron with $n(v)$ vertices, $n(e)$ edges and $n(f)$ faces, is converted in this way to an equation in reducible representations [16]:

$$\Gamma_{\sigma}(v) + \Gamma_{\sigma}(f) \times \Gamma_{\epsilon} = \Gamma_{\parallel}(e) + \Gamma_0 + \Gamma_{\epsilon} \quad (8)$$

where the subscripts σ and $\parallel$ denote a permutation representation and a representation of vectors along edges, respectively. Γ_0 is the totally symmetric representation, and Γ_{ϵ} is the determinantally antisymmetric representation in the point group of the polyhedron.

Similarly, in mechanics, the extended Maxwell condition for rigidity of bar and joint assemblies can be used to generate a relation between the permutation representations of the bars and joints and those of the states of self-stress and mechanisms of the assembled framework [17a,b].

In the present case, the extension of the scalar counting rules for $n(\delta)$ to symmetry theorems is straightforwardly achieved by replacing $n(\delta)$, $n(v)$, $n(e)$ $n(v_1)$ by the permutation representations $\Gamma_{\sigma}(\delta)$, $\Gamma_{\sigma}(v)$, $\Gamma_{\sigma}(e)$ and $\Gamma_{\sigma}(v_1)$ [13]. A permutation representation $\Gamma_{\sigma}(x)$, of a set of objects x has character $\chi(R)$ under operation (R) of the symmetry group of the undistorted framework, where $\chi(R)$ is equal to the number of objects *unshifted* under operation R . The subscript σ is often dropped if there is no danger of confusion. With these replacements, equation (4) becomes

$$\Gamma(\delta) = \Gamma(e) - \Gamma(v) \quad (9)$$

The translation of equation (5) into symmetry-extended form requires more discussion. A bipartite graph is one in which the vertices can be partitioned into two sets, starred and unstarred, say, such that every starred vertex has only unstarred neighbours and vice versa. The origin of the $+1$ in the scalar equation (5) is that it is possible to define a vector of coefficients on the vertices of a bipartite graph such that

each starred vertex carries coefficient $+1$ and each unstarred vertex -1 ; in the absence of pendant vertices, the two sets are of equal size, and the bipartite property then ensures that every edge of the graph links a coefficient $+1$ to a coefficient -1 . In this case of a bipartite graph without pendant vertices, if the coefficients in the vector are used to define a weighted combination of vertex sum constraints, each edge parameter will appear with equal and opposite signs and the weighted 'constraint' condition will be identically satisfied by any set of edge parameters. As noted earlier, this restores one edge freedom to the system.

The symmetry corresponding to the null constraint on the Heilbronner modes is the representation of the vector of ± 1 coefficients. This is a one-dimensional (1D) irreducible representation, $\Gamma_\star$, which has character $+1$ under those operations that permute vertices only within their starred and unstarred sets, and character -1 under all the other operations, those that permute starred with unstarred vertices. The symmetry $\Gamma_\star$ is that of the inactive vertex constraint. With it, the scalar relation $n(\delta) = n(e) - n(v) + 1$ becomes

$$\Gamma(\delta) = \Gamma(e) - \Gamma(v) + \Gamma_\star \quad (10)$$

For case (c), the scalar relation (6) for graphs with pendant vertices becomes

$$\Gamma(\delta) = \Gamma(e) - \Gamma(v) + \Gamma(v_1) \quad (11)$$

Equations (4)–(6) are, respectively, the characters $\chi(E)$ of equations (9)–(11) under the identity operation E . In the trivial group C_1 , the scalar and representation forms of the equations are the same, but whenever an undistorted molecular framework has some non-trivial symmetry, the symmetry-extended forms provide potentially useful extra information in that they reduce the set of Heilbronner modes to the minimum set of distinct distortions, and give their symmetry characteristics, which in many cases serve to define completely the distortions allowed by the model.

The significance of the symmetry treatment is that it shows explicitly which of the Heilbronner modes are inherently distortive. Any totally symmetric Heilbronner mode corresponds to readjustment of β parameters and hence of bondlengths, but without loss of symmetry. Since the point of departure of the model is that the molecule is already in its σ -optimal geometry, such modes can be ignored, and only the non-totally symmetric distorting modes retained.

The number of totally symmetric Heilbronner modes follows from counting of *orbits*. An orbit is a set of equivalent (structureless) objects, which are permuted amongst themselves by symmetry operations of the group: every operation of the group either leaves a given member of the orbit in place and unchanged, or moves it to another location. Thus the six edges of benzene, the two face centres of pentalene and the pair of terminal vertices of an $[n]$ -polyene chain, all form orbits. Each orbit has an associated permutation representation that contains the totally symmetric representation Γ_0 exactly once.

Totally symmetric Heilbronner modes are therefore counted in cases (a)–(c) by replacing the total numbers of components $n(e)$, $n(v)$, $n(v_1)$ by the respective numbers of orbits. The $+1$ entry in equation (5) is retained when $\Gamma_\star = \Gamma_0$

(i.e., when the starred and unstarred sets are each composed of whole orbits), and deleted otherwise. As an example, D_{2h} naphthalene has four orbits of edges (sets of 4, 4, 2, 1), and three orbits of vertices (4, 4, 2). As its starred and unstarred vertex sets contain partial orbits, $\Gamma_{\star} \neq \Gamma_0$ is a dipole symmetry for this molecular graph. Hence, naphthalene has $4 - 3 = 1$ totally symmetric Heilbronner modes, and one distortive mode consisting of alternating enhancement and depletion of β around the perimeter, with no contribution from the central bond.

Heilbronner mode symmetries have been tabulated for various series of π systems [13]. Some specific results are: in unbranched polyenes, the unique Heilbronner mode is either totally symmetric [(2n)-polyene] or has the symmetry of a dipole moment along the chain [(2n + 1)-polyene]; in [2n]-linear acenes the Heilbronner modes span $nA_g + nB_{1u}$ of D_{2h} , and in [2n + 1]-linear acenes have an extra B_{1u} component; the Heilbronner modes of the tetrahedron, cube and dodecahedron span $E(T_d)$, $E_g + T_{2u}(O_h)$, and $H_g + H_u(I_h)$, respectively, reducing the sets of modes to be considered from 2, 5 and 10 to just 1, 2, and 2 independent distortive modes which can be constructed easily ‘by hand’.

Symmetry also gives insight into how the scalar counts $n(\delta)$ are achieved. In benzene, for example, the edges and vertices are in different orbits of size 6, distinguished by their behaviour under C_2' and C_2'' operations. Standard spherical-harmonic analysis shows that both edge and vertex permutation representations contain s , p and d components corresponding to functions with components of angular momentum along the principal axis, Λ , equal to 0, ± 1 , ± 2 . The remaining sixth combination differs between the two permutation representations and is one of the orthogonal halves of the $|\Lambda| = 3$ pair of f -functions, intersected by three nodal lines in the molecular plane. Of this pair, the vertex combination is cancelled by $\Gamma_{\star}$, leaving as the only contribution to $\Gamma(\delta)$ the fully alternating edge combination. This, of course, is the Kekulé mode derived by the pencil-and-paper method.

The power of the spherical-harmonic argument is that it shows that the same cancellation process will occur for all even monocycles, always leaving $\Gamma(\delta)$ as the maximally sign-alternated combination of edges with the highest $|\Lambda|$ quantum number. Likewise for the odd monocycle, since edge and vertex orbits coincide exactly in the D_{2n+1h} groups of these systems, where all C_2' axes form a single class, Heilbronner modes of every conceivable symmetry must vanish identically, and the result $n(\delta) = 0$ is seen to have roots deeper than the simple equality of numbers of edges and vertices.

5. HEILBRONNER MODES IN POLYHEDRA

Symmetry also adds useful detail to the picture for polyhedral 3D π systems. A trivalent polyhedron obeys

$$\Gamma_{\sigma}(v) \times \Gamma_T = \Gamma_{\sigma}(e) + \Gamma_{||}(e) \quad (12)$$

where Γ_T is the representation of the three translations, as is easily verified by noting that if a trivalent polyhedron is marked with a pair of points at one-third and two-thirds of the way along each edge, the markings can be grouped in two ways: every edge carries a distinct pair of marks, by construction, and every vertex is surrounded by a distinct triangle of marks. Considered as edge pairings, the in- and out-of-phase combinations transform as a scalar on and a vector along the edge, but considered as vertex triples, the three independent combinations at a vertex transform as a radial vector (σ) and a pair of tangential vectors (π), matching the representation of a set of local xyz -axes on all vertices, hence

$$\Gamma_\sigma(v) + \Gamma_\pi(v) = \Gamma_\sigma(v) \times \Gamma_T = \Gamma_\sigma(e) + \Gamma_\parallel(e) \quad (13)$$

The edge-vertex difference function of equations (9) and (10) then becomes

$$\Gamma_\sigma(e) - \Gamma_\sigma(v) = \Gamma_\pi(v) - \Gamma_\parallel(e) \quad (14)$$

and so the Heilbronner symmetry $\Gamma(\delta)$ can be seen either as a difference of scalar functions on edges and vertices or of vector functions tangential to vertices and parallel to edges. Thus for trivalent polyhedra, equations (9) and (10) may be re-expressed as

$$\Gamma(\delta) = \Gamma_\pi(v) - \Gamma_\sigma(v) - \Gamma_\parallel(e) + (\Gamma_\star). \quad (15)$$

The extended Euler theorem can also be used to give a version of equation (15) in which vertex and face, but not edge, terms appear.

A special subclass of trivalent polyhedra, of special interest in the theory of the electronic structure of the fullerenes, is that of the leapfrogs [18a,b]. A leapfrog polyhedron is obtained from a general trivalent polyhedron by a transformation process which can be described combinatorially as first capping all faces and then taking the dual of the result, or as an operation on the graph in which every edge of the parent is first crossed by a new tangential edge, the ends of the new edges are joined to form faces inset in those of the parent, and then all vertices and edges of the parent are deleted. The leapfrog graph obtained from a trivalent polyhedron is itself the skeleton of a trivalent polyhedron, containing all the original faces of the parent in place but rotated, and with a new hexagonal face centred on every original trivalent vertex.

Leapfrogging a fullerene polyhedron produces another fullerene, of the same symmetry but with three times as many vertices and with a properly closed π shell (in this case, with a bonding HOMO and antibonding LUMO). The leapfrog construction gives rise to nearly all of the fullerenes that have this π -ideal electronic configuration. The set of crossing edges constitutes one-third of the edges of the enlarged fullerene. A Fries-type Kekulé structure achieving the maximum possible number of simultaneous benzenoid hexagons can be formed by treating the crossing edges as formally double and all others as formally single. In consequence, the symmetry of the occupied orbitals in a leapfrog fullerene is exactly that of the edges of the parent, $\Gamma_\sigma(e, P)$.

Consideration of the description of leapfrogging in terms of edge crossings suggests formulas for the permutational representations of the leapfrog polyhedron Lf in terms of structural representations of the parent, P . From

$$\Gamma_{\sigma}(e, Lf) = \Gamma_{\sigma}(e, P) + \Gamma_{\sigma}(v, P) \times \Gamma_T = 2\Gamma_{\sigma}(e, P) + \Gamma_{\parallel}(e, P) \quad (16)$$

and

$$\Gamma_{\sigma}(v, L) = \Gamma_{\sigma}(e, P) + \Gamma_{\perp}(e, P) \quad (17)$$

the symmetry of the Heilbronner modes of the leapfrog can be expressed in terms of parent properties, involving the difference in symmetry of tangential vectors along and across edges:

$$\Gamma(\delta, Lf) = \Gamma_{\sigma}(e, P) + \Gamma_{\parallel}(e, P) - \Gamma_{\perp}(e) + (\Gamma_{\star}) \quad (18)$$

where $\Gamma_{\star}$ is to be included only for bipartite polyhedra. (If P is a bipartite spherical polyhedron, then so is Lf .)

In general, $\Gamma_{\perp}(e)$ and $\Gamma_{\parallel}(e, P)$ are not equal, being related by a global twist

$$\Gamma_{\parallel}(e, P) = \Gamma_{\perp}(e) \times \Gamma_{\epsilon} \quad (19)$$

but the two are equal in some circumstances, as when P is chiral (implying $\Gamma_{\epsilon} = \Gamma_0$) or when all faces of P are of odd size, as in the tetrahedron or the dodecahedron.

Thus, for the icosahedral C_{60} fullerene, which is the leapfrog of the dodecahedron,

$$\Gamma(\delta, C_{60}) = \Gamma_{\sigma}(e, C_{20}) \quad (20)$$

and the Heilbronner modes span exactly the same 30-orbit of the I_h group as the edges of the dodecahedron, the formal double bonds of the dominant Kekulé structure of C_{60} , and the set of 30 occupied π orbitals of this, the smallest leapfrog fullerene.

The symmetry of the Heilbronner modes of C_{60} thus includes just one totally symmetric mode, already implicitly taken into account by the difference in length of the 60 long (pentagon–hexagon) and 30 short (hexagon–hexagon) edges of the σ framework. The potentially distortive Heilbronner modes of C_{60} span

$$\Gamma(\delta, C_{60}) = G_g + 2H_g + T_{1u} + T_{2u} + G_u + H_u \quad (21)$$

6. HEILBRONNER MODES AND LINE GRAPHS

A Heilbronner mode is defined by a set of scalar quantities attached to the edges of a graph, which suggests a possible connection with the eigenvectors of the edge-incidence matrix, i.e., the adjacency matrix of the line graph. The line graph $L(G)$ has one vertex for every edge of G , and two vertices of the line graph are adjacent if and only if the corresponding edges of G have a vertex of G in common.

We restrict attention to graphs G that have no pendant edges. For concreteness, take a graph G corresponding to a trivalent polyhedron P , where each edge has four

neighbouring edges. Let coefficients be attached to a central edge and its neighbours as in Fig. 3.

Now, if the local pattern of coefficients is part of a Heilbronner mode, we have

$$a_0 + a_1 + a_2 = 0 \quad (22)$$

$$a_0 + a_3 + a_4 = 0 \quad (23)$$

and similar equations centred in turn on every edge of P . On the other hand, if the local pattern of coefficients forms part of an eigenvector of the adjacency matrix of the line graph derived from G , then for each edge considered as a centre

$$-\lambda_i^L a_0 + a_1 + a_2 + a_3 + a_4 = 0 \quad (24)$$

for some eigenvalue λ_i^L . Comparison of equations (22) and (23) with equation (24) shows that any Heilbronner mode of a trivalent polyhedron must also be an eigenvector of the adjacency matrix of $L(G)$, with $\lambda_i^L = -2$.

Furthermore, any Heilbronner mode of any graph without pendant edges corresponds to such an eigenvector, as can be verified by deleting one but not both neighbouring edges at each vertex of the central edge, equivalent to setting some of the a_i to zero.

The reverse implication also holds. Suppose there is an eigenvector with $\lambda^L = -2$ that is not a Heilbronner mode. This would mean that a set $a_1, \dots, a_4$ satisfied equation (24) without satisfying either of equations (22) or (23). The central edge of that set must then have an excess at one vertex, $a_0 + a_1 + a_2 = x > 0$, say, balanced by a deficiency at the other, $a_0 + a_3 + a_4 = -x$. Condition (24) demands that the excess/deficiency propagate in a consistent pattern of $\pm$ signs on vertices such that every edge has a positive and a negative end with the same absolute value $|x|$. This is impossible if the graph is non-bipartite. Even if the graph is bipartite, it leads to a contradiction for $x \neq 0$ once edge parameters are assigned: on a walk along edges away from a given central edges, the assigned parameters have contributions of x or $-x$ multiplied by ever larger integers as the number of steps increases; since every

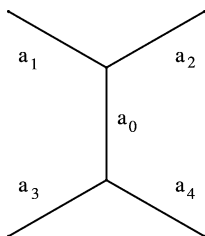


Fig. 3. Local pattern of coefficients on the edges of a trivalent graph.

edge occurs in a cycle, this leads sooner or later to equality of x with a multiple of x and hence $x = 0$ (see Fig. 4 for an example).

In the case of regular graphs (i.e., those where all vertices of G are of equal degree), the one-to-one correspondence between Heilbronner modes and edge-adjacency eigenvectors can also be easily proved from a mathematical result for the spectra of their line graphs. The eigenvalues of an adjacency matrix are the roots of the characteristic polynomial of the graph. The characteristic polynomial of the line graph $L(G)$ is related to that of G by [19]

$$\mathbf{P}_{L(G)}(\lambda) = (\lambda + 2)^{n(e)-n(v)} \mathbf{P}_G(\lambda - d + 2) \quad (25)$$

where d is the degree of G (assumed regular), and $n(e)$ and $n(v)$ are the numbers of edges and vertices of G , as before. For $d = 3$,

$$\mathbf{P}_{L(G)}(\lambda) = (\lambda + 2)^{n(v)/2} \mathbf{P}_G(\lambda - 1) \quad (26)$$

and so the eigenvalue spectrum of $L(G)$ contains a shifted copy of the spectrum of G , plus $n(e) - n(v) = n(v)/2$ roots -2 . Every root -3 of $\mathbf{P}_G$ generates an additional -2 root of $\mathbf{P}_{L(G)}$. Thus we have $n(e) - n(v)$ eigenvalues -2 for non-bipartite G and $n(e) - n(v) + 1$ for bipartite G , as a connected trivalent bipartite graph has exactly one adjacency eigenvalue $\lambda^A = -3$. As these are exactly the values of $n(\delta)$ for the two cases (a) and (b), the one-to-one nature of the correspondence between Heilbronner modes and $\lambda^L = -2$ eigenvectors is demonstrated.

Monocycles offer an easy example of this match; a monocycle G is its own line graph and has $d = 2$; an even monocycle has one eigenvalue $\lambda^A = \lambda^L = -2$ and $n(\delta) = 1$; an odd monocycle has no -2 eigenvalue, and indeed $n(\delta) = 0$.

The link with line graphs could be used to generate Heilbronner modes (inefficiently) by diagonalisation of the adjacency matrix of the line graph, but more interestingly, it gives symmetry information about the eigenspaces of line graphs themselves. The structure of the spectrum of the line graphs of fullerenes and other trivalent polyhedra has already been noted in passing in the study of ‘decorated’ fullerenes [20], where various transformations of the polyhedra lead to spectra that

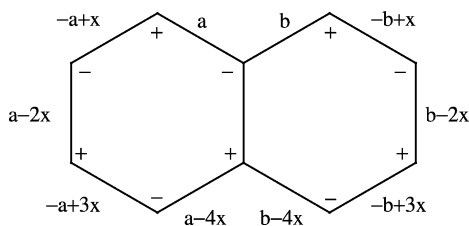


Fig. 4. Demonstration that a pattern of edge parameters obeying $\lambda^L = -2$ is also a Heilbronner mode. The signs indicate the presumed excess/defect $\pm x$ in each vertex sum. Propagation clockwise from b and anticlockwise from a leads to a contradiction on the central edge unless $-a - b - x = -a - b + 8x$, $x = 0$.

consist of heavily degenerate special eigenvalues plus one or more distorted copies of the spectrum of the original graph. The copies arise where the eigenvalues of the decorated structure are roots of polynomial equations whose coefficients are functions of the original eigenvalues λ^A .

In the case of the line graph of a fullerene C_n , the spectrum consists of the entire adjacency spectrum of the fullerene itself (shifted by a constant),

$$\lambda_i^L = \lambda_i^A + 1, \quad i = 1, \dots, n \quad (27)$$

with $\lambda_n^L > -2$, together with an $n/2$ -fold degenerate eigenvalue

$$\lambda_i^L = -2 \quad i = n + 1, \dots, 3n/2. \quad (28)$$

The eigenvectors of $L(G)$ span $\Gamma(e, G)$, as the basis is a set of scalar quantities on the edges of the graph G , and the correspondence with Heilbronner modes then shows that the eigenvectors of $L(C_n)$ span $\Gamma(v)$ for $i = 1, \dots, n$ and $\Gamma(\delta) = \Gamma(e) - \Gamma(v)$ for $i = n + 1, \dots, 3n/2$. Given an eigenvector of the fullerene graph, with coefficients c_i on vertices, an eigenvector of $L(G)$ in the $\Gamma(v)$ subspace follows by assigning to each edge the sum of the coefficients on its end vertices; given an eigenvector on $L(G)$ in this space, the process can be reversed, using the implied eigenvalue, to find an eigenvector of G .

7. WHEN DOES DISTORTION OCCUR?

Interesting though the Heilbronner modes may be as graph theoretical objects, their chemical interest lies in their utility or otherwise in predicting distortion of a π framework. A formal theory of the distortive tendencies of π systems was proposed in an early paper by Binsch *et al.* [12] and gives a point of reference for the simpler model.

The bond-polarisability matrix is a second-order perturbation property whose elements $\pi_{ij,kl}$ define the derivative of the π bond order of ij with respect to the β integral of bond kl . Bond order is defined from the product of the orbital coefficients for the two ends of the bond, summed over all occupied spin orbitals, and elements $\pi_{ij,kl}$ are functions of the energies and coefficients of occupied and unoccupied orbitals, and hence follow directly from the adjacency matrix. With additional approximations, which are more severe for non-bipartite systems, the eigenvectors that result from diagonalisation of the $n(e) \times n(e)$ bond-polarisability matrix correspond to the principal directions of distortion by which the π system can lower its energy. The eigenvectors of this matrix span the full permutation representation of the edges, $\Gamma(e)$; its eigenvalues give the curvature of the π energy with respect to distortion of β integrals along the eigenvector and hence can be used to predict whether distortion will actually occur. Estimation of the variation of bond length with β , and typical force constants, leads to a rule of thumb that a π system will distort if the bond-polarisability matrix has an eigenvalue larger than $\sim 1.7\beta^{-1}$ [12].

The classic case for application of the rule is pentalene. The 9×9 bond-polarisability matrix of this system has one large eigenvalue ($2.357\beta^{-1}$), corresponding to a b_{2g} vector that leads away from the maximum D_{2h} symmetry of the graph to the twisted C_{2h} structure that is found in full *ab initio* optimisations. This is clearly a success for the bond-polarisability model. However, application of the simple Heilbronner model gives directly, without calculation, a single mode of the correct symmetry, almost indistinguishable from the eigenvector of the bond-polarisability matrix [10]; the large second derivative of E_π is easily confirmed by a single-point energy calculation.

More generally, the Heilbronner vectors have a strong tendency to pick out the most distortive modes of the π system [13]. As noted earlier, the symmetry rule (9) gives the Heilbronner modes for dodecahedral C_{20}^{2+} as the pair of 5-fold degenerate sets $H_g + H_u$; of these H_u shadows exactly the most distortive bond-polarisability eigenvector [13]. Symmetry gives an immediate pictorial explanation, showing the cylindrically symmetric component of the distortion mode as an alternating expansion and contraction of bonds along the equator of the dodecahedron. Likewise for neutral C_{60} , the Heilbronner modes that were noted earlier to span the permutation representation of the formal double bonds of the fully symmetric Kekulé structure, give 7 distinct E_π profiles, all clustering around the most distortive of the eigenvectors of the 90×90 bond-polarisability matrix [13]. In neither fullerene is the distortion threshold reached, but the model gives a clear indication of the modes that are closest to achieving distortion. Distortion has been predicted for some fullerenes [21] and in scanning for the very large isomer sets for further possibilities, the advantages of the simple model, either by itself or as a method of rationalising bond-polarisability results, are evident.

An alternative approach to the prediction of distortive behaviour in closed-shell systems uses the well-established language of the second-order Jahn–Teller effect. Nakajima *et al.* [11] derived a rule of thumb for the type of symmetry loss to be expected in non-bipartite polycyclic systems: the irreducible representation of the symmetry breaking mode should be one that is present in the product of the HOMO and LUMO representations in the higher group. Prediction of whether, by how much, and with what detailed geometric changes the molecule actually distorts along a pathway of the favoured symmetry then requires an explicit calculation. Within the limits of the information that it can provide, the approach is generally successful for the non-bipartite (non-alternant) molecules for which it was designed [11]. It has nothing to say about possible distortions of bipartite (alternant) systems, where the HOMO–LUMO product symmetry contains $\Gamma_\star$, which in many cases is not a possible Heilbronner-mode symmetry [13]. The rule is also less specific for non-alternants of high symmetry, where degeneracies may imply that the HOMO–LUMO product spans several symmetries, with no guide to which will be the symmetry of the softest mode.

The crucial advantage of the Heilbronner-mode approach is that both symmetry and detailed form of potential distortions are predicted, without requiring knowledge of the electronic structure. Its success in picking out the most distortive

modes from amongst the eigenvectors of the bond-polarisability matrix stems from its recognition of the oscillatory nature of the response of conjugated systems to perturbation: modification of one bond integral tends to produce alternating strengthening and weakening of bonds along chains away from the perturbed site. The bond-polarisability matrix elements reflect this trend [12], and Heilbronner's intuitive constraint is therefore an ideal device for concentrating attention on the eigenvectors of maximum eigenvalue.

8. DISTORTION AND AROMATICITY

The picture of a π system that emerges from the work of Heilbronner, Shaik and others is one where delocalisation is a consequence rather than a cause of the regular geometry in systems such as benzene. On this view, an important characteristic of π electrons is the tolerance of π bonding to geometric constraints. Recent progress in calculation and interpretation of the magnetic properties of π systems sheds further light on this aspect in that it shows the geometric resilience of characteristic ring currents.

Ring currents are inferred in experiment from ^1H NMR chemical shifts at sites attached to the carbon skeleton [5], and by analogy, are often inferred in calculation from calculated ring-centre shifts [6]. However, it is now possible to calculate the pattern of current density induced in a molecule by an external magnetic field directly, and to assign ring-current aromaticity on the basis of the current-density map itself. A key advance in *ab initio* methods was the proposal [22a–d] to use a distributed-gauge method for computation of current density in which the origin of vector potential is a function of the point at which the current density is to be calculated. In the simplest version, current density at each point is calculated with the point itself taken as the origin of vector potential. This *ipsocentric* [7a,b] choice yields maps of excellent quality, even with basis sets of only moderate size, and the maps can be used routinely to discuss the sense, intensity and physical location of ring currents.

Orbital contributions to the perturbed wavefunction are sum-over-states expressions with several special features: (i) each term is a transition integral divided by an orbital energy difference; (ii) the integrals define virtual excitations from occupied to unoccupied molecular orbitals – there is no remixing of occupied orbitals; (iii) the terms leading to diamagnetic (paramagnetic) circulations in planar molecules in the presence of a perpendicular magnetic field obey *in-plane translational* (*rotational*) selection rules. As has been discussed extensively elsewhere, these features lead to an interpretation of the current map as governed, in delocalised systems, by transitions from a few occupied frontier orbitals. The sense of a current can often be deduced from the symmetry characteristics of the HOMO, LUMO and nearby orbitals, and even simple Hückel calculations may be sufficient to give these symmetries. Orbital contributions defined in this way also have a unique physical status, in allowing first-order prediction of the changes in

maps caused by electron gain or loss, or chemically modification of substituents on the ring, in terms of blocking and opening up of channels for occupied-virtual excitations.

For example, a pure symmetry argument based on the angular-momentum characteristics of π molecular orbitals implies diamagnetic ring currents for $4n + 2\pi$ monocycles, and paramagnetic ring currents for $4n\pi$ monocycles, and furthermore ascribes essentially all the ring current in each case to the activity of 4 HOMO electrons for the aromatic (diatropic) and 2 HOMO electrons for the antiaromatic (paratropic) systems [7a,b].

The few-electron character of ring currents uncovered by the ipsocentric approach prompts many questions about the links between aromaticity/strobilism and distortivity. Just two examples from recent work [14] will be discussed briefly here.

The classic case of pentalene is one where the sense of the ring current and the direction of the distortion are linked. Bond-polarisability, Heilbronner-mode analysis and the HOMO–LUMO rule all agree in this case. The unique Heilbronner distortion has the symmetry of the HOMO–LUMO product which is also the symmetry of a rotation about the out-of-plane C_2 axis. The HOMO–LUMO gap is small. Thus, the D_{2h} molecule is predicted to be unstable to distortion and to exhibit a strong paratropic ring current, both predictions being confirmed by *ab initio* calculation of the geometry and the current map [14c]. One and the same transition supplies a large bond-polarisability eigenvalue, drives the distortion of the framework, and gives a ring current with the paratropic sense expected for an 8π antiaromatic perimeter. Significantly, the paratropic current persists, albeit with reduced intensity, even after the distortion has taken place (Fig. 5); this is to be expected on a perturbation argument as the topologies of HOMO and LUMO remain essentially unchanged by the symmetry breaking.

A spectacular example of resilience of π currents in the presence of σ constraints is given by the current densities of various clamped benzenes. Production of a

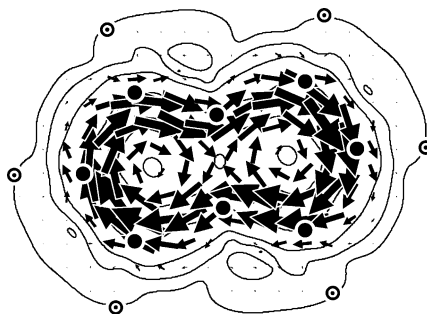


Fig. 5. Computed map of the π current density calculated in the ipsocentric approach for pentalene optimised at the RHF/6-31G**level [14c]. Arrows show the projection of the current density induced by unit perpendicular magnetic field in the plane 1 bohr above the molecule. The clockwise sense indicates paramagnetic (anti-Lenz) circulation.

localised 1,3,5-cyclohexatriene form of the benzene ring has been a long-standing target of the art and sport of synthetic organic chemistry. Significant bond alternation in the benzene ring can be induced by annelation with rigid clamping groups, and π localisation has been claimed for several molecules synthesised on this pattern [23a,b].

Mapping of the current densities in these and a wide range of hypothetical clamped systems gives a surprising result [14a,b]. Substantial bond alternation can coexist with the characteristic 4-electron diatropic ring current of benzene, but systems with similar alternation can also be found where the current is quenched.

The orbital picture based on the ipsocentric approach gives a systematic rationale for these findings. Essentially, current is retained where the topology of the HOMO and LUMO orbitals is retained, and quenched where it is not. In systems where the geometric change is produced by σ clamping groups, the frontier orbitals remain benzene-like, and the current associated with the benzene HOMO $\rightarrow$ LUMO transition is present. In those systems where the clamping involves groups that retain a π system, new π and π^* orbitals are introduced into the frontier region, pushing the benzene-based orbitals further apart, and the strong transitions responsible for the specific ring current of the central ring are lost by attenuation and mixing. An entirely similar dichotomy explains the retention and loss of paratropic ring current in various σ and π -clamped planarised cyclooctatetraene molecules.

The message from both pentalene and benzene/cyclohexatriene examples is of the persistence of the mobility of π electrons under constraints imposed by a σ framework. This resilience and π -distortivity are opposite sides of the same coin.

REFERENCES

- [1] M. K. Cyranski, T. M. Krygowski, A. R. Katritzky and P. von R. Schleyer, *J. Org. Chem.*, 2002, **67**, 1333.
- [2] Interchange between E. Heilbronner and G. Binsch, in discussion of G. Binsch in *Aromaticity, Pseudo-aromaticity, Anti-aromaticity* (eds E. D. Bergmann and B. Pullman), Israel Academy of Sciences, Jerusalem, 1971, p. 25.
- [3] J. F. Labarre and F. Gallais, in *Aromaticity, Pseudo-aromaticity, Anti-aromaticity* (eds E. D. Bergmann and B. Pullman), Israel Academy of Sciences, Jerusalem, 1971, p. 48.
- [4] (a) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 1961, 859; (b) P. von R. Schleyer and H. Jiao, *Pure Appl. Chem.*, 1996, **68**, 209.
- [5] J. A. Pople, *J. Chem. Phys.*, 1956, **24**, 1111.
- [6] P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317.
- [7] (a) E. Steiner and P. W. Fowler, *J. Phys. Chem.*, 2001, **105**, 9553; (b) E. Steiner and P. W. Fowler, *Chem. Commun.*, 2001, 2220.
- [8] (a) S. Shaik, A. Shurki, D. Danovich and P. Hiberty, *Chem. Rev.*, 2001, **101**, 1501; (b) K. Jug, P. C. Hiberty and S. Shaik, *Chem. Rev.*, 2001, **101**, 1477.
- [9] E. Heilbronner, *J. Chem. Ed.*, 1989, **66**, 471.
- [10] E. Heilbronner and S. Shaik, *Helv. Chim. Acta*, 1992, **75**, 539.
- [11] T. Nakajima, A. Toyota and S. Fujii, *Bull. Jpn. Chem. Soc.*, 1972, **45**, 1022.
- [12] G. Binsch, E. Heilbronner and J. N. Murrell, *Mol. Phys.*, 1966, **11**, 305.

- [13] P. W. Fowler and A. Rassat, *PCCP*, 2002, **4**, 1105.
- [14] (a) P. W. Fowler, R. W. A. Havenith, L. W. Jenneskens, A. Soncini and E. Steiner, *Chem. Commun.*, 2001, 2386; (b) A. Soncini, R. W. A. Havenith, P. W. Fowler, L. W. Jenneskens and E. Steiner, *J. Org. Chem.*, 2002, **67**, 4753; (c) R. W. A. Havenith, F. Lugli, P. W. Fowler and E. Steiner, *J. Phys. Chem. A*, 2002, **106**, 5703.
- [15] H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 275.
- [16] A. Ceulemans and P. W. Fowler, *Nature*, 1991, **353**, 52.
- [17] (a) S. Pellegrino and C. R. Calladine, *Int. J. Solids Struct.*, 1986, **22**, 409; (b) P. W. Fowler and S. D. Guest, *Int. J. Solids Struct.*, 2000, **37**, 1793.
- [18] (a) P. W. Fowler and J. I. Steer, *J. Chem. Soc. Chem. Commun.*, 1987, 1403; (b) P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Oxford University Press, Oxford, 1995.
- [19] D. Cvetković, M. Doob and H. Sachs, *Spectra of Graphs – Theory and Application*, Johann Ambrosius Barth Verlag, Heidelberg–Leipzig, 1995.
- [20] P. W. Fowler and K. M. Rogers, *J. Chem. Soc. Faraday*, 1998, **94**, 1019.
- [21] P. W. Fowler and J. P. B. Sandall, *J. Chem. Soc. Perkin*, 1994, **2**, 1917.
- [22] (a) T. A. Keith and R. F. W. Bader, *Chem. Phys. Lett.*, 1993, **210**, 223; (b) T. A. Keith and R. F. W. Bader, *J. Chem. Phys.*, 1993, **99**, 3669; (c) R. Zanasi, P. Lazzeretti, M. Malagoli and F. Piccinini, *J. Chem. Phys.*, 1995, **102**, 7150; (d) R. Zanasi, *J. Chem. Phys.*, 1996, **105**, 1460.
- [23] (a) N. L. Frank, K. K. Baldrige and J. S. Siegel, *J. Am. Chem. Soc.*, 1995, **117**, 2102; (b) R. Diercks and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1986, **108**, 3150.

Jahn–Teller Effect in Circulenes

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Abstract

To compare with the Jahn–Teller effect in [5]circulene, corannulene monoanion, ESR spectra of [6]circulene, coronene monoanion was observed in solution. Although the ESR spectra of doped corannulene monoanion have shown complicated hyperfine splitting due to the Jahn–Teller effect, those of coronene monoanion exhibited equally spaced 13 peaks due to the 12 equivalent hydrogens and no hyperfine structure due to the Jahn–Teller effect down to 183 K, which signifies that the energy barrier between the minima of coronene monoanion is lower than that of corannulene monoanion. The quantum chemical calculations were performed to obtain the Jahn–Teller potential of corannulene and coronene monoanion. For corannulene, the calculated barrier between the equivalent minima was 7.9 meV for the $E_2(16)$ mode which is the strongest coupling mode, while that for coronene monoanion was 0.2 meV. In order to elucidate the warping terms on the potentials, it is important to include nonlinear terms, at least fifth-order and sixth-order anharmonic vibration for corannulene and coronene, respectively, and fourth-order nonlinear vibronic coupling for both molecules. The symmetries of the Jahn–Teller potentials and the optimized structures of a minimum and a saddle point are discussed from the group-theoretical point of view.

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1. INTRODUCTION

The class of hydrocarbons, $[n]$ circulene, $C_{4n}H_{2n}$, is a group of polycyclic aromatic hydrocarbons (PAH) in which n benzene rings are arranged annulately to form a ring [1,2]. [5]circulene (corannulene) [3,4], [6]circulene (coronene), and [7]circulene [5] have been synthesized so far. The discovery of fullerenes has stimulated studies on the chemistry of circulenes. After the discovery of fullerenes and nanotubes, π conjugated systems with positive or negative curvature have attracted interests. Circulene is such a molecule with various curvature due to the n -membered ring.

Corannulene, $C_{20}H_{10}$, dibenzo[*ghi, mno*] fluoranthene, shown in Fig. 1(a), is a bowl-shaped PAH with 5-fold symmetry [6], and has a one-third skeleton of C_{60} (see Figs 1(c) and (d)). Recently, convenient synthesis for corannulene [7,8] has been developed. On the other hand, coronene, $C_{24}H_{12}$, hexabenzobenzene, shown in Fig. 1(b), has a flat structure with a 6-fold symmetry axis.

The lowest unoccupied molecular orbitals (LUMO) of corannulene are rather low-lying and doubly degenerate as shown in Fig. 2 [10,11], which signifies that

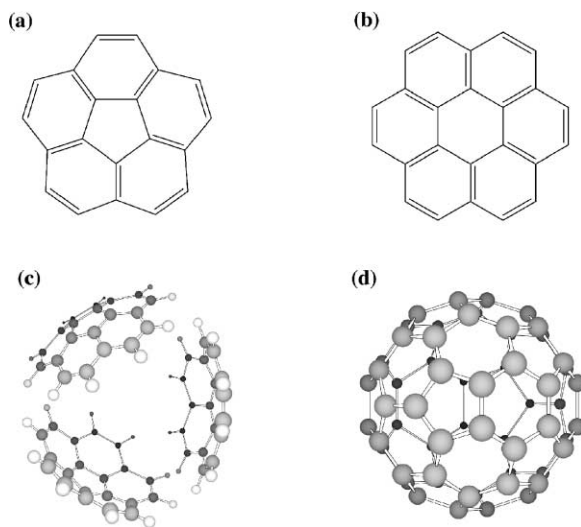


Fig. 1. Structures of (a) [5]circulene, corannulene and (b) [6]circulene, coronene. Three corannulene (c) skeletons give the C_{60} structure (d).

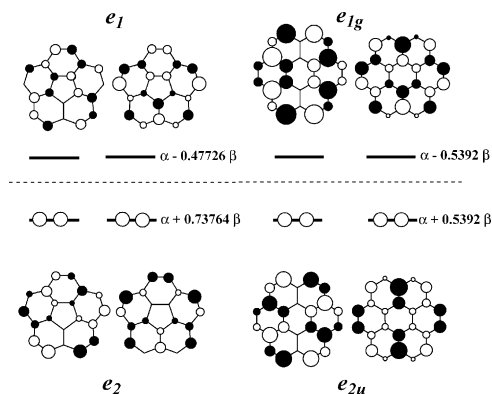


Fig. 2. Frontier orbitals of corannulene (left) and coronene (right). Degenerate LUMOs can give rise to Jahn–Teller distortion in the monoanionic state.

the reduced states of corannulene could be stable even in highly anionized state, similar to C_{60} . Actually all of the anionic state from the monoanion to the tetraanion have been observed [12–15]. As shown in Fig. 2, the energy level of the LUMO is doubly degenerate for corannulene and coronene. Therefore, according to the Jahn–Teller (JT) theorem [16], we can expect the JT effect in these monoanions.

Recently, the occurrence of JT Effect in the monoanionic state of corannulene has been predicted [11], and observed the JT effect in the monoanion using ESR [17]. It has been found that the JT distortion from the C_{5v} configuration to the C_s could make the 10 hydrogen atoms inequivalent. The solution ESR spectra of sodium-doped corannulene monoanion from r.t. to 273 K have been composed of 11 equally spaced peaks with hyperfine coupling (HFC) constant, $a_H = 0.156$ mT. It has been concluded that all the peripheral hydrogen atoms are equivalent, and at low temperatures below 253 K, the spectra have become complicated ones because of the JT effect. It can be interpreted in terms of the pseudorotation about the C_{5v} Jahn–Teller crossing. Fifth-order anharmonicity of molecular vibration gives rise to five equivalent C_s wells in the adiabatic potential surface. The energy barrier between the wells has been estimated to be 2.2 meV from the temperature dependence of the ESR spectra.

In this article, we report solution ESR spectra of coronene monoanion, to compare with that of corannulene monoanion. Moreover, we present *ab initio* molecular orbital (MO) calculation on the JT potentials of monoanionic state of corannulene and coronene, and consider the temperature dependence of the ESR spectra based on these results. Furthermore, the analytical JT potential surfaces of corannulene monoanion and coronene monoanion are derived using group theory.

2. JAHN–TELLER EFFECT

2.1. Corannulene

The electronic state of corannulene anion with C_{5v} symmetry is ${}^2E_1$. The symmetric product representation of E_1 is decomposed as follows:

$$[E_1^2] = A_1 \oplus E_2 \quad (1)$$

Hence, the JT-active vibrational mode is E_2 .

The point group of a JT distorted molecule is a subgroup of the point group G of the parent molecule without JT distortion. In the JT active configuration space v , there exists a minimal subgroup which consists of such symmetry operations g in G that leave all allowed distortions invariant. Such a subgroup will be referred to as a *kernel* of v in G , $K(G, v)$:

$$K(G, v) = \{g \in G | g(a) = a; \forall a \in v\} \quad (2)$$

A subgroup which conserves a subspace w of v is termed as an *epikernel* of v in G , $E(G, v)$:

$$E(G, v) = \{h \in G | h(a) = a; \forall a \in w \subset v\} \quad (3)$$

Epikernels are intermediate subgroups between the parent group and the kernel group:

$$G \supset E(G, v) \supset E'(G, v) \supset K(G, v) \quad (4)$$

Ceulemans *et al.* has proposed the following *epikernel principle* concerning the symmetry of the JT surface assuming quadratic vibronic interaction [18–20]: “Extremum points on a JT surface prefer epikernels to kernel; they prefer maximal epikernels to lower ranking ones. As a rule, stable minima are to be found with structures of maximal epikernel symmetry”. The symmetry group of the configuration space v corresponds to the quotient group $G/K(G, v)$. This group is referred to as a homomorphic image of G in v , $H(G, v)$, because the division of G by $K(G, v)$ defines a homomorphism.

In this case, the kernel, epikernel, and homomorphic image are expressed by

$$K(C_{5v}, e_2) = C_1, \quad E(C_{5v}, e_2) = C_s \quad (5)$$

$$H(C_{5v}, e_2) = C_{5v}/K = C_{5v}/C_1 \cong C_{5v} \quad (6)$$

According to the epikernel principle, the symmetry of the stable minima of the corannulene ion is C_s . If corannulene monoanion is a static JT system, the 11 peaks of the hyperfine structure with intensity ratio 1:10:45:120:210:252:210:120:45:10:1 due to the 10 equivalent hydrogens can be split into $3^5 = 243$ peaks.

2.2. Coronene

The electronic term of coronene monoanion with D_{6h} symmetry is ${}^2E_{1g}$. The symmetric product is decomposed as

$$[E_{1g}^2] = A_{1g} \oplus E_{2g} \quad (7)$$

For coronene monoanion, the kernel and epikernel are expressed by

$$K(D_{6h}, e_{2g}) = C_{2h}, \quad E(D_{6h}, e_{2g}) = D_{2h} \quad (8)$$

and the homomorphic image of D_{6h} in e_{2g} space is

$$H(D_{6h}, e_{2g}) = D_{6h}/K = D_{6h}/C_{2h} \cong C_{3v} \quad (9)$$

According to the epikernel principle, the symmetry of the coronene ion is D_{2h} . If coronene monoanion is a static JT system, the 13 peaks with intensity ratio 1:12:66:220:495:792:924:792:495:220:66:12:1 due to the 12 equivalent hydrogens can be split into $3^6 = 729$ peaks.

3. EXPERIMENTAL

Coronene (Aldrich, 99%; m.p. 438–440 °C) was crystallized from toluene, and sublimed under vacuum. Under nitrogen atmosphere, 1.2 mg of coronene was dissolved into 5 ml of THF dried over sodium. A piece of lithium metal (ca. 50 mg) without further purification and 0.5 ml of the coronene solution was placed into the glass tube equipped with a quartz sample tube. The solution was degassed under high vacuum four times. The tube was sealed, and the solution was left to contact the metal for 9 h. After the solution had turned into green, it was moved into the quartz tube to remove the metal, and an ESR spectrum was recorded. Sodium was, on the other hand, purified by sublimation in a glass tube to give a mirror on the surface of the glass tube. Then the solution was left to contact the alkali-metal mirror.

ESR spectra were recorded on JEOL JES-SRE2X at X-band frequency (9.43 GHz), and g -value was determined by third and fourth signals of MnO_2 (1.981 and 2.034) as a standard. Low temperature measurement down to 183 K was performed until the freezing temperature of the solution.

4. METHOD OF CALCULATION

We employed Hartree–Fock (HF) method for the geometry optimizations and the JT potential calculation. Radom has reviewed computational studies on various molecular anions that includes only first row elements [21]. It has been concluded that reliable structural predictions may be made from single-determinant MO calculations with double-zeta basis sets. Furthermore, we applied second-order Møller–Plesset (MP2) perturbation theory for the optimized geometries with HF

calculations to estimate the spin density. Since polarization function is important to obtain reliable bond angles [22], we used 6-31G** basis set for both carbon and hydrogen. The GAUSSIAN 98 program [23] on SGI Origin3800 have been employed for carrying out both the HF MO calculations and the post HF calculations. Restricted Hartree–Fock (RHF) method was applied for the optimizations of neutral coronene. On the other hand, for the open shell systems, coronene and corannulene monoanion, unrestricted Hartree–Fock (UHF) method was employed. Vibrational analysis was performed for the optimized structures to confirm the stable minimum and the saddle point on the potential surface.

5. RESULTS AND DISCUSSION

5.1. ESR spectra

The solution ESR spectra of sodium-doped coronene monoanion is shown in Fig. 3. All the spectra are composed of 13 equally spaced peaks with an HFC constant,

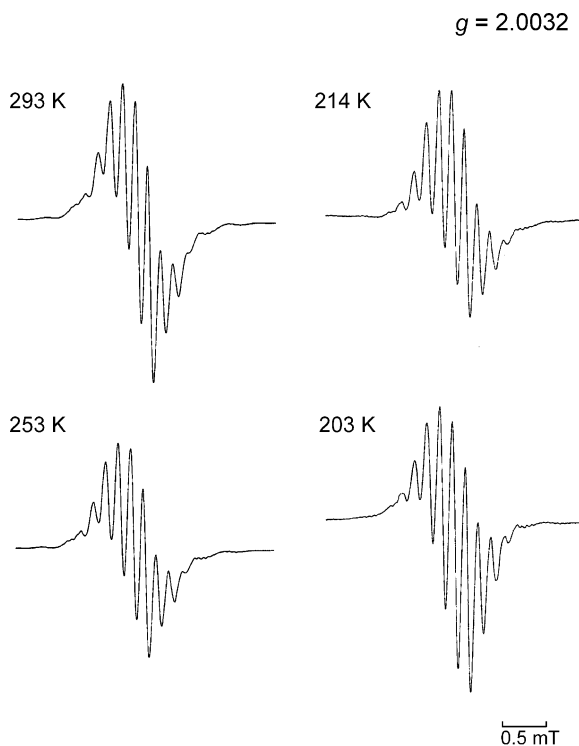


Fig. 3. Temperature dependence of the observed ESR spectra of sodium-doped coronene anion.

$a_{\text{H}} = 0.148$ mT. This means that all the hydrogens are equivalent even at low temperatures. In other words, in contrast to corannulene monoanion, the ESR observation exhibited no JT effect down to 183 K. The observed g -value is 2.0033, which is consistent with the published value, 2.0032 [9]. Moreover, it was independent of temperature.

Figure 4 shows ESR spectra for lithium-doped coronene monoanion in THF solution. There is no significant difference between the lithium-doped sample and the sodium-doped one. Hence, the observed signals are due to the monoanion itself. In Section 5.2, we consider the reason why JT Effect was not observed in this system using *ab initio* calculation.

5.2. *Ab initio* calculation

The stable structures of the neutral and monoanionic state of coronene are depicted in Fig. 5. The optimized structure of the neutral state of coronene has D_{6h} symmetry and that of the monoanion does not have D_{2h} symmetry expected from the epikernel

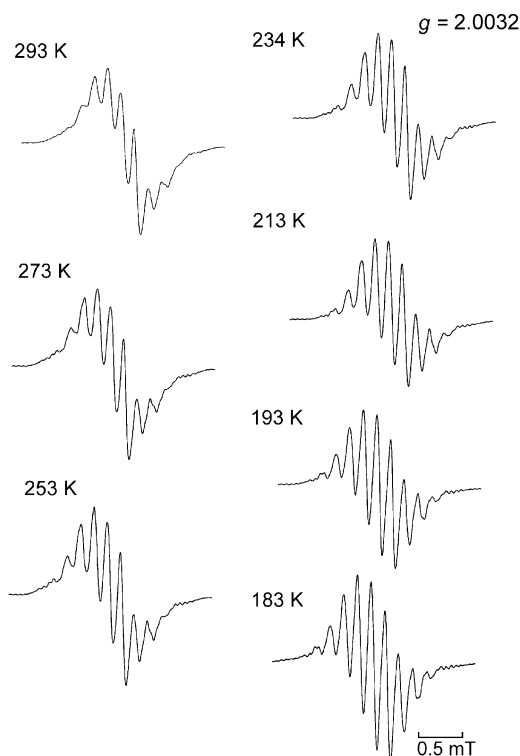


Fig. 4. Temperature dependence of the observed ESR spectra of lithium-doped coronene anion.

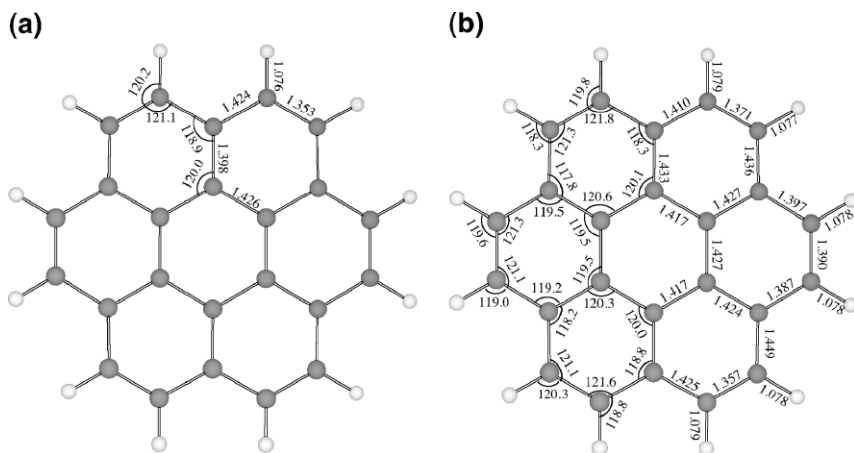


Fig. 5. (a) Stable structure of neutral coronene and (b) coronene monoanion. Bond lengths and bond angles are shown in Å and degrees.

principle, but has C_{2h} symmetry, and the ground electronic state is ^2B_g . The JT stabilization energy E_{JT} is 297 meV.

The optimized structure with D_{2h} symmetry, shown in Fig. 6(a), has one imaginary mode. The vibrational mode with an imaginary frequency is also depicted in Fig. 6(b). The imaginary mode will move the D_{2h} structure to C_{2h} one. Hence the D_{2h} symmetry structure is a saddle point between the stable C_{2h} structures. The energy barrier ΔE between the C_{2h} minima is 0.2 meV. It should be noted that ΔE

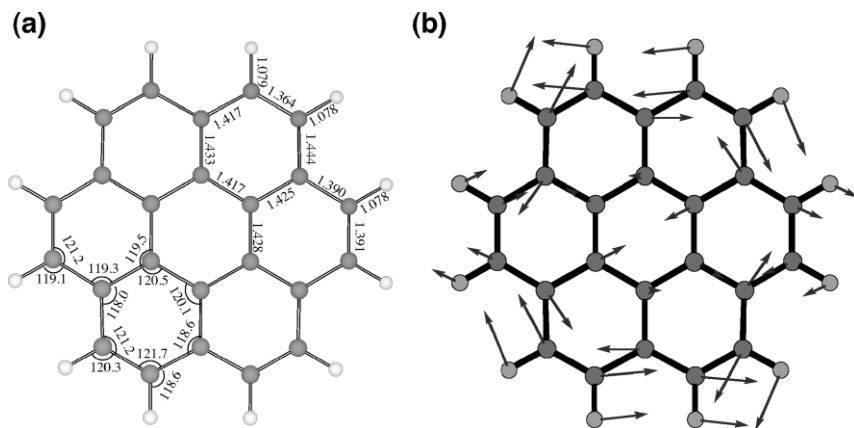


Fig. 6. (a) Optimized structure of coronene monoanion with D_{2h} symmetry and (b) the vibrational mode with imaginary frequency, 330i cm^{-1} . The optimized structure with D_{2h} symmetry is a saddle point.

estimated from the ESR spectra of the corannulene anion, 2.2 meV, is 10 times as large as that of the coronene anion.

Since the *ab initio* calculation on coronene monoanion indicates that the stable configuration has C_{2h} symmetry, we must take higher-order anharmonic terms up to sixth order into consideration which is not considered in the derivation of the epikernel principle to obtain a JT surface with the adequate structure. We will discuss this point later.

5.3. Spin density and HFC constant

Based on the result of the calculation, we will discuss the ESR spectra using the calculated spin density.

For π -conjugated hydrocarbon radicals, it is well known that the HFC constant of a hydrogen, a_H , is proportional to the spin density of π orbital on a carbon atom bonded with the hydrogen atom, ρ_C , which is the so-called McConnell relation:

$$a_H = Q\rho_C \tag{10}$$

where Q is a constant which is usually taken to be from 2.25 to 3.0 mT.

Substituting the magnitude of spin density ρ_C of the corannulene anion and the coronene anion obtained by MO calculation into equation (10), the calculated a_H is tabulated in Table 1.

To estimate the inequivalence of hydrogen due to the JT distortion, it is assumed that the observation of 12 equivalent hydrogen of coronene monoanion is due to some averaging of these hydrogen atoms. Using this assumption, we determined Q for the McConnell’s relation from the average value of the spin density $\overline{\rho_C}$ and the observed HFC constant, $a_H = 0.148$ mT for the coronene ion. We estimated Q as 2.16 for the coronene anion. Applying McConnell’s relation using this Q value and ρ_C on a carbon atom bonded with hydrogen, we estimated a_H as tabulated in Table 1. If the potential barrier ΔE of the coronene anion were comparable to that of the corannulene anion, hyperfine structure due to six kinds of hydrogen atoms would

Table 1. Calculated HFC constants of corannulene monoanion taken from Ref. [11] and coronene monoanion and spin density calculated using MP2/6-31G(d,p)//HF/6-31G(d,p)

Corannulene		Coronene	
ρ_C	a_H (mT)	ρ_C	a_H (mT)
−0.0210	−0.072	0.5540	1.197
−0.2531	−0.863	−0.4341	−0.938
0.3289	1.122	−0.6045	−1.306
0.2315	0.790	0.8104	1.752
−0.0560	−0.191	−0.3383	−0.731
		0.4232	0.915

have been observed at low temperatures, since the magnitude of a_H is almost the same as that of the corannulene anion.

However, the ESR spectra for coronene monoanion did not exhibit such complicated peaks as corannulene monoanion. This suggests that ΔE in the coronene ion is smaller than that of the corannulene ion. In fact, the calculated energy barrier ΔE of one of the D_{2h} saddle points between the stable C_{2h} structures is 0.2 meV, which is smaller than that of corannulene as mentioned previously. Therefore, the pseudorotation about the D_{6h} JT crossing makes the HFC constant averaged and all the peripheral hydrogen atoms equivalent even at low temperatures.

To elucidate the difference between corannulene and coronene, we will consider JT potential surfaces in the Section 5.4.

5.4. Jahn–Teller surfaces

The vibrational modes of corannulene are

$$\Gamma_{\text{vib}} = 9A_1 \oplus 7A_2 \oplus 16E_1 \oplus 18E_2 \quad (11)$$

Among the 18 JT-active E_2 modes, our preliminary calculation shows that the $E_2(16)$ mode has the strongest interaction. The vibrational modes of coronene are

$$\begin{aligned} \Gamma_{\text{vib}} = & 6A_{1g} \oplus 5A_{2g} \oplus 2A_{1u} \oplus 3A_{2u} \oplus 2B_{1g} \oplus 4B_{2g} \oplus 6B_{1u} \oplus 6A_{2u} \oplus 15E_{1g} \\ & \oplus 12E_{2g} \oplus 11E_{1u} \oplus 6E_{2u} \end{aligned} \quad (12)$$

Among 12 JT-active E_{2g} modes, our preliminary calculation shows that the strongest coupling mode is $E_{2g}(10)$.

Figure 7 shows the JT surface on the $E_2(16)$ mode of corannulene monoanion. Five equivalent minima and five equivalent saddle points can be seen on the surface, since the e_2 configuration space has $C_{5v}/C_1 \cong C_{5v}$ symmetry.

We also estimated the barrier height for corannulene monoanion on the $E_2(16)$ mode. The calculated ΔE for corannulene is 7.9 meV. Since calculated potential barrier by HF method tends to be overestimated, this value agrees fairly well with the experimental value, 2.2 meV [11]. In addition, the barrier could be much less, since this calculated value is an upper bound.

Figure 8 shows the JT surface of coronene monoanion on the $E_{2g}(10)$ mode. Six equivalent minima and six equivalent saddle points appear to exist on the surface. Strictly speaking, however, these saddle points consist of two kinds of structures with a very small energy difference less than 10^{-4} meV, since the e_{2g} configuration space has $D_{6h}/C_{2h} \cong C_{3v}$ symmetry.

The energy barrier on the $E_{2g}(10)$ mode is 4.3 meV, which is rather larger than the calculated value from the global minimum and the saddle point mentioned previously. This means that the minimum on the $E_{2g}(10)$ mode is not a global one and there exists another path.

From the present calculation, we can conclude that the upper bound of the energy barrier for the corannulene anion and coronene anion is 7.9 and 0.2 meV, respectively.

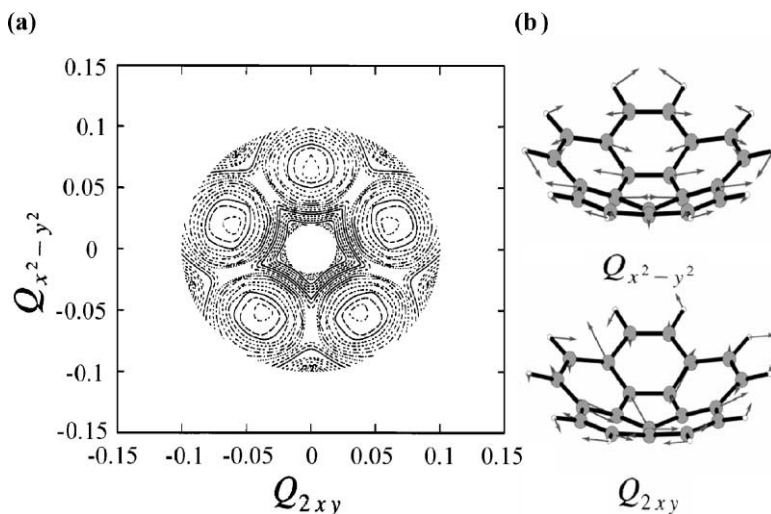


Fig. 7. (a) Lower Jahn–Teller potential surface of corannulene monoanion on the $E_2(16)$ mode. The energy barrier between the minima is 7.9 meV. (b) The vibrational vectors of the $E_2(16)$ mode, the symmetric one (top) and the asymmetric one (bottom).

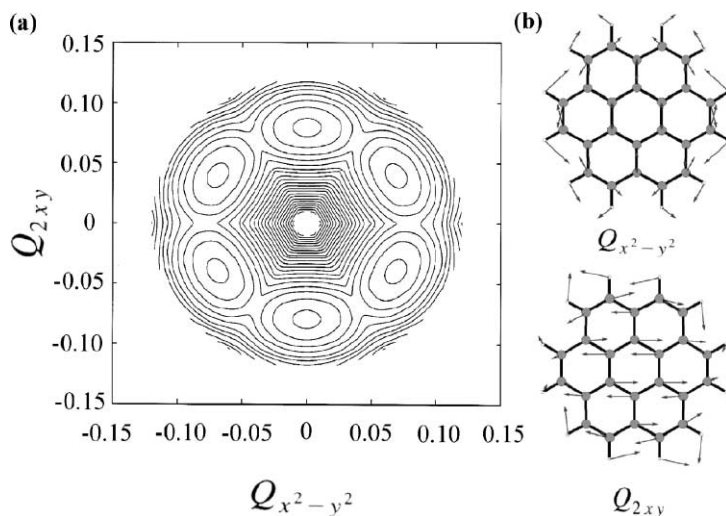


Fig. 8. (a) Lower Jahn–Teller potential surface of coronene monoanion on the $E_{2g}(10)$ mode. The energy barrier between the minima is 4.3 meV. (b) The vibrational vectors of the $E_{2g}(10)$ mode, the symmetric one (top) and the asymmetric one (bottom).

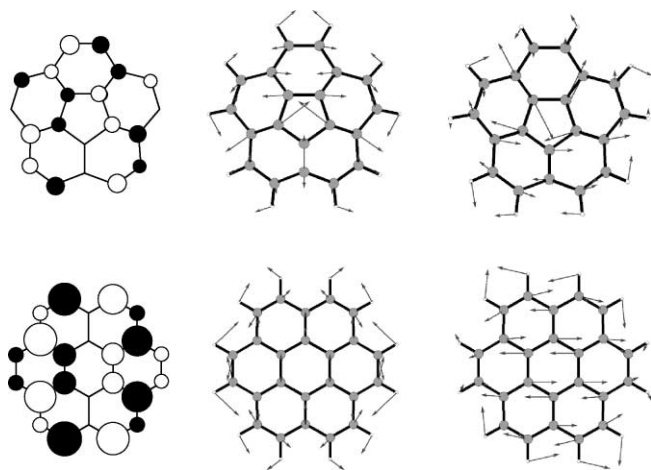


Fig. 9. Orbital pattern of singly occupied molecular orbital and Jahn–Teller active mode. Both SOMOs are antisymmetric with respect to the σ plane. For corannulene (top) the tangential direction along the pseudorotational path at the minimum corresponds to the antisymmetric vibration, while, for coronene (bottom), the symmetric vibration corresponds to the tangential direction at the minimum.

Why is the barrier height ΔE so different between the monoanionic states of corannulene and coronene? The symmetry matching between one of the degenerate JT modes, which corresponds to the tangential direction along the pseudorotational path at the minimum and the singly occupied molecular orbital might play an important role as shown in Fig. 9. For corannulene monoanion with the A'' electronic ground state, A'' vibration is the tangential direction; on the other hand, A_g vibration corresponds to the tangential direction for coronene with the B_g electronic ground state.

5.5. Analytical expressions for Jahn–Teller surfaces

In this section, we will derive the analytical JT potential for corannulene and coronene monoanion using group theory to elucidate roles of anharmonic vibration and nonlinear vibronic coupling.

Both of the JT active modes E_2 and E_{2g} transform according to $(x^2 - y^2, 2xy)$. We denote these normal coordinates as $(Q_{x^2-y^2}, Q_{2xy})$. Note that the base employed here is somewhat different from that appears in the standard text book [24].

The static JT Hamiltonian with the anharmonic vibration and the nonlinear vibronic coupling terms is expressed by

$$\hat{\mathcal{H}} = \frac{1}{2} k (Q_{x^2-y^2}^2 + Q_{2xy}^2) \hat{\mathbf{1}} + \sum_{n=3} U^{(n)} \hat{\mathbf{1}} + \hat{\mathbf{V}} \quad (13)$$

where $\hat{\mathbf{1}}$ is a 2×2 unit matrix, the first term is the harmonic potential with a force constant k , the second one the vibrational anharmonicity, and the third one describes

the vibronic coupling expressed by

$$\hat{V} = g_1(\hat{\sigma}_z Q_{x^2-y^2} + \hat{\sigma}_x Q_{2xy}) + \sum_{n=2} g_n \{ \hat{\sigma}_z I_{x^2-y^2}^n(Q_{x^2-y^2}, Q_{2xy}) + \hat{\sigma}_x I_{2xy}^n(Q_{x^2-y^2}, Q_{2xy}) \} \quad (14)$$

where $\hat{\sigma}_z$ and $\hat{\sigma}_x$ are Pauli matrices:

$$\hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (15)$$

$I_{x^2-y^2}^n(Q_{x^2-y^2}, Q_{2xy})$, $I_{2xy}^n(Q_{x^2-y^2}, Q_{2xy})$ the n th order polynomials of $(Q_{x^2-y^2}, Q_{2xy})$ transforming as $(x^2 - y^2, 2xy)$, and g_n a constant. The first term in equation (14) is the linear coupling, and the second one describes the nonlinear couplings.

5.5.1. Corannulene

The anharmonic potentials, the second term in equation (13), transform as A_1 representation, while the I^n in the nonlinear vibronic term, the second term in equation (14), transform as E_2 representation. The product representations are decomposed as

$$E_2 \times E_2 = A_1 \oplus A_2 \oplus E_1 \quad (16)$$

$$E_2 \times E_2 \times E_2 = E_1 \oplus 3E_2 \quad (17)$$

$$E_2 \times E_2 \times E_2 \times E_2 = 3A_1 \oplus 3A_2 \oplus 4E_1 \oplus 3E_2 \quad (18)$$

It should be noted that the quadratic vibronic interaction is vanishing in the corannulene anion, since $E_2 \times E_2$ does not contain E_2 representation in equation (16).

The anharmonic potentials are expressed by

$$U^{(3)} = 0 \quad (19)$$

$$U^{(4)} = W_4(Q_{x^2-y^2}^2 + Q_{2xy}^2)^2 \quad (20)$$

$$U^{(5)} = W_5(Q_{x^2-y^2}^5 - 10Q_{x^2-y^2}^3 Q_{2xy}^2 + 5Q_{2xy}^5) = W_5 \rho^5 \cos 5\theta \quad (21)$$

where W_4 , W_5 are constants. Note that angular dependence appears in the fifth-order.

The polynomials $(I_{x^2-y^2}^n, I_{2xy}^n)$ are expressed by

$$\begin{aligned} (I_{x^2-y^2}^3, I_{2xy}^3) &= (Q_{x^2-y^2}(Q_{x^2-y^2}^2 + Q_{2xy}^2), Q_{2xy}(Q_{x^2-y^2}^2 + Q_{2xy}^2)) \\ &= (\rho^3 \cos \theta, \rho^3 \sin \theta) \end{aligned} \quad (22)$$

$$\begin{aligned} (I_{x^2-y^2}^4, I_{2xy}^4) &= (Q_{x^2-y^2}^4 - 6Q_{x^2-y^2}^2 Q_{2xy}^2 + Q_{2xy}^4, -4Q_{x^2-y^2} Q_{2xy}(Q_{x^2-y^2}^2 - Q_{2xy}^2)) \\ &= (\rho^4 \cos 4\theta, -\rho^4 \sin 4\theta) \end{aligned} \quad (23)$$

Note that the second order polynomial is vanishing as mentioned above.

By diagonalization of equation (13), the analytical JT potential function is obtained as

$$E_{\pm} = \frac{1}{2}k\rho^2 + W^{(4)}\rho^4 + W^{(5)}\rho^5 \cos 5\theta \pm [\rho^2\{g_1^2 + 2g_1g_3\rho^2 + g_3^2\rho^4 + 2g_4\rho^3(g_1 + g_3\rho^3)\cos 5\theta\}]^{1/2} \quad (24)$$

From equation (24), the warping terms arise from the fifth-order anharmonic vibration and the fourth-order nonlinear vibronic coupling.

5.5.2. Coronene

The product representations of the JT-active E_{2g} mode are decomposed as

$$E_{2g} \times E_{2g} = A_{1g} \oplus A_{2g} \oplus E_{2g} \quad (25)$$

$$E_{2g} \times E_{2g} \times E_{2g} = A_{1g} \oplus A_{2g} \oplus 3E_{2g} \quad (26)$$

$$E_{2g} \times E_{2g} \times E_{2g} \times E_{2g} = 3A_{1g} \oplus 3A_{2g} \oplus 15E_{2g} \quad (27)$$

The anharmonic potentials are expressed by

$$U^{(3)} = W_3(Q_{x^2-y^2}^3 - 3Q_{x^2-y^2}Q_{2xy}^2) = W_3\rho^3 \cos 3\theta \quad (28)$$

$$U^{(4)} = W_4(Q_{x^2-y^2}^2 + Q_{2xy}^2)^2 = W_4\rho^4 \quad (29)$$

$$U^{(5)} = W_5(Q_{x^2-y^2}^2 + Q_{2xy}^2)(Q_{x^2-y^2}^3 - 3Q_{x^2-y^2}Q_{2xy}^2) = W_5\rho^5 \cos 3\theta \quad (30)$$

$$U^{(6)} = W_6(Q_{x^2-y^2}^6 - 15Q_{x^2-y^2}^4Q_{2xy}^2 + 15Q_{x^2-y^2}^2Q_{2xy}^4 - Q_{2xy}^6) = W_6\rho^6 \cos 6\theta \quad (31)$$

where W_3 , W_4 , W_5 , W_6 are constants. Note that the third, fifth, sixth orders have angular dependence.

The polynomials ($I_{x^2-y^2}^n, I_{2xy}^n$) are expressed by

$$(I_{x^2-y^2}^2, I_{2xy}^2) = (Q_{x^2-y^2}^2 - Q_{2xy}^2, -2Q_{x^2-y^2}Q_{2xy}) = (\rho^2 \cos 2\theta, -\rho^2 \sin 2\theta) \quad (32)$$

$$(I_{x^2-y^2}^3, I_{2xy}^3) = (Q_{x^2-y^2}^3(Q_{x^2-y^2}^2 + Q_{2xy}^2), Q_{2xy}(Q_{x^2-y^2}^2 + Q_{2xy}^2)) = (\rho^3 \cos \theta, \rho^3 \sin \theta) \quad (33)$$

$$(I_{x^2-y^2}^4, I_{2xy}^4) = (Q_{x^2-y^2}^4 - 6Q_{x^2-y^2}^2Q_{2xy}^2 + Q_{2xy}^4, 4Q_{x^2-y^2}Q_{2xy}(Q_{x^2-y^2}^2 - Q_{2xy}^2)) = (\rho^4 \cos 4\theta, \rho^4 \sin 4\theta) \quad (34)$$

The analytical JT potential function is obtained by

$$E_{\pm} = \frac{1}{2}k\rho^2 + W^{(3)}\rho^3 \cos 3\theta + W^{(4)}\rho^4 + W^{(5)}\rho^5 \cos 3\theta + (W^{(6a)} + W^{(6b)} \cos 6\theta)\rho^6 \pm [\rho^2\{g_1^2 + g_2^2\rho^2 + 2g_1g_3\rho^2 + g_3^2\rho^4 + 2\rho(g_1 + g_3\rho^2)(g_2 + g_4\rho^2)\cos 3\theta + 2g_2g_4\rho^3 \cos 6\theta\}]^{1/2} \quad (35)$$

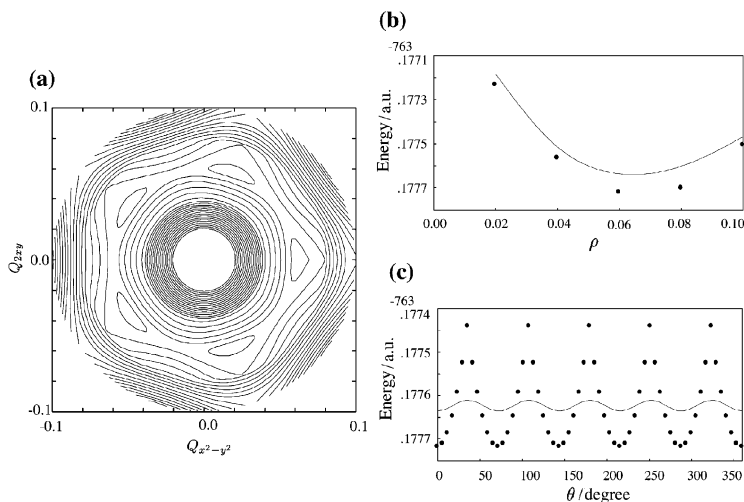


Fig. 10. (a) Lower potential surface of corannulene monoanion using equation (24), (b) cross-section along $\theta = 0.0$, and (c) cross-section along $\rho = 0.06$.

From equation (35), the 3θ -warping terms arise from the third-order and fifth-order anharmonic vibration and the quadratic vibronic coupling, and the 6θ -warping terms arise from the sixth-order anharmonic vibration and the fourth-order non-linear vibronic coupling.

5.5.3. Fitting analytical expressions to calculate Jahn–Teller potentials

Figures 10 and 11 show JT surfaces calculated by equations (24) and (35) using nonlinear fitting to the JT potential, Figs 7 and 8.

The behaviors in the radial direction (see Figs 10(b) and 11(b)) and the location of the minima and saddle points (see Figs 10(c) and 11(c)) are well reproduced. However, the amplitudes of the warping is too small as shown in Figs 10(c) and 11(c).

6. SUMMARY

We observed solution ESR spectra of corannulene and coronene monoanion and performed *ab initio* calculation. We also applied group-theoretical calculation to the JT systems to explain the experimental and computational findings. The major findings are as follows:

1. For the corannulene anion, complicated hyperfine structures due to the JT effect has been observed at low temperatures. The potential barrier between the JT-distorted minima has been estimated to be 2.2 meV. On the other hand, for

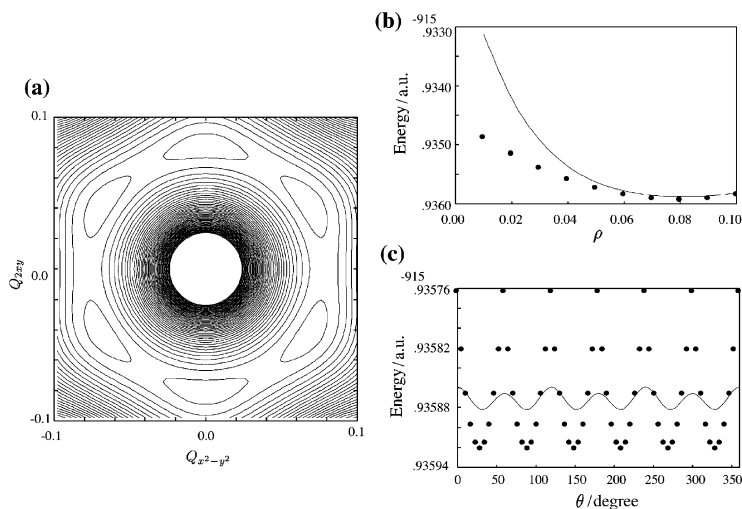


Fig. 11. (a) Lower Jahn–Teller potential surface of coronene monoanion using equation (35), (b) cross-section along $\theta = 30.0$, and (c) cross-section along $\rho = 0.08$.

the coronene anion, we could observe no hyperfine splitting due to the JT distortion down to 183 K.

2. The present HF calculations show that there are five and six equivalent minima for the corannulene and the coronene anion, respectively. The symmetry of the stable minima is C_s and C_{2h} , respectively. The JT potentials are also obtained. The calculated energy barrier between the distorted minima is 7.9 and 0.2 meV for the corannulene ion and the coronene ion, respectively. This is the reason why JT distortion could not be observed in the coronene ion.
3. For the corannulene anion, the quadratic vibronic interaction is vanishing due to its symmetry, and it is necessary to include the fifth-order vibrational anharmonicity and fourth-order vibronic interaction to explain the five equivalent minima. For coronene, on the other hand, if the quadratic vibronic interaction is considered, the interaction gives rise to three minima on the JT surface of the coronene anion. However, this is not the case. It is necessary for the sixth-order vibrational anharmonicity and fourth-order nonlinear vibronic interaction to give rise to the six equivalent minima.

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REFERENCES

- [1] J. H. Dopper and H. Wynberg, *Tetrahedron Lett.*, 1972, **13**, 763.
- [2] J. H. Dopper and H. Wynberg, *J. Org. Chem.*, 1975, **40**, 1957.
- [3] W. E. Barth and R. G. Lawton, *J. Am. Chem. Soc.*, 1966, **88**, 380.
- [4] W. E. Barth and R. G. Lawton, *J. Am. Chem. Soc.*, 1971, **93**, 1730.
- [5] K. Yamamoto, T. Harada, M. Nakazaki, T. Naka, Y. Kai, S. Harada and N. Kasai, *J. Am. Chem. Soc.*, 1983, **105**, 71713.
- [6] J. C. Hanson and C. E. Nordman, *Acta Crystallogr.*, 1976, **B32**, 1147.
- [7] L. T. Scott, M. M. Hashemi, D. T. Meyer and H. B. Warren, *J. Am. Chem. Soc.*, 1991, **113**, 7082.
- [8] L. T. Scott, P.-C. Cheng, M. H. Hashemi, M. S. Bratcher, D. T. Meyer and H. B. Warren, *J. Am. Chem. Soc.*, 1997, **119**, 10963.
- [9] M. Sato, K. Yamamoto, H. Sonobe, K. Yano, H. Matsubara, H. Fujita, T. Sugimoto and K. Yamamoto, *J. Chem. Soc. Perkin Trans.*, 1998, **2**, 1909.
- [10] S. J. Cyvin, E. Brendsdal, J. Brunvoll and M. Skaret, *J. Mol. Struct.*, 1991, **247**, 119.
- [11] T. Sato, A. Yamamoto and T. Yamabe, *J. Phys. Chem. A*, 2000, **104**, 130.
- [12] J. Janata, J. Gendell, C.-Y. Ling, W. Barth, L. Backes, Jr., H. B. Mark and R. G. Lawton, *J. Am. Chem. Soc.*, 1967, **89**, 30567.
- [13] A. Ayalon, M. Rabinovitz, P.-C. Cheng and L. T. Scott, *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 1636.
- [14] A. Ayalon, A. Sygula, P.-C. Cheng, M. Rabinovitz, P. W. Rabideau and L. T. Scott, *Science*, 1994, **265**, 1065.
- [15] M. Baumgarten, L. Gherghel, M. Wagner, A. Weitz, M. Rabinovitz, P.-C. Cheng and L. T. Scott, *J. Am. Chem. Soc.*, 1995, **117**, 6254.
- [16] H. A. Jahn and E. Teller, *Proc. R. Soc. Lond. Ser. A*, 1937, **161**, 220.
- [17] T. Sato, A. Yamamoto and H. Tanaka, *Chem. Phys. Lett.*, 2000, **326**, 573.
- [18] A. Ceulemans, D. Beyens and L. G. Vanquickenborne, *J. Am. Chem. Soc.*, 1984, **106**, 5824.
- [19] A. Ceulemans, *J. Chem. Phys.*, 1987, **87**, 5374.
- [20] A. Ceulemans and L. G. Vanquickenborne, *Struct. Bonding*, 1989, **71**, 125.
- [21] L. Radom, in *Applications of Electronic Structure Theory* (ed. H. F. Schaefer, III), Plenum Press, New York, 1977, p. 333.
- [22] J. A. Pople, in *Applications of Electronic Structure Theory* (ed. H. F. Schaefer, III), Plenum Press, New York, 1977, p. 1.
- [23] M. J. Frisch, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, Jr., J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople. GAUSSIAN 98, Revision A.11, Gaussian, Inc., Pittsburgh PA, 1998
- [24] F. A. Cotton, *Chemical Applications of Group Theory*, Wiley, New York, 1971.

Vibronic Interactions and Jahn–Teller Effects in Charged Hydrocarbons

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Abstract

The relationships between the strengths of the electron–phonon coupling and the molecular sizes and structures in charged hydrocarbons are studied. We suggest that calculated electron–phonon coupling becomes weaker with an increasing in molecular size both in negatively charged acene-edge-type hydrocarbons and in phenanthrene-edge-type hydrocarbon crystals. But the vibronic coupling is stronger in phenanthrene-edge-type hydrocarbons than in acene-edge-type hydrocarbons. Therefore, not only molecular sizes but also molecular edge structures have relevance to the strength of the electron–phonon coupling. We also study the Jahn–Teller effects and possible superconductivity in negatively charged coronene and corannulene from a viewpoint that coronene can be viewed as a fragment of one-sheet of graphite and corannulene as a fragment of fullerene C₆₀.

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1. INTRODUCTION

The search for new organic metals and superconductors has attracted a great deal of attention in synthetic chemistry and material science since the discovery of high electrical conductivity in conjugated polymers such as polyacetylene [1]. Lots of theoretical studies have been carried out in order to understand the mechanism of conductivity and superconductivity in the conjugated polymers and related

materials, and to reveal the interconnection between chemical and electronic structures. In modern physics and chemistry, the effect of vibronic interaction in molecules and crystals [2] has been an important topic.

The alkali-doped A_3C_{60} complexes [3] exhibit superconducting transition temperatures T_c s of more than 30 K [4] and 40 K under pressure [5]. Several researchers suggested that pure intramolecular Raman-active modes are important in a BCS-type strong coupling scenario in superconductivity in alkali-doped fullerenes [6]. Haddon [7] discussed the rehybridization of the π orbitals and the 2s atomic orbitals which may also be useful in order to understand the high T_c superconductivity of the A_3C_{60} complexes. It was proposed that the electron–phonon interactions dominate the charge transport in the crystals of naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$), tetracene ($C_{18}H_{12}$), and pentacene ($C_{22}H_{14}$) [8–10]. Interestingly, from a theoretical viewpoint, possible superconductivity of polyacene has been proposed [11,12]. We can reasonably expect that many other nano-sized molecular crystals might also exhibit superconductivity in view of the interesting molecular superconductivity in fullerene and organic compounds.

In this paper, we analyze the vibronic interactions and estimate possible T_c s in the monoanions [13] of acene-edge-type hydrocarbons such as benzene (C_6H_6), naphthalene, anthracene, tetracene, and pentacene, and in the monoanions of phenanthrene-edge-type hydrocarbons such as phenanthrene ($C_{14}H_{10}$), chrysene ($C_{18}H_{12}$), and benzo[a]chrysene ($C_{22}H_{14}$) [14]. Furthermore, we also study the Jahn–Teller effects and possible superconductivity in negatively charged coronene ($C_{24}H_{12}$) and corannulene ($C_{20}H_{10}$) [15] from a viewpoint that coronene can be viewed as a fragment of one-sheet of graphite and corannulene as a fragment of fullerene C_{60} . Since intermediate character between σ and π orbital interaction characters owing to the bowl-shaped structure of corannulene makes orbital interactions between two neighboring carbon atoms strong, the calculated electron–phonon coupling constant for the monoanion of corannulene is much larger than that of the monoanion of planar coronene. Finally, we discuss how the differences of the molecular structures and sizes have relevance to the strengths of the electron–phonon interactions.

2. OPTIMIZED STRUCTURES

The structures of neutral acene- and phenanthrene-series were optimized, using the hybrid Hartree–Fock (HF)/density-functional-theory (DFT) method of Becke [16] and Lee, Yang, and Parr [17] (B3LYP) and the 6-31G* basis set [18]. GAUSSIAN 98 program package [19] was used for our theoretical analyses. This level of theory is, in our experience, sufficient for reasonable descriptions of the geometric, electronic, and vibrational structures of hydrocarbons. Optimized structures of acene- and phenanthrene-series are shown in Fig. 1. We can see that in the D_{6h} structure of benzene there is no bond alternation and all C–C bond lengths are approximately

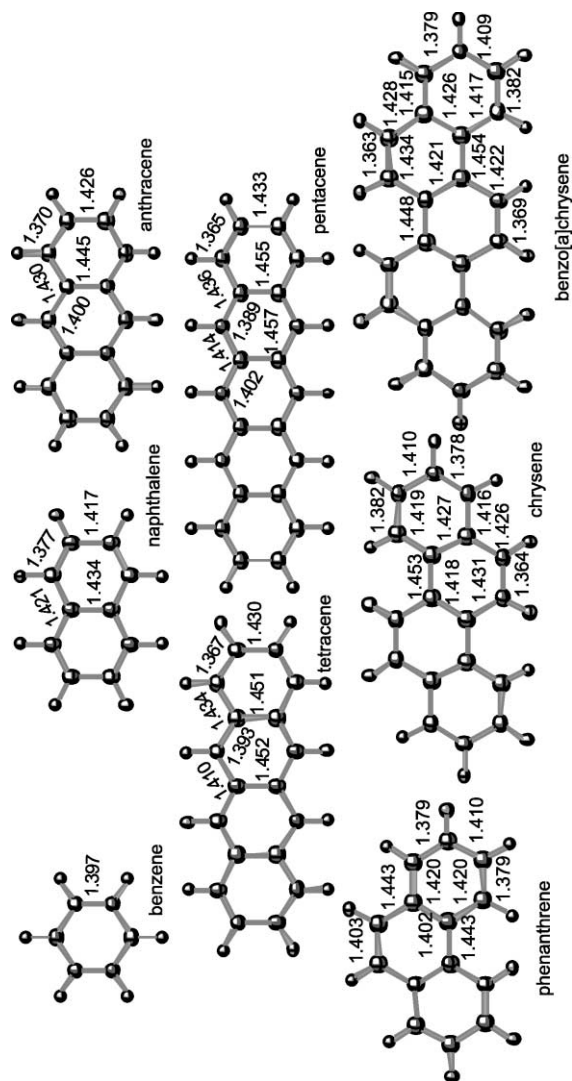


Fig. 1. Optimized structures of acene- and phenanthrene-series.

1.4 Å. In the optimized structures of acenes and phenanthrenes, there is a distinct variation in the C–C distances.

3. ELECTRON–PHONON COUPLING IN THE MONOANIONS OF ACENE- AND PHENANTHRENE-EDGE-TYPE HYDROCARBONS

We carried out vibrational analyses of these acene- and phenanthrene-edge-type hydrocarbons at the B3LYP/6-31G* level of theory. Selected vibrational modes of these molecules are shown in Fig. 2. We next calculated first-order derivatives at this equilibrium structure on each orbital energy surface by distorting the molecule along these vibrational modes of these molecules in order to obtain orbital vibronic coupling constants $g_{\text{LUMO}}(\omega_m)$. We can estimate the electron–phonon coupling constants $I_{\text{LUMO}}(\omega_m)$ from the dimensionless diagonal linear orbital vibronic coupling constants. The calculated electron–phonon coupling constants in the monoanions of acene-edge-type hydrocarbons are shown in Fig. 3. Let us take a look at the electron–phonon coupling of the A_{1g} and E_{2g} vibrational modes to the e_{2u} LUMO in benzene. We can see from Fig. 3 that the E_{2g} mode of 1656 cm^{-1} strongly couples to the e_{2u} LUMO in benzene. This can be understood in view of the orbital patterns of the e_{2u} LUMO and vibrational modes of benzene. When benzene is distorted along this E_{2g} mode towards the direction as shown in Fig. 2, the antibonding (bonding) interactions between C_{1b} and C_{1c} in the LUMO (A) (LUMO (B)) become strong, and the antibonding interactions between C_{1a} and C_{1b} and between C_{1c} and C_{1d} in the LUMO (B) become weak. Therefore, the LUMO (A) (LUMO (B)) is significantly destabilized (stabilized) in energy. On the other hand, when benzene is distorted towards the opposite direction along the arrow of this mode, the LUMO (A) (LUMO (B)) is significantly stabilized (destabilized) in energy. This is the reason why the E_{2g} mode of 1656 cm^{-1} strongly couples to the e_{2u} LUMO in benzene. Let us next look at the electron–phonon coupling of the A_g vibrational modes to the b_{1g} LUMO in naphthalene. Figure 3 demonstrates that the C–C stretching A_g modes of 1417 and 1630 cm^{-1} strongly couple to the b_{1g} LUMO. In the two frequency modes, the displacements of C atoms are very large compared with any other A_g mode of naphthalene, and the b_{1g} LUMO is completely localized on C atoms. It is rational that a frequency mode in which normal displacements are large for atoms, and where there exists considerable orbital amplitude can strongly couple to the molecular orbital. Identical discussions can be made in anthracene, tetracene, pentacene, and hexacene; the C–C stretching A_g modes of 1400 – 1600 cm^{-1} and the lowest frequency A_g mode strongly couple to the LUMOs.

Let us take a look at the electron–phonon coupling of A_1 vibrational modes to a_2 LUMO in phenanthrene. Electron–phonon coupling constants in the monoanions of phenanthrene-edge-type hydrocarbons are shown in Fig. 4. We see from this figure that the C–C stretching A_1 mode of 1434 cm^{-1} strongly couples to the a_2 LUMO in phenanthrene. In a similar way, the C–C stretching A_1 mode of 1670 cm^{-1} strongly couples to the a_2 LUMO in phenanthrene. It should be noted

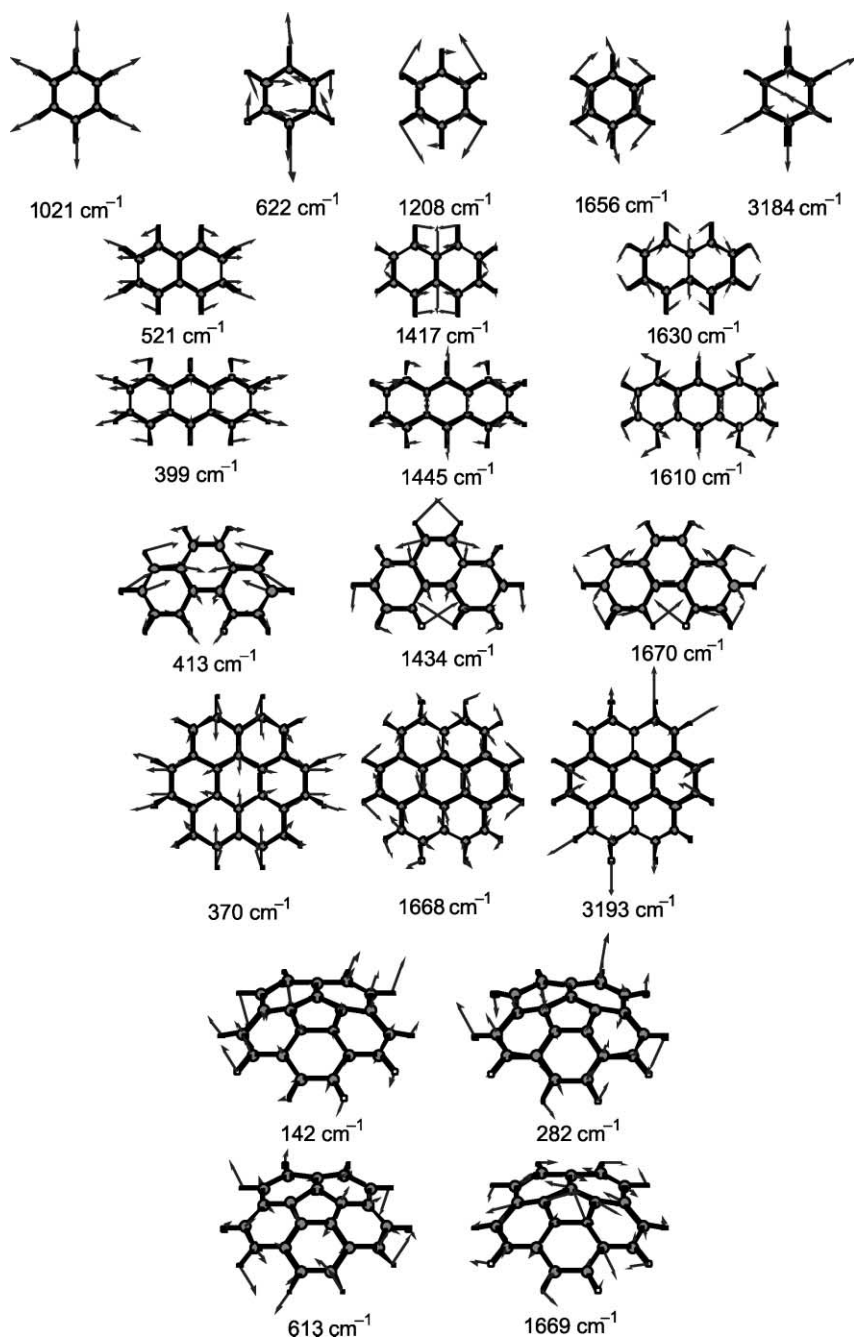


Fig. 2. Selected vibrational modes of hydrocarbons.

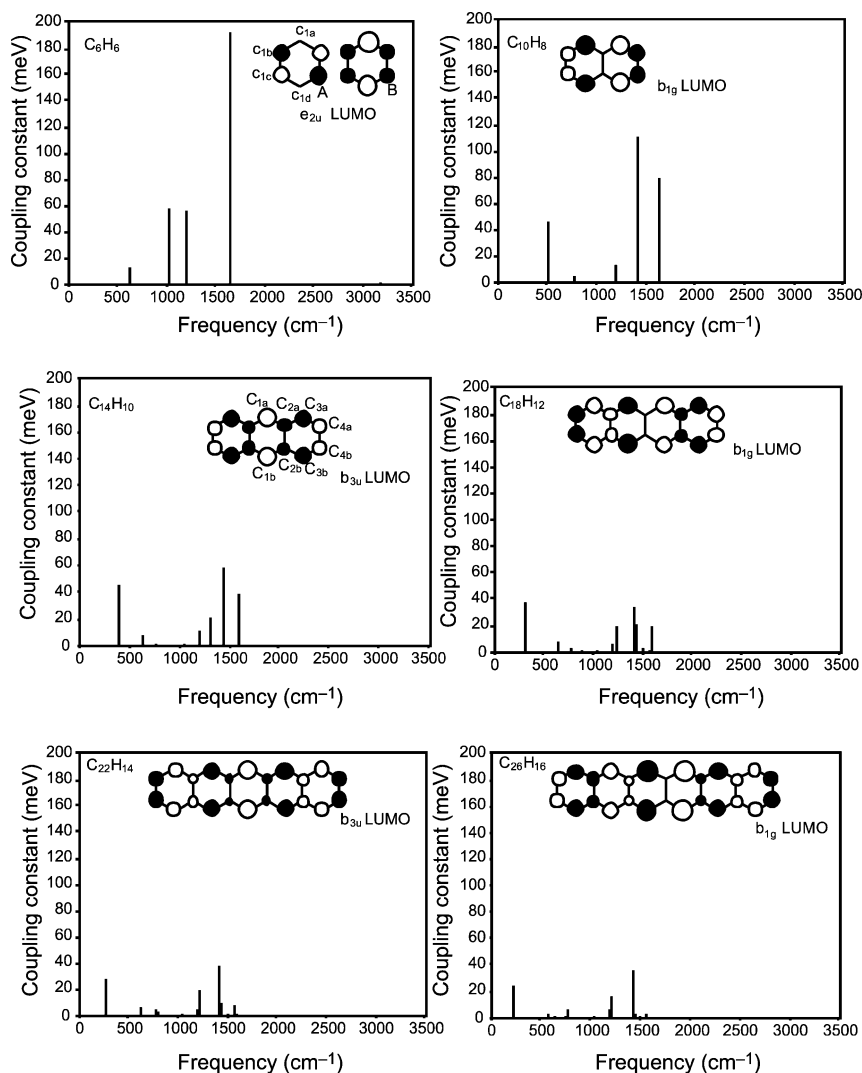


Fig. 3. Electron–phonon coupling constants for the monoanions of acene-edge-type hydrocarbons.

that the electron–phonon coupling constants in the monoanion of phenanthrene are larger than those in the monoanion of anthracene. That is because the frontier orbitals of anthracene is somewhat localized on C_{1a}, C_{3a}, C_{1b}, and C_{3b}, whereas those of phenanthrene are distributed evenly over the carbon structure. That is, the frontier orbitals of anthracene have nonbonding characters and thus these orbitals cannot strongly couple to the A_g vibrational modes. This is also the case for other

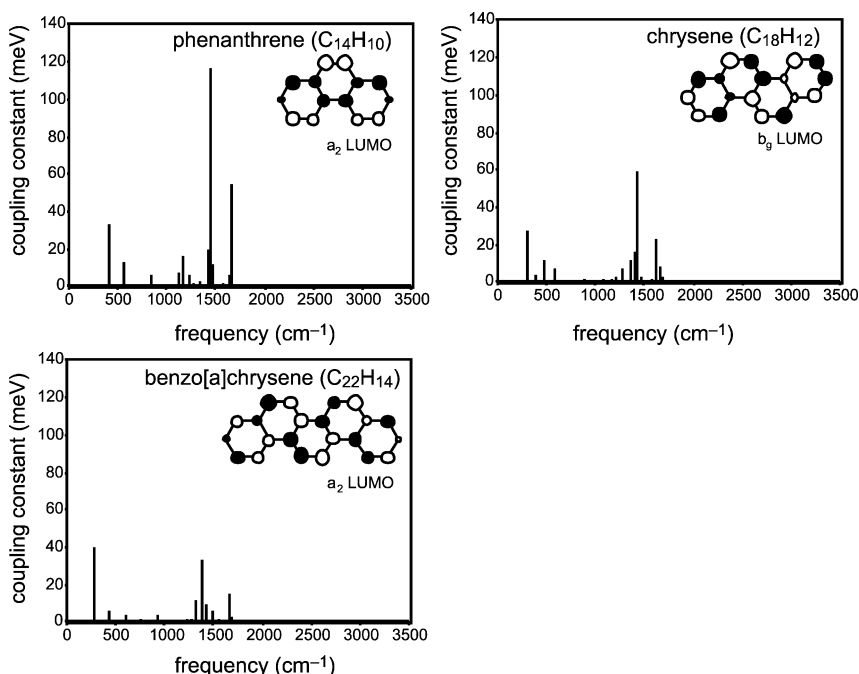


Fig. 4. Electron–phonon coupling constants for the monoanions of phenanthrene-edge-type hydrocarbons.

acene-edge-type hydrocarbons. The lowest frequency mode and the C–C stretching modes strongly couple to the LUMO also in other acene- and phenanthrene-edge-type hydrocarbons.

The calculated total electron–phonon coupling constants (l_{LUMO}) in the monoanions of acene- and phenanthrene-edge-type hydrocarbons are shown in Fig. 5. The coupling constants were estimated to be 0.322, 0.254, 0.186, 0.154, 0.127, and 0.106 eV in the monoanions of benzene, naphthalene, anthracene, tetracene, pentacene, and hexacene, respectively, and 0.300, 0.194, and 0.179 eV in the monoanions of phenanthrene, chrysene, and benzo[a]chrysene, respectively. Therefore, the coupling constants generally decrease with an increase in the number of carbon atoms in both acene- and phenanthrene-edge-type hydrocarbons. The coupling constant for the monoanion of phenanthrene (0.300 eV) is larger than that for the monoanion of anthracene (0.186 eV) although both molecules have the same molecular formula (C₁₄H₁₀). Furthermore, the coupling constant for chrysene monoanion (0.194 eV) is larger than that for tetracene monoanion (0.154 eV), and that for benzo[a]chrysene monoanion (0.179 eV) is larger than that for pentacene monoanion (0.127 eV). Therefore, the molecular edge structures as well as the molecular sizes are closely related to the strengths of the electron–phonon interactions in negatively charged hydrocarbons.

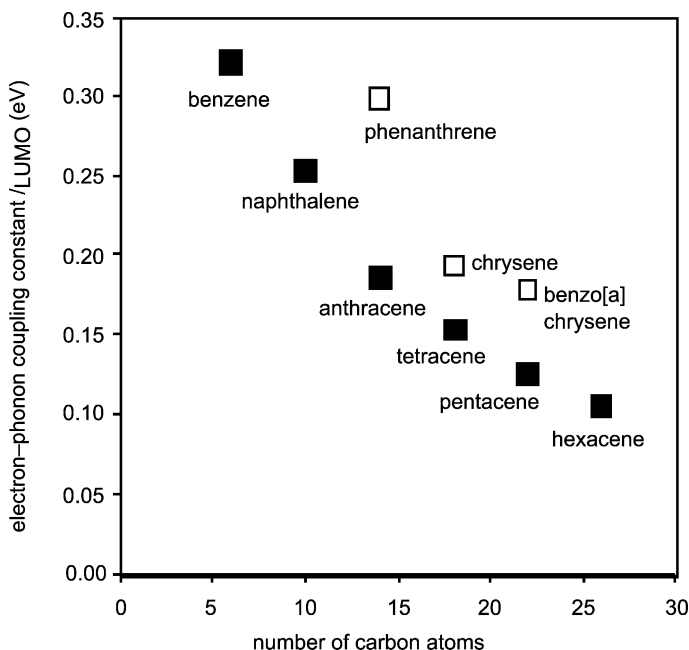


Fig. 5. Electron–phonon coupling constants l_{LUMO} as a function of the number of carbon atoms.

4. POSSIBLE T_c S FOR THE MONOANIONS OF ACENE- AND PHENANTHRENE-EDGE-TYPE HYDROCARBON CRYSTALS

We are now able to estimate T_c for the hydrocarbon monoanions by using the approximate solution of the Eliashberg equation [20]. On the basis of the calculated BCS electron–phonon coupling constants [21], we estimate T_c s using McMillan’s formula [22,23]. McMillan’s formula was derived from a three-dimensional formalism, while the electron carriers in acene-edge-type molecules form a quasi-two-dimensional system. But we believe that McMillan’s formula is still available for qualitative discussions. For $\lambda < 1.5$, this is available for an approximate solution to the Eliashberg equations

$$T_c = \frac{\omega_{\text{ln}}}{1.2} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right] \quad (1)$$

where μ^* is the Coulomb pseudopotential describing the electron–electron repulsion, and ω_{ln} is the logarithmically averaged phonon frequency [23].

Since $n(0)$ was estimated to be about four states per spin per molecule for the electronically twofold degenerate benzene monoanion [6(1)], we can roughly estimate the values for the electronically nondegenerate monoanions of acene- and

phenanthrene-edge-type molecules to be about two by considering that weak van der Waals interactions between molecules and thus a similar broadening of the molecular states will characterize the molecular crystals [6,13–15]. However, $n(0)$ is obviously sensitive to the overlap (the transfer integral) between the LUMOs on neighboring molecules, and consequently to the distance and the orientation between the molecules and to the extent and the position of the nodes of the LUMO. Therefore, let us estimate possible T_c s for the monoanions of acene- and phenanthrene-series as a function of $n(0)$ as well as μ^* . Calculated T_c s for the monoanions of acene- and phenanthrene-series as a function of $n(0)$ and μ^* are listed in Table 1. We can expect from Table 1 that these small molecules would have high superconducting transition temperatures T_c s if these molecules exhibit superconductivity. For example, the T_c for the monoanion of benzene is estimated to be very high; 194.60–128.35 K for $n(0) = 4$ and $\mu^* = 0.10$ –0.20. And the T_c for the monoanion of naphthalene is estimated to be 22.48–2.39 K for $n(0) = 2$ and $\mu^* = 0.10$ –0.20. We expect from these data that the monoanions of phenanthrene-edge-type hydrocarbons would have higher T_c s than the monoanions of acene-edge-type hydrocarbons if we assume that both type hydrocarbons with the same molecular formula have approximately similar values of $n(0)$ and μ^* . For example, the T_c for the monoanion of phenanthrene is estimated to be high; 39.54 K for $n(0) = 2.0$ and $\mu^* = 0.10$, 46.55 K for $n(0) = 2.5$ and $\mu^* = 0.15$, and 50.13 K for $n(0) = 3.0$ and $\mu^* = 0.20$, under the same condition, the T_c for the monoanion of anthracene was estimated to be about 4 K [13]. The T_c for the monoanion of chrysene is also estimated to be higher than that for the monoanion of tetracene; 15.56 K for $n(0) = 2.5$ and $\mu^* = 0.10$, 15.51 K for $n(0) = 3.0$ and $\mu^* = 0.15$, and 14.48 K for $n(0) = 3.5$ and $\mu^* = 0.20$, under the same condition, the T_c for

Table 1. Calculated T_c s (K) for the monoanions of acene- and phenanthrene-edge-type hydrocarbons as a function of $n(0)$ and μ^*

	μ^*	$n(0) = 2.0$	$n(0) = 3.0$	$n(0) = 4.0$
Benzene	0.10	56.04	131.86	194.60
	0.15	32.43	99.72	160.97
	0.20	15.21	70.38	128.35
Naphthalene	0.10	22.48	73.62	124.28
	0.15	9.30	49.05	95.82
	0.20	2.39	28.75	69.48
Phenanthrene	0.10	39.54	101.16	154.55
	0.15	21.17	74.19	125.64
	0.20	8.72	50.13	97.90
Chrysene	0.10	5.08	30.17	63.78
	0.15	0.94	15.51	43.03
	0.20	0.04	5.96	25.70

the monoanion of tetracene was estimated to be about 3 K [13]. Therefore, molecular edge structures as well as molecular sizes have relevance to the values of the T_c s.

5. POSSIBLE T_c S FOR THE MONOANIONS OF CORONENE AND CORANNULENE

Let us take a look at the electron–phonon coupling of the E_{2g} modes to the E_{1g} electronic state in the monoanion of coronene. The calculated electron–phonon coupling constants in the monoanions of coronene and corannulene [15] are shown in Fig. 6. We can see from Fig. 6 that the C–C stretching E_{2g} mode of 1668 cm^{-1} strongly couples to the E_{1g} electronic state in the monoanion of coronene. Let us next look at the electron–phonon coupling of the E_2 vibrational modes to the E_1 electronic state in the monoanion of corannulene. Figure 6 demonstrates that the lowest frequency E_2 mode of 142 cm^{-1} the most strongly couples to the E_1 electronic state in the monoanion of corannulene. In addition to this mode, the low frequency E_2 modes of 282 and 613 cm^{-1} and the C–C stretching E_2 mode of 1669 cm^{-1} afford large electron–phonon coupling constants. The high frequency modes are mostly tangential in character, while the low frequency modes have mostly a radial character in corannulene. The calculated total electron–phonon coupling constants in the monoanions of coronene and corannulene are 0.076 and 0.269 eV, respectively. Therefore, the total electron–phonon coupling constant in the monoanion of corannulene is much larger than that in the monoanion of coronene. As mentioned above, not only the C–C stretching mode but also the low frequency modes play a role in the electron–phonon coupling in the monoanion of corannulene, while only the C–C stretching mode plays an essential role in the electron–phonon coupling in the monoanion of coronene. Therefore, the essential role of the low frequency modes in the electron–phonon coupling in the monoanion of corannulene is the main reason that the total electron–phonon coupling is much stronger in the monoanion of corannulene than in the monoanion of coronene. Such a remarkable contrast in their electron–phonon interactions is expressed by structural difference between coronene and corannulene as follows. Orbital interactions between two neighboring carbon atoms in coronene have pure π -character because of its planar structure, whereas those in corannulene have intermediate character between σ - and π -characters because of the curvatures, and thus orbital interactions between two neighboring carbon atoms in corannulene are stronger than those in coronene. As a consequence, the electron–phonon coupling is stronger in the monoanion of corannulene than in the monoanion of coronene. Furthermore, because in planar coronene the inner six-membered ring is combined with the outer 18-membered ring through the six spoke bonds, the D_{6h} framework of coronene would be rather rigid. Although in corannulene there are also spoke bonds that combine the inner five-membered ring and the outer 15-membered ring, C_{5v} framework of corannulene is not so rigid, as confirmed from facts that the carbon framework of corannulene is easily inverted at room temperature [24–26]

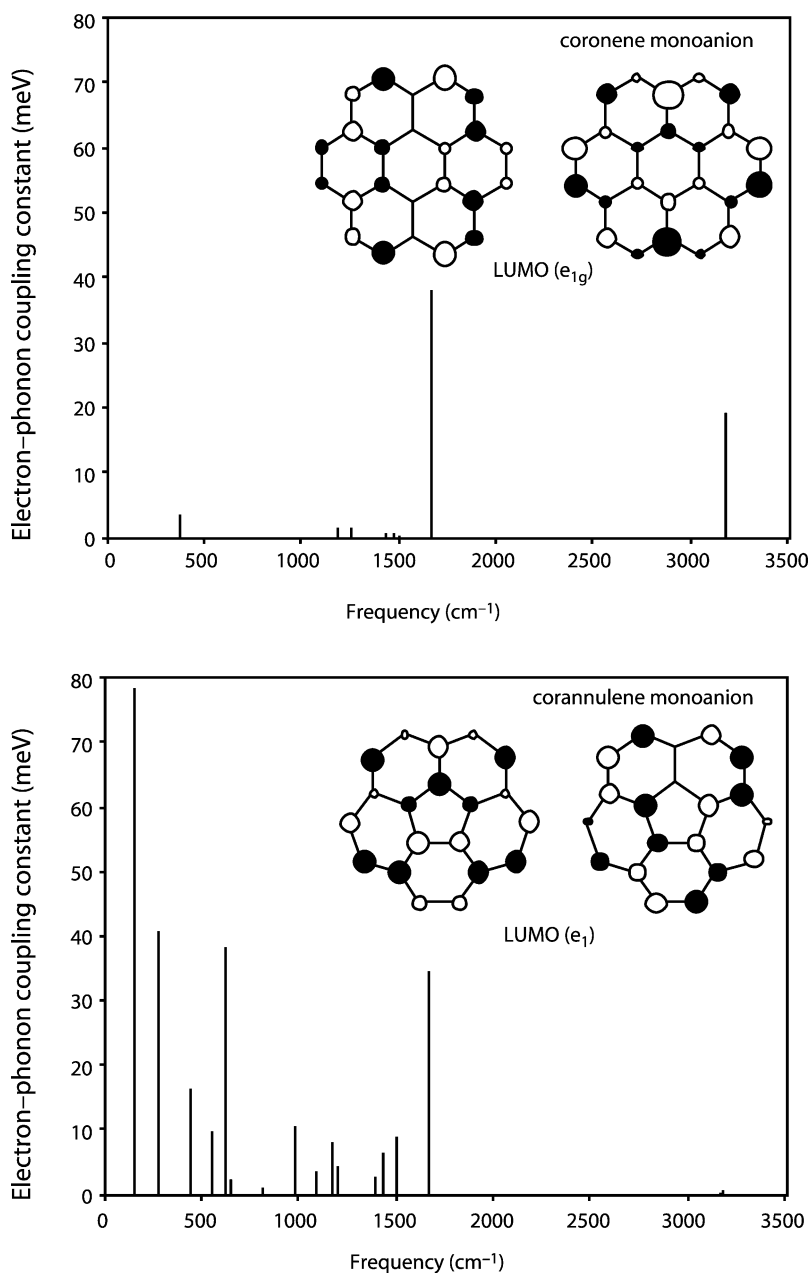


Fig. 6. Electron–phonon coupling constants in the monoanions of coronene and corannulene.

and the relative bowl depth is significantly decreased by electron doping. The low frequency Jahn–Teller active E_2 modes of vibration which have mostly a radial character have relevance to the interesting molecular motion. On the other hand, the Jahn–Teller active E_{2g} modes of coronene and the resultant molecular distortions in its anions are strictly fixed on the molecular plane by symmetry [27]. We can thus conclude that the low frequency flexible Jahn–Teller E_2 modes in which the atomic motion is somewhat vertical to the bowl-shaped structure of corannulene should lead to large electron–phonon coupling constants. Calculated T_c s for the monoanions of coronene and corannulene as a function of $n(0)$ and μ^* are indicated in Table 2.

According to our calculations, the T_c s for the monoanion of corannulene is expected to be by an order of magnitude higher than that for the monoanion of coronene if we assume that the monoanions of both coronene and corannulene whose electronic states are twofold degenerate would have similar $n(0)$ values, and usual μ^* values of 0.10–0.20. For example, the calculated values of T_c s for the monoanions of coronene and corannulene are about 0.05–8.86 and 29.17–65.56 K, respectively, in the range of $n(0) = 4$ –5 and $\mu^* = 0.10$ –0.20. Of course, strong electron–phonon coupling generally causes a charge density wave (CDW) and make the system insulating and we cannot rule out such a possibility.

The graphite intercalation compounds (GICs) exhibit superconductivity [28], but in contrast to the A_3C_{60} complexes the T_c values of the GICs are low, the highest T_c being 5.5 K in C_4K [29]. On the other hand, the alkali-doped fullerenes (A_3C_{60}) have high T_c s: 33 K [4] and even 40 K under pressure [5]. Considering that GICs and A_3C_{60} have the T_c s of -5 and -40 K, respectively, and that the T_c s for the monoanions of coronene and corannulene are estimated, for example, to be about 0.05–8.86 and 29.17–65.56 K under some conditions, respectively, we can characterize the electronic features of coronene and corannulene in that coronene and corannulene can be viewed as fragments of one-sheet of graphite and C_{60} , respectively. The main difference between structures of coronene and one-sheet of graphite and those of corannulene and C_{60} is induced by the curvatures of the latter. Orbital interactions between two neighboring carbon atoms in coronene and one-sheet of graphite have pure π -character because of their planar structures,

Table 2. Calculated T_c s (K) for the monoanions of coronene and corannulene as a function of $n(0)$ and μ^*

	μ^*	$n(0) = 3.0$	$n(0) = 4.0$	$n(0) = 5.0$
Coronene	0.10	0.03	1.59	8.86
	0.15	–	0.05	1.52
	0.20	–	–	0.05
Corannulene	0.10	30.58	49.78	65.56
	0.15	21.13	39.15	54.74
	0.20	13.09	29.17	44.19

whereas those in corannulene and C_{60} have intermediate character between σ - and π -characters owing to bowl-shaped structures, and thus orbital interactions between two neighboring carbon atoms in corannulene and C_{60} are stronger than those in coronene and one-sheet of graphite. As a consequence, the vibronic couplings (electron–phonon couplings) are much stronger in corannulene and C_{60} than in coronene and graphite. This may be one of the principal reasons that A_3C_{60} exhibits higher temperature superconductivity than GICs, and accordingly the monoanion of corannulene is expected to exhibit much higher temperature superconductivity than the monoanion of coronene.

6. CONCLUDING REMARKS

We have studied vibronic interaction and its role in the occurrence of possible superconductivity in hydrocarbons. We have computed the electron–phonon coupling constants. The total electron–phonon coupling constants for the monoanions of anthracene, tetracene, and pentacene are estimated to be 0.186, 0.154, and 0.127 eV, respectively, whereas those for the monoanions of phenanthrene, chrysene, and benzo[a]chrysene are estimated to be 0.300, 0.194, and 0.179 eV, respectively. Therefore, the electron–phonon coupling constants decrease with an increase in the number of carbon atoms in both acene- and phenanthrene-edge-type hydrocarbons. The total electron–phonon coupling constants for the monoanions of phenanthrene-edge-type hydrocarbons are larger than those for the monoanions of acene-edge-type hydrocarbons. Therefore, not only molecular sizes but also molecular edge structures have relevance to the strength of the electron–phonon coupling. We estimated possible T_c s for the monoanions of phenanthrene-edge-type hydrocarbons. According to our calculation, the monoanions of phenanthrene-edge-type hydrocarbons would have higher T_c s than the monoanions of acene-edge-type hydrocarbons if the monoanions of phenanthrene-edge-type hydrocarbons exhibit superconductivity.

We have also studied electron–phonon coupling and its role in the occurrence of possible superconductivity in the monoanions of coronene and corannulene. Our calculational result shows that the C–C stretching E_{2g} mode of 1668 cm^{-1} plays an essential role in the electron–phonon coupling in the monoanion of coronene and that the low frequency E_2 modes which have mostly a radial character and the C–C stretching E_2 mode of 1669 cm^{-1} which has a tangential character afford large electron–intramolecular-phonon coupling constants in the monoanion of corannulene. The calculated total electron–intramolecular-phonon coupling constant for the monoanion of corannulene (0.269 eV) is much larger than that for the monoanion of coronene (0.076 eV). We estimated possible T_c values for the monoanions of coronene and corannulene. The calculated T_c value for the monoanion of corannulene is by an order of magnitude larger than that for the monoanion of coronene. The main structural difference between coronene and corannulene is induced by the curvature of the latter. Because of the planar structure,

orbital interactions between two neighboring carbon atoms in coronene have pure π -character, whereas those in corannulene have intermediate character between σ - and π -characters owing to the bowl-shaped structure, and thus orbital interaction between two neighboring carbon atoms in corannulene are stronger than those in coronene. As a consequence, the electron–phonon couplings are much stronger in the monoanion of corannulene than in the monoanion of coronene. Therefore, the monoanion of corannulene is expected to have higher T_c than the monoanion of coronene if these anions exhibit superconductivity caused by intramolecular vibronic interactions and Jahn–Teller effects. In a similar way, strong orbital interactions between two neighboring carbon atoms due to bowl-shaped structure of C_{60} may be one of the main reasons that A_3C_{60} exhibits higher temperature superconductivity than GICs.

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REFERENCES

- [1] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1977, **578**, 1977.
- [2] (a) I. B. Bersuker, *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry*, Plenum, New York, 1984; (b) I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, Berlin, 1989.
- [3] (a) A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, 1991, **350**, 600; (b) M. J. Rosseinsky, A. P. Ramirez, S. H. Glarum, D. W. Murphy, R. C. Haddon, A. F. Hebard, T. T. M. Palstra, A. R. Kortan, S. M. Zahurak and A. V. Makhija, *Phys. Rev. Lett.*, 1991, **66**, 2830.
- [4] K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo and S. Kuroshima, *Nature*, 1991, **352**, 222.
- [5] T. T. M. Palstra, O. Zhou, Y. Iwasa, P. E. Sulewski, R. M. Fleming and B. R. Zegarski, *Solid State Commun.*, 1995, **93**, 327.
- [6] (a) C. M. Varma, J. Zaanen and K. Raghavachari, *Science*, 1991, **254**, 989; (b) M. Lannoo, G. A. Baraff, M. Schlüter and D. Tomanek, *Phys. Rev. B*, 1991, **44**, 12106; (c) Y. Asai and Y. Kawaguchi, *Phys. Rev. B*, 1992, **46**, 1265; (d) J. C. R. Faulhaber, D. Y. K. Ko and P. R. Briddon, *Phys. Rev. B*, 1993, **48**, 661; (e) V. P. Antropov, O. Gunnarsson and A. I. Lichtenstein, *Phys. Rev. B*, 1993, **48**, 7651; (f) A. Auerbach, N. Manini and E. Tosatti, *Phys. Rev. B*, 1994, **49**, 12998; (g) N. Manini, E. Tosatti and A. Auerbach, *Phys. Rev. B*, 1994, **49**, 13008; (h) O. Gunnarsson, *Phys. Rev. B*, 1995, **51**, 3493; (i) O. Gunnarsson, H. Handschuh, P. S. Bechthold, B. Kessler, G. Ganteför and W. Eberhardt, *Phys. Rev. Lett.*, 1995, **74**, 1875; (j) J. L. Dunn and C. A. Bates, *Phys. Rev. B*, 1995, **52**, 5996; (k) O. Gunnarsson, *Rev. Mod. Phys.*, 1997, **69**, 575; (l) A. Devos and M. Lannoo, *Phys. Rev. B*, 1998, **58**, 8236.
- [7] R. C. Haddon, *Acc. Chem. Res.*, 1992, **25**, 127.
- [8] E. A. Silinch and V. Capek, *Organic Molecular Crystals*, AIP, New York, 1994.
- [9] W. Warta and N. Karl, *Phys. Rev. B*, 1985, **32**, 1172.

- [10] W. Warta, R. Stehle and N. Karl, *Appl. Phys. A*, 1985, **36**, 163.
- [11] S. Kivelson and O. L. Chapman, *Phys. Rev. B*, 1983, **28**, 7236.
- [12] A. Mishima and M. Kimura, *Synth. Met.*, 1985, **11**, 75.
- [13] T. Kato and T. Yamabe, *J. Chem. Phys.*, 2001, **115**, 8592.
- [14] T. Kato, K. Yoshizawa and K. Hirao, *J. Chem. Phys.*, 2002, **116**, 3420.
- [15] T. Kato and T. Yamabe, *J. Chem. Phys.*, 2002, **117**, 2324.
- [16] (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- [17] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
- [18] (a) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; (b) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
- [19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, in *GAUSSIAN 98*, Gaussian Inc., Pittsburgh, PA, 1998.
- [20] (a) G. M. Eliashberg, *Zh. Eksp. Teor. Fiz.*, 1960, **38**, 966; (b) G. M. Eliashberg, *Zh. Eksp. Teor. Fiz.*, 1960, **39**, 1437; (c) G. M. Eliashberg, *Sov. Phys. JETP*, 1960, **11**, 696; (d) G. M. Eliashberg, *Sov. Phys. JETP*, 1961, **12**, 1000.
- [21] P. B. Allen, *Phys. Rev. B*, 1972, **6**, 2577.
- [22] W. L. McMillan, *Phys. Rev.*, 1968, **167**, 331.
- [23] M. Schlüter, M. Lannoo, M. Needels, G. A. Baraff and D. Tomanek, *J. Phys. Chem. Solids*, 1992, **53**, 1473.
- [24] L. T. Scott, M. M. Hashemi and M. S. Bratcher, *J. Am. Chem. Soc.*, 1992, **114**, 1920.
- [25] R. L. Disch and J. M. Schulman, *J. Am. Chem. Soc.*, 1994, **116**, 1533.
- [26] A. Sygula and P. W. Rabideau, *J. Chem. Soc., Chem. Commun.*, 1994, 1497.
- [27] T. Kato, K. Yoshizawa and T. Yamabe, *J. Chem. Phys.*, 1999, **110**, 249.
- [28] N. B. Hannary, T. H. Geballe, B. T. Matthias, K. Andress, P. Schmidt and D. MacNair, *Phys. Rev. Lett.*, 1965, **14**, 225.
- [29] I. T. Belash, A. D. Bronnikov, O. V. Zharikov and A. V. Palnichenko, *Synth. Met.*, 1990, **36**, 283.

The Spin Hamiltonian Effective Approach to the Vibronic Effects – Selected Cases

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Abstract

Here we propose and apply the use of spin Hamiltonian for the effective analytic description and fit to the computed spectrum of correspondingly selected states as a strategy to describe the potential energy surfaces and related vibronic effects in terms of physically meaningful valence bond picture. In order to achieve numerical precision and a physically consistent parameterization we introduced here new terms to the spin Hamiltonian, equated in the intercentric biquadratic form, invested with the meaning of interbond interaction, avoiding the artifact of large next nearest neighbor direct spin coupling constants in the numerical fit. This model was applied for prototypic vibronic cases: (i) the Jahn–Teller effect H_3 molecule regarded as a spin-frustration topology and (ii) the bond length alternation *vs.* homogeneity in conjugated hydrocarbons (C_4H_4 and C_6H_6) as manifestation *vs.* silence, respectively, of a pseudo-Jahn–Teller effect involving states effectively described by the spin Hamiltonian.

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1. INTRODUCTION

The Heisenberg–Dirac–van Vleck (HDDVV) spin Hamiltonian [1] is a well-known phenomenological model that became very popular and routinely used in the last

decade, in conjunction with the vogue of molecular magnetism in chemistry [2]. At the same time, the spin Hamiltonian was used in elegant modeling of electronic spectra of polyenes [3] and bond-alternation in Peierls distortion [4]. Other works concerned formal development and application in large systems like fullerenes and extended chains and networks, including the relation with graph theory [5]. Acknowledging that the red line of such applications of the spin Hamiltonian points toward its utility in the modeling Jahn–Teller (JT) and pseudo Jahn–Teller (PJT) cases we advocate here for the systematic renewed attention devoted to the spin Hamiltonian, investigating its limits and the necessary extensions. We note that this line should be regarded distinguished from the realm of physical problems involving the interplay of spin interactions with the orbital degeneracy [6] and vibronic effects in phenomena like magnetic anisotropy, double exchange and huge magneto-resistance.

The spin Hamiltonian is conceptually rooted in Valence Bond (VB) theory being amended with the phenomenological assumption that parameters having the formal shape of exchange integrals are effective including many other contributions from the total Hamiltonian (e.g. kinetic exchange, overlap terms). The Valence Bond, in its CASVB modern form [7,8] is suited for accurate quantum approach, taking the advent of multideterminant wavefunctions, essential for good description of the electronic structure, especially in the calculation of potential energy surfaces and curve crossing problems. At the same time, the VB language, in a very qualitative form, is a longstanding tool of the current chemical intuition, investing this kind of approach with transparency towards a larger public.

The above synoptic picture determined us explore in this key selected prototypic cases (H_3 , as the simplest system with $e \otimes E$ JT effect, the bond alternation in cyclobutadiene as PJT effect). Keeping in mind the technical relationship between CASSCF and CASVB methods we performed corresponding CASSCF calculations for a selected number of states as function of active distortion coordinates. Then the subsequent fit by means of effective spin Hamiltonian model was approached, accomplishing the task of expressing the vibronic quantities in terms of Valence Bond concepts.

2. THE SPIN HAMILTONIAN AND ITS GENERALIZATION

The starting point is the observation that the genuine HDVV spin Hamiltonian is able to describe the double degenerate state of an equilateral triangle of centers with the spin 1/2. This gives a primary suggestion for the utility of HDVV-like frame in particular JT problems. Another direction concerns the view of bond alternation in antiaromatic systems (e.g. cyclobutadiene C_4H_4 , cyclo-octatetraene C_8H_8) [9] as a formal PJT effect with respect of the homogenous structure. Conversely, the aromaticity appears as resistance against this type of distortion. A natural incidence with the spin Hamiltonian is reached in the view that the chemical bond in conjugated systems is better understood in the frame of VB resonance structures.

The customary form of the spin Hamiltonian is

$$\hat{H} = -2 \sum_{j < i} J_{ij} \hat{S}_i \cdot \hat{S}_j \quad (1)$$

This expression is sufficient in the simplified simulation of magnetic susceptibility in polynuclear coordination compounds, where the case of very weakly interacting centers occurs. A non-trivial inquire is whether the HDVV is literally valid for strongly bonded system—the present discussion having as implicit goal the corresponding answer.

The generalization of spin Hamiltonian including biquadratic $J_{ij}(\hat{S}_i \cdot \hat{S}_j)^2$ or antisymmetric terms $a_{ij}\hat{S}_i \otimes \hat{S}_j$ is proven necessary for certain detailed purposes of theory and experiment in polymetallic systems [10,11]. However, a computational test for further necessary terms of spin Hamiltonian is scarcely approachable for weakly interacting metal ions, given the difficult goal of obtaining precision of few cm^{-1} in large systems with many metal and ligand atoms, even though some efforts in this direction were attempted [6].

To be distinguished, the use of HDVV paradigm in systems with firm covalent bonds may really reveal the extension to which the model itself is applicable and to suggest the further necessary terms. This is indeed the case encountered in our approach. We found that for an improved description of selected set of states, the spin Hamiltonian has to be expanded with new terms, proposed here as the intercentric generalization of the traditional biquadratic terms. We propose and use here the following extended form:

$$\hat{H} = -2 \sum_{j < i} (J_{ij} + 1/2) \hat{S}_i \cdot \hat{S}_j + 8 \sum_{j < i} \sum_{l < k} B_{ij,kl} (\hat{S}_i \cdot \hat{S}_j) (\hat{S}_k \cdot \hat{S}_l) \quad (2)$$

Note that when the absolute energies of states are targeted, the $J_{ij} + 1/2$ factor should be used instead of simple J_{ij} , sufficient only when the energy gaps are needed. The factor 8 in the front of biquadratic terms was conventionally chosen to avoid fractional expressions in the case of half-integer spins. The need for biquadratic part is shortly explained taking the example of a rectangular system with 1/2 spins. In this case the usual HDVV Hamiltonian has two parameters (along two different rectangle edges) while there are five distinct energy states to be reproduced. Similarly, making the system a perfect square there are four different states while only one spin-coupling constant. In the rectangle–square case one may gain a further HDVV parameter including the interaction between centers placed along diagonal. According to the physical intuition, this is expected to be small. However, actual application tested that during the fitting this parameter tends to have large magnitude. It is reasonable to accept that the full spectrum cannot be reproduced within pure HDVV limitation looking then for a possible extension.

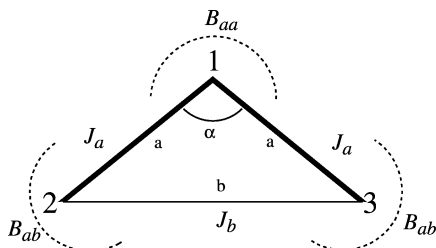
We suggest here that the non-nearest center interaction can be regarded as having indirect nature *via* intercentric biquadratic terms of the form $(\hat{S}_i \cdot \hat{S}_j)(\hat{S}_i \cdot \hat{S}_k)$ and $(\hat{S}_i \cdot \hat{S}_j)(\hat{S}_k \cdot \hat{S}_l)$. Such terms look like the generalization of the traditional biquadratic form $(\hat{S}_i \cdot \hat{S}_j)^2$ initially proposed for dimmers, justified from experiment as useful

correction [12]. The biquadratic terms can be regarded as perturbational supplement to the spin Hamiltonian [13]. If dichotomize the total Hamiltonian in monoelectronic, h , and bielectronic parts, g , with the excitations separated in single to quadruple components (T_1 to T_4) then the above-mentioned biquadratic terms stand for different terms of coupled-cluster type expansion, e.g. $[g, T_4]$, $[[g, T_2], T_2]$, $\times [[h, T_2], T_2], T_3]$, $[[h, T_2], T_4]$, etc., taken with respect of a reference which is generally not a solution of a Fock operator. As a technical detail, note that the biquadratic intercentric parameters are symmetric in the sense $B_{ij,kl} = B_{kl,ij}$ and $B_{ik,jk} = B_{jk,ik}$. The tetracentric operator is also symmetric to pair permutations $(\hat{S}_i \cdot \hat{S}_j)(\hat{S}_k \cdot \hat{S}_l) \equiv (\hat{S}_k \cdot \hat{S}_l)(\hat{S}_i \cdot \hat{S}_j)$, while the tricentric one is not, the symmetrized form $B_{ik,jk}((\hat{S}_i \cdot \hat{S}_k)(\hat{S}_j \cdot \hat{S}_k) + (\hat{S}_j \cdot \hat{S}_k)(\hat{S}_i \cdot \hat{S}_k))$ being necessary if restrict the summation on independent couples of pairs. For sake of generality the Hamiltonian (2) is given for run over all pairs of pairs.

3. A JAHN–TELLER SYSTEM MODELED THROUGH GENERALIZED SPIN HAMILTONIAN: THE H_3 MOLECULE

The H_3 regular triangle is an $e \otimes E$ JT system whose ground and excited states, ${}^2E'$ and ${}^4A_2'$ in D_{3h} are reproduced also by the simple HDVV Hamiltonian. The orbital degenerate spin doublet is intrinsically related to the problem of spin frustration in triangular systems [14]. The analysis of potential energy surface, the conical intersection and the dynamics of the H_3 system are thoroughly approached in the literature [15]. We do not follow here the challenge of improving the calculations up to spectral accuracy and comparison to experiment, taking the quantum calculation (CASSCF(3,3)/6-311G with three electrons fully excited over the a_1' and e' orbitals) as a convenient, qualitatively salient source for the fit in terms of spin Hamiltonian. The purpose is merely the formal development, while the numeric goals are confined to the semiquantitative level.

For sake of simplicity we will treat explicitly only the θ mode of the degenerate e' instability coordinate, accounted as function of the top angle, α , driving the triangle from equilateral to isosceles (see Scheme 1). The radial part was taken imposing for



Scheme 1.

the edges denoted with ‘ a ’ the bond length (1.2711 Å) found after minimizing the energy of D_{3h} system with state averaging over the two degenerate components. The state averaging was kept also for the CASSCF along the distortion. The calculations in this work were performed with the GAMESS code [16].

The spin Hamiltonian particularized from general form (2) to the isosceles depicted in the Scheme 1 is

$$\begin{aligned}\hat{H} = & K(\alpha) - J_a - J_b/2 - 2J_a(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3) - 2J_b\hat{S}_2 \cdot \hat{S}_3 \\ & + 8B_{aa}[(\hat{S}_1 \cdot \hat{S}_2)(\hat{S}_1 \cdot \hat{S}_3) + (\hat{S}_1 \cdot \hat{S}_3)(\hat{S}_1 \cdot \hat{S}_2)] + 8B_{ab}[(\hat{S}_1 \cdot \hat{S}_2)(\hat{S}_2 \cdot \hat{S}_3) \\ & + (\hat{S}_2 \cdot \hat{S}_3)(\hat{S}_1 \cdot \hat{S}_2) + (\hat{S}_1 \cdot \hat{S}_3)(\hat{S}_2 \cdot \hat{S}_3) + (\hat{S}_2 \cdot \hat{S}_3)(\hat{S}_1 \cdot \hat{S}_3)]\end{aligned}\quad (3)$$

where $K(\alpha)$ together accomplish the role of positive harmonic force constant in the JT formalisms, J_a and J_b are the regular HDVV parameters along the different edges and finally B_{aa} and B_{ab} being the newly introduced parameters having the aspect of bond–bond interactions. Note that the traditional monocentric biquadratic terms do not play any role in systems with 1/2 spin centers, the newly proposed formula (2) being a natural extension to get the supplementary parameters that are technically necessary for the full account of curve crossing, including the excited spin quartet state.

As an illustration for the necessity of richer parametric scheme note that in the frame of simple HDVV the barycenter of ${}^2E'$ term is constant. At the same time, the gap between one component of spin doublet and the quartet is $-3J_a$. In the limit of angular distortion, keeping constant the bond length ‘ a ’, this practically means an equal spacing of these states. The *ab initio* calculations do not retrieve such constant relationships among the splitted terms along distortion. Therefore the supplementary parameters are taking implicitly the role of ‘bond-in-molecule’ dependence of the HDVV part allowing to keep J as function of intercenter distances only. The HDVV coupling parameters as function of geometry are taken as an exponential dependence on the intercenter distance R_{ij} .

$$J_{ij} = \sum_{k=1}^2 a_k \exp(-b_k R_{ij}) \quad (4)$$

In our case the two HDVV parameters are implicitly a unique function of the angle α , $J_a = J(\alpha)$ and $J_b = J(90 - \alpha/2)$, becoming equal, $J_a = J_b = J(60^\circ)$, at symmetrized structure. A similar reason is hold for the B_{aa} and B_{ab} parameters for which the numerical was convenient also with an exponential form similar to equation (4).

With equation (3), the energies of spin doublet equating the JT problem are ascribed in the matrix form as follows:

$$E_{S=1/2}(\alpha) = \begin{pmatrix} K(\alpha) - B_{aa} - 2B_{ab} - \varepsilon & J_a - J_b + 2B_{aa} - 2B_{ab} \\ J_a - J_b + 2B_{aa} - 2B_{ab} & K(\alpha) - B_{aa} - 2B_{ab} - \varepsilon \end{pmatrix} \quad (5)$$

the remaining spin quartet being correspondingly,

$$E_{S=3/2}(\alpha) = K(\alpha) - 2J_a - J_b + B_{aa} + 2B_{ab} \tag{6}$$

where $K(\alpha)$ is a positive force constant (taken as a fourth order polynomial).

The computed adiabatic potential energy curves (marked points) together with their fit to the model (continuous and dashed lines) are shown in Fig. 1. Note that the H_3 is notoriously a non-bonded system [15]. Therefore the minimum at acute angles is relative and the section of the potential energy surface of the e' term does not have at opposite distortion the well-known profile related with the ‘mexican-hat’ or ‘tricorn’ pattern. The strong anharmonicity of the curves suggests the need for a Hamiltonian beyond usual perturbation model of JT effect, the present approach offering an opening of this kind.

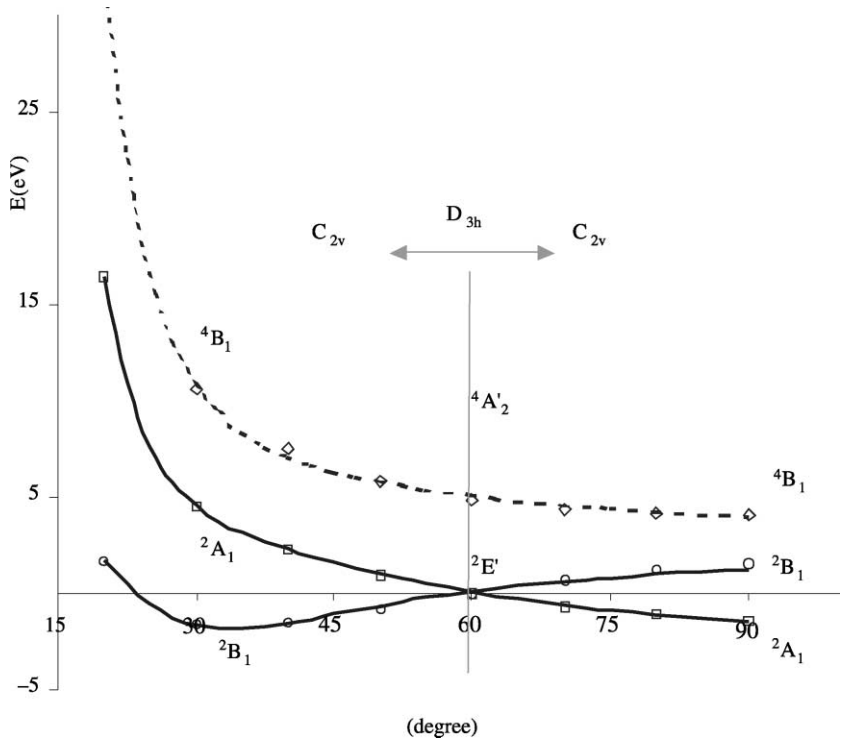


Fig. 1. The potential energy curves with respect of the top angle in H_3 isosceles triangle as illustration of θ coordinate of the $e \otimes E$ JT distortion. The marked points shows the CASSCF computed values, the continuous and dashed lines corresponding to the fit with Hamiltonian of equation (3).

In the actual construction the vibronic constant taken as the coordinate derivative of non-diagonal matrix element in equation (5) took a form depending on the spin-Hamiltonian effective parameters:

$$V_{JT}^E = \frac{d}{d\alpha} (J(\alpha) - J(90 - \alpha) + 2B(\alpha) - 2B(90 - \alpha)) = 0.076 \text{ (eV/degree)} \quad (7)$$

where the angular dependence is taken from equation (4).

The VB simplified model of ground-state potential energy surface H_3 system considered as transition state and stabilization valleys of the $H + H_2$ reaction is also an early problem, belonging to the history of physical chemistry under the name London–Eyring–Polanyi–Sato (LEPS) model that continues to serve as basis of further related developments [17,18]. The actual analysis is a new a focus on the JT point of this potential energy surface able to absorb results of further renewed CASCCF type calculations on this important system.

4. A PSEUDO-JAHN–TELLER SYSTEM MODELED THROUGH GENERALIZED SPIN HAMILTONIAN: THE C_4H_4 MOLECULE

In the following we will apply the strategy of spin Hamiltonian fit of the adiabatic potential energy surfaces for a system addressing the problem of bond alternation in antiaromatic conjugated system, interpreted as a PJT effect. The simplest system of this type is the cyclobutadiene, considering its distortion with respect of regular square (D_{4h}) to rectangle, (D_{2h}) as the $(a_{1g} + b_{1g}) \otimes B_{1g}$ PJT effect (symmetry notation is valid for the molecular orientation that have the C–C bonds intersected by the C_2' axes, while the C_2'' ones are passing through atoms).

The optimum geometry in the given calculations (using CASSCF(4,4)/6-31G over the four π orbitals and electrons) is a rectangle with two types of bond lengths, $r_a = 1.3657 \text{ \AA}$ and $r_b = 1.5533 \text{ \AA}$ corresponding to double and single bonds respectively. Enforcing a square geometry, the optimized unique bond length is $r_a = r_b = r_0 = 1.4521 \text{ \AA}$. Noting that rectangular and square geometries keep almost the same radius of carbon atoms with respect of molecular barycenter (1.034 vs. 1.026 $\text{\AA}$, respectively) we confined for sake of clarity to the use of simple nuclear coordinate, namely the radius of r_a tuned from shorter to longer, while r_b results from the condition $r_a^2 + r_b^2 = 2r_0^2$. This coordinate passes very close to the absolute minima, being a convenient choice for a one-dimensional potential energy curve. The other geometry parameters (CH bond length and CCH bond angles) were subject of optimization along the distortion coordinate [16].

The shallow double well shape of the ground-state energy curve has the well-known pattern of PJT effect corresponding to different directions of square elongation. Among the many excited states, two spin singlets, three spin triplets, and

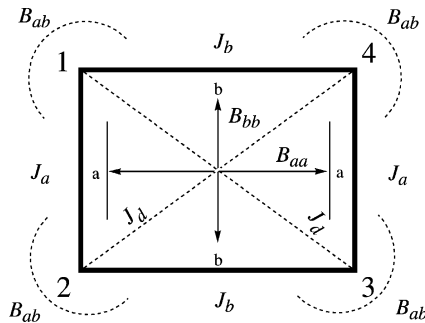
one spin quintet are described by the spin Hamiltonian, being correspondingly selected from the whole CASSCF result.

The used spin Hamiltonian is presented in equation (8),

$$\begin{aligned}
 \hat{H} = & K(q) - J_a - J_b - 2J_a(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_4) - 2J_b(\hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3) \\
 & + 16B_{aa}(\hat{S}_1 \cdot \hat{S}_2)(\hat{S}_3 \cdot \hat{S}_4) + 16B_{bb}(\hat{S}_1 \cdot \hat{S}_4)(\hat{S}_2 \cdot \hat{S}_3) + 8B_{ab}[(\hat{S}_1 \cdot \hat{S}_2)(\hat{S}_1 \cdot \hat{S}_4) \\
 & + (\hat{S}_1 \cdot \hat{S}_4)(\hat{S}_1 \cdot \hat{S}_2) + (\hat{S}_2 \cdot \hat{S}_1)(\hat{S}_2 \cdot \hat{S}_3) + (\hat{S}_2 \cdot \hat{S}_3)(\hat{S}_2 \cdot \hat{S}_1) + (\hat{S}_3 \cdot \hat{S}_2)(\hat{S}_3 \cdot \hat{S}_4) \\
 & + (\hat{S}_3 \cdot \hat{S}_4)(\hat{S}_3 \cdot \hat{S}_2) + (\hat{S}_4 \cdot \hat{S}_1)(\hat{S}_4 \cdot \hat{S}_3) + (\hat{S}_4 \cdot \hat{S}_3)(\hat{S}_4 \cdot \hat{S}_1)]
 \end{aligned} \quad (8)$$

along with Scheme 2 showing the meaning of parameters. The $J_a = J(r_a)$ and $J_b = J(r_b)$ are the regular coupling constants assigned to the different bonds, fitted by an exponential form like equation (4). The J_d is a diagonal term, corresponding to non-bonded coupling. This was set to zero in order to prevent results offending the physical intuition but was formally kept in the energy expressions (9)–(12). A look into these formulas reveals that without the newly introduced terms of biquadratic coupling, the pattern of HDVV-type spectrum selected from *ab initio* results cannot be described without the non-physical help of J_d . It is then seen that the biquadratic terms are accounting for long-range interactions while keeping for the traditional HDVV part the account of bonded interactions only. In a rectangular shape the B_{ab} parameter can be intuitively interpreted as interaction between spin pairs located on double bond and single bond sides. The B_{aa} and B_{bb} represent the interaction between spin pairs located on the parallel bonds.

The spin singlet states of HDVV Hamiltonian are those forming the problem of PJT effect related to the bond alternation. Using the symmetry labels of D_{4h} one may write the following model Hamiltonian whose non-diagonal matrix element



Scheme 2.

vanishes at square geometry:

$${}^1A_g, {}^1B_{1g} : \begin{pmatrix} K_0 + J_a + J_b - 2J_d + 7B_{aa} + 7B_{bb} + 4B_{ab} - \varepsilon & \sqrt{3}(J_a - J_b + 2B_{aa} - 2B_{bb}) \\ \sqrt{3}(J_a - J_b + 2B_{aa} - 2B_{bb}) & K_0 - J_a - J_b + 2J_d + 3B_{aa} + 3B_{bb} - 12B_{ab} - \varepsilon \end{pmatrix} \quad (9)$$

It is interesting to note that the spin triplet states of the HDVV-type have an orbital degenerate state at D_{4h} which can be presented as an excited state JT effect, the corresponding matrix formulation being:

$${}^3E_u : \begin{pmatrix} K_0 - J_a - J_b - B_{aa} - B_{bb} - 4B_{ab} - \varepsilon & J_a - J_b - 2B_{aa} + 2B_{bb} \\ J_a - J_b - 2B_{aa} + 2B_{bb} & K_0 - J_a - J_b - B_{aa} - B_{bb} - 4B_{ab} - \varepsilon \end{pmatrix} \quad (10)$$

Another triplet state has the following formula:

$${}^3B_{2g} : K_0 - 2J_d - 3B_{aa} - 3B_{bb} + 4B_{ab} \quad (11)$$

being located between the two singlet states and finally, the quintet

$${}^5A_g : K_0 - 2J_a - 2J_b - 2J_d + B_{aa} + B_{bb} + B_{ab} \quad (12)$$

the highest state of HDVV spectrum (though not of the full $\pi-\pi$ spectrum containing higher singlet and triplet states with ionic nature). For all the states a common background given by an oscillator estimated with quadratic and quartic terms was added under the term of K_0 . For the PJT Hamiltonian this forms the non-vibronic part of the curvature, together with the other terms on the first diagonal in equation (9).

We encountered in this case the interesting situation of expressing the PJT and a JT vibronic constants by an unique set of parameters offered by the spin Hamiltonian expansion:

$$\begin{aligned} V_{\text{PJT}} &= \sqrt{3} \frac{d}{dr} \left(J(r) - J\left(\sqrt{2r_0^2 - r^2}\right) \right) + 2\sqrt{3} \frac{d}{dr} \left(B_{aa}(r) - B_{aa}\left(\sqrt{2r_0^2 - r^2}\right) \right) \\ &= 5.71 \text{ (eV/\AA)} \\ V_{\text{JT}} &= \frac{d}{dr} \left(J(r) - J\left(\sqrt{2r_0^2 - r^2}\right) \right) + 2 \frac{d}{dr} \left(B_{aa}(r) - B_{aa}\left(\sqrt{2r_0^2 - r^2}\right) \right) \\ &= 10.49 \text{ (eV/\AA)} \end{aligned} \quad (13)$$

For sake of gaining precision in the description of PJT and JT problems we performed the fit imposing the preponderant weight on the corresponding states, presented in Fig. 2. The other states (the remaining triplet and the quintet) were

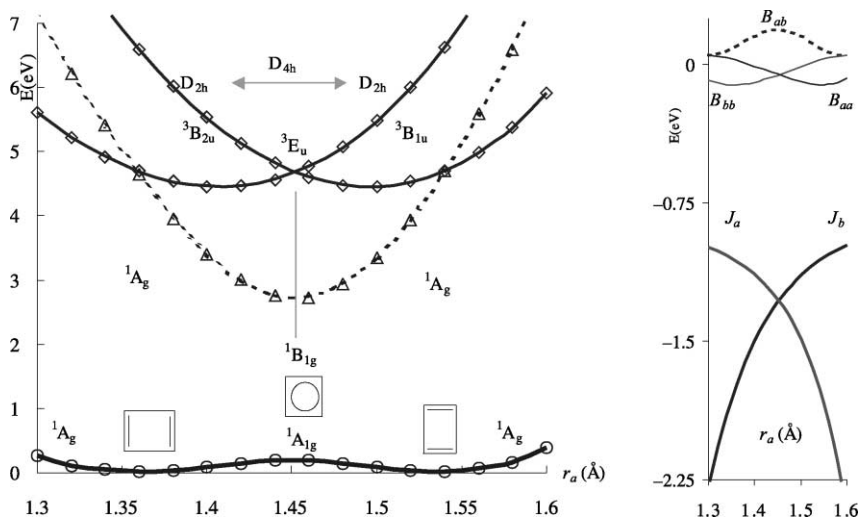


Fig. 2. (a) Selected states representing the $(a_{1g} + b_{1g}) \otimes B_{1g}$ PJT and the $e \otimes E$ effect excited state JT effect in the square C_4H_4 . The marked points show the CASSCF computed values, the continuous and dashed lines corresponding to the fit with Hamiltonian of equation (8) (left side); (b) the corresponding geometry dependence of spin Hamiltonian parameters that fit the energy spectrum (right side).

discarded from the actual parametric problem. The fit can be judged as physically reasonable, noting that the J coupling constants have the exponential pattern undoubtedly revealed from the preliminary evaluation of singlet–triplet gap in ethylene as function of bond length. Moreover, these take values about 1.5 eV in the range of genuine double bonds (as expected, from comparison with ethylene). The newly introduced quadratic B parameters were technically worked with polynomial expansion, revealing relatively small absolute values in comparison to the J ones. Being aware of possible non-uniqueness of the fit, as a general problem in complex systems, we emphasize the semiquantitative meaning of the abstracted parameters, advocating in turn for their qualitative validity in the light of the above considerations.

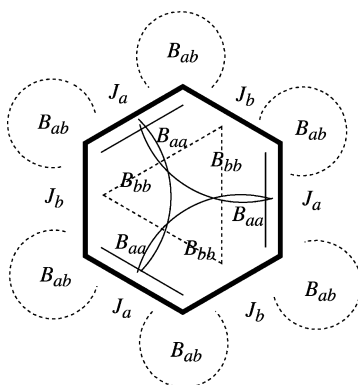
5. THE COMPARISON WITH C_6H_6 – THE VIBRONIC PERSPECTIVE ON RESONANCE STABILIZATION AND AROMATICITY

The benzene itself is obviously not a JT problem, but its cationic [19] and anionic forms [20] are. Here we will discuss the bond homogeneity in C_6H_6 as a natural counter-problem to PJT determined bond alternation in C_4H_4 . The benzene is the

cornerstone and the most illustrative test of the VB electronic structure theories [8,21]. Using the *ab initio* data as basis for the actual extended spin Hamiltonian model, we performed a series of CASSCF(6,6)/6-31G calculations including full configuration interaction of the aromatic sextet into the corresponding six π orbitals. The switch between the D_{6h} symmetry with equal $r_0 = 1.38837$ bond length and D_{3h} distorted ones was conventionally taken along a one-dimensional coordinate keeping the equal radial placement of the carbon atoms (with the relation $r_b = \sqrt{3(r_0^2 - r_a^2/4)} - r_a/2$ between the r_a and r_b different bond lengths). This choice subjects the benzene system to the premises comparable to those used for cyclobutadiene analysis. Within this choice the calculations were conducted as relaxed potential energy surfaces type [16]. Here the coordinate possesses b_{2u} symmetry (in D_{6h}). Given the increased complexity of six-spin modeling we will equate here only the singlet states. There are five spin singlets, in direct relation with the number of celebrated resonance structures (2 Kekule + 3 Dewar). Scheme 3 shows the parameters implementing the actual spin Hamiltonian approach to the VB nature of electronic structure of benzene.

It is interesting to note that the ground and first excited states, which, in line with the state-of-the-art VB calculation are revealed to have a Kekule preponderant parentage [8] span the symmetry related to the bond alternation due to vibronic mixing effects.

Even though the system is stable in symmetric form, a vibronic part acts in the inner resorts of the electronic structure. Anticipating, the aromaticity can be presented as the situation when the distortion tendency does not overcome the non-vibronic positive harmonic constant maintaining the high symmetry. The ^1A_g ground state have the aspect of in-phase combination of the Kekule resonance structures, whereas the first excited $^1B_{2u}$ state results from their out-of-phase mixing. These states are mixed *via* the b_{2u} distortion coordinate of bond alternation. Additionally



Scheme 3.

there is another ^1A_g excited state resulted from equal combination of Dewar structures. This excited ^1A_g state and the $^1B_{2u}$ one are also connected by vibronic coupling, the full block of the problem being given below, with the diagonal elements ordered with respect of ^1A_g , $^1B_{2u}$, ^1A_g labels in D_{6h} :

$$\begin{pmatrix} K_0 + \frac{1}{2}(J_a + J_b) + 16(B_{aa} + B_{bb}) - \varepsilon & \sqrt{6}(J_a - J_b + 5B_{aa} - 5B_{bb}) & \frac{3}{2}(J_a + J_b) + 3(B_{aa} + B_{bb}) + 6B_{ab} \\ \sqrt{6}(J_a - J_b + 5B_{aa} - 5B_{bb}) & K_0 + 9(B_{aa} + B_{bb}) - 6B_{ab} - \varepsilon & 3\sqrt{6}(B_{aa} - B_{bb}) \\ \frac{3}{2}(J_a + J_b) + 3(B_{aa} + B_{bb}) + 6B_{ab} & 3\sqrt{6}(B_{aa} - B_{bb}) & K_0 - \frac{3}{2}(J_a + J_b) - \varepsilon \end{pmatrix} \quad (14)$$

There are two other combinations of Dewar resonances forming a degenerate set ($^1E_{2g}$ in D_{6h}) having no role in the bond alternation factors:

$$K_0 - (J_a + J_b) - 5(B_{aa} + B_{bb}) - 6B_{ab} \quad (15)$$

The computed and fitted potential energy surfaces and their symmetry and resonance assignment are shown in Fig. 3a. Figure 3b shows the parameter geometry dependence that accomplishes the fit of the singlet states. Their semiquantitative relevance is validated by the same reasons discussed in the previous section.

The ground state of benzene has positive curvature along the b_{2u} distortion, the aromaticity being therefore interpreted as resistance against the PJT effect. One

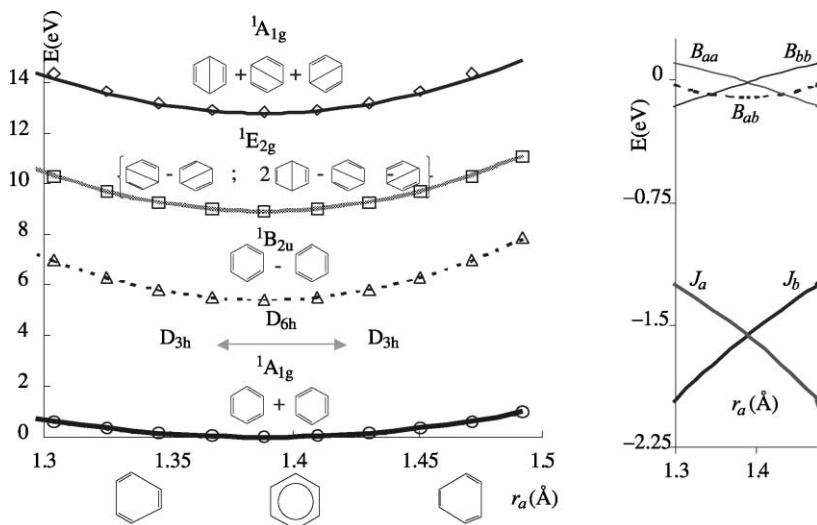


Fig. 3. (a) The singlet states originating from Kekule and Dewar resonances in benzene. The marked points show the CASSCF computed values, the continuous and dashed lines corresponding to the fit with Hamiltonian of equation (14) (left side); (b) the geometry dependence of spin Hamiltonian parameters (right side).

heuristic reason can be found in the presence of higher totally symmetric state made by Dewar resonances. To be distinguished from the customary two state model of PJT here we have a three-state case, where the excited state with the symmetry related with those of distortion is ‘sandwiched’ between the total symmetric states, proportional to $J_a + J_b$ is also enhanced by distortion, contributing to a supplementary gap between the states able for vibronic coupling, preventing then the PJT effect.

After equating, *via* HDVV, the energies of states conceived as having a VB meaning, the resonance stabilization can be defined subtracting the average of non-interacting resonance structures simulated by the sum of HDVV terms for dimmer units made with atoms joint by double bonds.

For cyclobutadiene, keeping the K_0 term as necessary to describe the background exerted by σ skeleton, the average of the two Kekule structures is $K_0 - J_a - J_b$. Correspondingly, for benzene, confined also to Kekule structures, the non-resonant part can be conventionally defined as $K_0 - 3J_a/2 - 3J_b/2$. In this way we estimate a resonance stabilization for benzene of -8.56 kcal/mol, comparable with the CASVB calculation [22] giving -7.4 kcal/mol. Here one should note that with respect to the adopted definition and the method of estimation, the resonance energy is disputed in a very large interval (-5 to -95 kcal/mol) [23]. The representation in

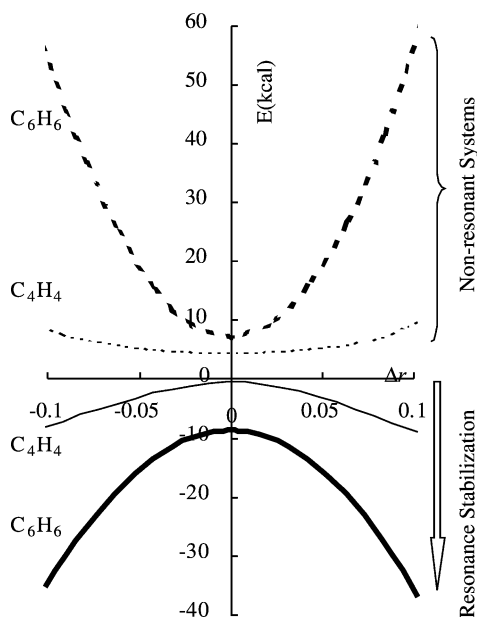


Fig. 4. The hypothetical non-resonant energy in cyclobutadiene and benzene and the corresponding resonance stabilization (in kilocalories per mole) obtained with the help of fitted spin Hamiltonian parameters (as function of bond altering distortion).

Fig. 4 shows that the defined non-resonant superposition of states increases in energy with distortion with a higher slope and curvature for benzene. Correspondingly, the magnitude of resonance energy taken as difference with respect to the correct ground-state energy increases with the distortion. This clearly emphasizes an aspect which otherwise can be confusingly understood from the usual textbook treatment of the problem. Namely, the resonance is not a phenomenon pertaining to the symmetric structures only. It persists and even enhances with the distortion.

6. CONCLUSION

The combined use of vibronic and adapted spin Hamiltonian models allow valuable translation of JT and PJT factors within the VB language. In this approach JT systems are related with the topological effect of spin frustration and particular cases (here considering the conical intersection of H_3 molecule) suggests useful applications in various analytical potential energy models in terms explicitly accounting for the bonds existing in the activated complex and breaking along a distortion coordinate.

The electronic states accounted by the spin Hamiltonian were proven adequate to discuss the bond alternation in conjugated hydrocarbons as a PJT effect. Comparative analysis of cyclobutadiene and benzene allowed a new insight in the inner details of the aromaticity. Following the language of PJT effects, the vibronic contribution to the potential energy curvature K_v can be regarded as having effective π nature, paralleling the resonance stabilization. Conversely, the non-vibronic part K_0 that cumulates many non-explicit factors can be effectively regarded as essentially matching the resistance of the σ skeleton against distortion. In non-aromatic systems the negative K_v exceeds the positive K_0 determining the bond alternation while this effect does not occur in aromatic ones. From this point we can note that a key role in aromaticity problem is comprised in the σ skeleton. In C_4H_4 the rectangular C–C–C bond angle either cannot be accomplished with hybrid orbitals (the bond angle imposing genuine p ones) or certain hybridization is allowed on the expense of non-favorable bent bond. In both cases the σ bonding will be rather weak, explaining the relative smallness of the K_0 term. By contrary, in C_6H_6 the σ bond strength is optimally ensured by the sp^2 planar hybrids yielding the stronger K_0 term. Without entering the details here we shortly point that the concept of hybridization used in non-trivial quantitative manner [24] and with full quantum background could be revived as a powerful tool in particular structural problems, as is here the case of its imbrications with the aromatic delocalization factors.

The apparently striking role of σ skeleton as important in the intimate resorts of aromaticity was revealed in several previous discussions [25]. In addition, the vibronic language helps to illuminate new details on the rather controversial aromaticity problem which deserves still further attention, because of its position at the hearth of molecular structure ideas. Still incompletely explored areas of the aromaticity manifestation are in the field of inorganic and organometallic cycles and

clusters [26]. Promising application of the HDVV-VB type vibronic schemes provided from the state-of-the-art multireference electronic structure calculations in the polyene series [27] concern the extrapolation to the problem of Peierls distortion in conjugated infinite hydrocarbon chains.

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REFERENCES

- [1] W. Z. Heisenberg, *Phys.*, 1928, **49**, 619; J. H. van Vleck and A. Sherman, *Rev. Mod. Phys.*, 1953, **7**, 167; P. W. Anderson, *Phys. Rev.*, 1959, **115**, 2.
- [2] O. Kahn, *Molecular Magnetism*, VCH Publisher, New York, 1993; C. Benelli and D. Gatteschi, *Chem. Rev.*, 2002, **102** (6), 2369; A. Muller, F. Peters, M. T. Pope and D. Gatteschi, *Chem. Rev.*, 1998, **98** (1), 239.
- [3] M. Said, D. Maynau and J. P. Malrieu, *J. Am. Chem. Soc.*, 1984, **106** (3), 580; N. Guihery, N. Benamor, D. Maynau and J. P. Malrieu, *J. Chem. Phys.*, 1996, **104** (10), 3701.
- [4] M. A. Garciasbach, P. Blaise and J. P. Malrieu, *Phys. Rev. B – Condens. Matter.*, 1992, **46** (24), 15645; S. Capponi, N. Guihery, J. P. Malrieu, B. Miguel and D. Poilblanc, *Chem. Phys. Lett.*, 1996, **255** (4–6), 238.
- [5] J. Cioslowski, *Chem. Phys. Lett.*, 1987, **134** (6), 507; N. Flocke and T. G. Schmalz, *Chem. Phys. Lett.*, 1998, **298** (1–3), 71–78; N. Flocke, T. G. Schmalz and D. J. Klein, *J. Chem. Phys.*, 1998, **109** (3), 873–880; M. A. Garciasbach, R. Valenti and D. J. Klein, *Phys. Rev. B – Condens. Matter.*, 1997, **56** (4), 1751–1761; D. J. Klein, H. Zhu, R. Valenti and M. A. Garciasbach, *Int. J. Quantum Chem.*, 1997, **65** (5), 421–438.
- [6] A. Ceulemans, G. A. Heylen, L. F. Chibotaru, T. L. Maes, K. Pierloot, C. Ribbing and L. G. Vanquickenborne, *Inorg. Chim. Acta*, 1996, **251**, 15; J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, A. V. Palii and B. S. Tsukerblat, *Chem. Phys.*, 2001, **274** (2–3), 131.
- [7] M. Raimondi and D. L. Cooper, *Top. Curr. Chem.*, 1999, **203**, 105; D. L. Cooper, T. Thorsteinsson and J. Gerratt, *Adv. Quant. Chem.*, 1999, **32**, 51; T. Thorsteinsson and D. L. Cooper, *Int. J. Quantum Chem.*, 1998, **70** (4–5), 637.
- [8] K. Hirao, H. Nakano, K. Nakayama and M. Dupuis, *J. Chem. Phys.*, 1996, **105**, 9227; H. Nakano, K. Sorakubo, K. Nakayama and K. Hirao, in *Valence Bond Theory* (ed. D. L. Cooper), Elsevier Science, Amsterdam, 2002, pp. 55–77.
- [9] T. Taketsugu and T. Hirano, *J. Mol. Struct. (Theochem)*, 1994, **116**, 169.
- [10] A. Ceulemans, L. F. Chibotaru, G. A. Heylen, K. Pierloot and L. G. Vanquickenborne, *Chem. Rev.*, 2000, **100** (2), 787.
- [11] J. Borrás-Almenar, J. M. Lementé-Juan, E. Coronado and B. S. Tsukerblat, *Inorg. Chem.*, 1999, **38** (26), 6081.
- [12] P. C. Benson and E. C. Dugdale, *J. Phys. C: Solid State Phys.*, 1975, **8**, 3872; K. Wieghardt, P. Chaudhuri, B. Nuber and J. Weiss, *Inorg. Chem.*, 1982, **21** (8), 3086–3090; B. Leuenberger, A. Stebler, H. U. Gudel, A. Furrer, R. Feile and J. K. Kjems, *Phys. Rev. B*, 1984, **30**, 6300.
- [13] T. Iwashita and N. Uryu, *J. Phys. Soc. Jpn*, 1974, **36**, 48; K. Harada and N. Kawashima, *Phys. Rev. B*, 2002, **65** (5), 2403.

- [14] O. Kahn, *Chem. Phys. Lett.*, 1997, **265** (1–2), 109.
- [15] S. Mahapatra and H. Köppel, *Phys. Rev. Lett.*, 1998, **81**, 3116; F. Hagelberg, *Int. J. Quantum Chem.*, 1999, **75**, 367; I. Mistrik, R. Reichle, U. Muller, H. Helm, M. Jungen and J. A. Stephens, *Phys. Rev. A*, 2000, **61** (3), 3410.
- [16] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su and T. L. Windus, *J. Comput. Chem.*, 1993, **14**, 1347.
- [17] U. Kleinekathofer, K. T. Tang, J. P. Toennies and C. L. Yiu, *J. Chem. Phys.*, 1999, **111**, 3386.
- [18] H. Nakano, K. Nakayama and K. Hirao, *J. Mol. Struct. (Theochem)*, 1999, **461**, 55.
- [19] H. Kato, K. Hirao and M. Sano, *J. Mol. Struct. (Theochem)*, 1983, **13** (3–4), 489; M. Döschner, H. Köppel and P. G. Szalay, *J. Chem. Phys.*, 2002, **117** (6), 2645; T. A. Barckholtz and T. A. Miller, *J. Phys. Chem. A*, 1999, **103**, 2321.
- [20] K. Yoshizawa, T. Kato and T. Yamabe, *J. Chem. Phys.*, 1998, **108** (18), 7637; T. Kato, K. Yoshizawa and T. Yamabe, *Syn. Met.*, 2001, **119** (1–3), 217.
- [21] D. L. Cooper, J. Gerratt and M. Raimondi, *Nature*, 1986, **323**, 699.
- [22] J. H. van Lenthe, F. Dijkstra and R. W. A. Havenith, in *Valence Bond Theory* (ed. D. L. Cooper), Elsevier Science, Amsterdam, 2002, pp. 79–116.
- [23] Y. Mo, W. Wu and Q. Zhang, *J. Phys. Chem.*, 1994, **98**, 10048; R. Janoshek, *J. Mol. Struct. (Theochem)*, 1991, **229**, 197; H. Kollmar, *J. Am. Chem. Soc.*, 1979, **101**, 4832.
- [24] M. Ferbinteanu, H. W. Roesky, F. Cimpoesu, M. Atanasov, S. Köpke and R. Herbst-Irmer, *Inorg. Chem.*, 2001, **40**, 4947.
- [25] S. S. Shaik, P. C. Hiberty, J.-M. Lefour and G. Ohanessian, *J. Am. Chem. Soc.*, 1987, **109**, 363; T. Nakajima and M. Kataoka, *Theor. Chim. Acta*, 1993, **85**, 27; E. D. Glendening, R. Faust, A. Streitwieser, K. P. C. Vollhardt and F. Weinhold, *J. Am. Chem. Soc.*, 1993, **115**, 10952; P. C. Hiberty, D. Danovich, A. Shurki and S. Shaik, *J. Am. Chem. Soc.*, 1995, **117**, 7760; K. Jug, P. C. Hiberty and S. Shaik, *Chem. Rev.*, 2001, **101**, 1477; S. Shaik, A. Shurki, D. Danovich and P. C. Hiberty, *Chem. Rev.*, 2001, **101**, 1267.
- [26] C. M. Cui, H. W. Roesky, H. G. Schmidt, M. Noltemeyer, H. J. Hao and F. Cimpoesu, *Angew. Chem. Int. Ed.*, 2002, **39** (23), 4274–4277; A. Stasch, M. Ferbinteanu, J. Prust, W. Zheng, F. Cimpoesu, H. W. Roesky, J. Magull, H.-G. Schmidt and M. Noltemeyer, *J. Am. Chem. Soc.*, 2002, **124**, 5441–5448.
- [27] K. Nakayama, H. Nakano and K. Hirao, *Int. J. Quant. Chem.*, 1998, **66**, 157.

Jahn–Teller Distortions and Excitation Energies in C_{60}^{n+}

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Abstract

Based on previously computed parameters for the electron–phonon couplings and the Coulomb exchange, we compute and classify the static Jahn–Teller (JT) distortions, i.e., the minima of the lowest adiabatic potential energy surface, of C_{60}^{n+} , for all values of charge $1 \leq n \leq 9$ and spin. We compute the intra-band electronic excitation energies in the different optimal geometries in the sudden approximation, and find a spread of the electronic states of roughly 1 eV. We also obtain the leading vibronic quantum corrections to the ground-state energy, equal to zero-point energy lowering due to the softening of the phonons at the adiabatic JT minima: these nonadiabatic corrections are so large that for $4 \leq n \leq 6$ states of different spin symmetry turn lower than the high-spin adiabatic ground state.

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1. INTRODUCTION

Low-spin states are associated to larger distortions, thus larger energy gains, than high-spin states in degenerate electron–phonon coupled molecules and impurity centers. Electron–electron Coulomb repulsion opposes this tendency, favoring high-spin states instead, in accord to the first of Hund’s rules. The Jahn–Teller (JT)

systems C_{60}^{n+} are no exception to this rule: if electron–phonon coupling was the only relevant interaction, then the n -holes ground state would be either of spin $S = 0$ (even n) or $S = \frac{1}{2}$ (odd n). As was recently shown [1], in positive fullerene ions the size of Coulomb interaction is sufficiently large to enforce Hund’s rule: the ground states of C_{60}^{n+} was calculated to always be high spin ($S = n/2$ for $n \leq 5$, $S = (10 - n)/2$ for $n > 5$) in the adiabatic approximation. This result is confirmed for $n = 2$ by NMR investigation of solid-state compounds [2]. The JT distortions in C_{60}^{n+} , though strongly counteracted by the larger electron–electron repulsion, yet represent an important, and still largely unexplored, contribution to the energetics of C_{60}^{n+} . Investigation of this contribution, and in particular of the corrections to the adiabatic approximation, is the main subject of this work.

The JT model relevant for C_{60}^{n+} is conventionally indicated as $h^n \otimes (A + G + H)$, where h refers to the fivefold-degenerate highest occupied molecular orbital (HOMO), and A , G , H refer to the two nondegenerate A_g , six fourfold-degenerate G_g and eight fivefold-degenerate H_g molecular vibration modes that are linearly coupled to the h_u states according to icosahedral symmetry [1,3,4]. We investigate this model by treating the normal coordinates for these vibrational modes as classical variables, and searching the minima of the adiabatic potential energy surface in the 66-fold dimensional space of these distortions. Each of these static JT configurations is characterized by a reduced symmetry from icosahedral to some (usually) lower symmetry. New vibrational frequencies arise at these local minima: we determine these frequencies by evaluation of the Hessian matrix at the minimum [5]. The lowering of the vibrational frequencies gives the leading quantum correction to the adiabatic approximation. The original icosahedral symmetry of the problem is restored once the presence of several equivalent optimal distortions is recognized, and quantum tunneling between these wells is allowed. Proper accounting of tunneling gives the next-order quantum correction, but in the present work, we limit ourselves to the study of the local properties of the wells and the connectivity of the sets of minima in distortion space, for all values of charge n and spin S .

The competing intra-molecular exchange of Coulomb origin and the JT interaction both contribute to the computed spectrum of excitations. Differences in energies of the fully relaxed configurations at different spin compare directly with spin gaps as could be measured in ‘slow’ spectroscopies such as electron or nuclear magnetic resonance. In contrast, the electronic excitation energies computed keeping the molecular geometry fixed in the lowest minimum compare directly with the vertical excitations probed by fast optical spectroscopies. Both these classes of quantities are reported in this work.

This paper is organized as follows: Section 2 introduces the model and the parameters used in this calculation, which is then described in Section 3, along with the properties of the JT minima for all values n and S ; Section 4 contains the vertical excitation spectra. The zero-point nonadiabatic corrections are described in Section 5. The results are discussed in Section 6, and connectivity matrices are collected in Appendix.

2. THE MODEL HAMILTONIAN

We report here for completeness of the model Hamiltonian previously introduced in Ref. [1] to describe the physics of the holes in the h_u HOMO of C_{60} fullerene:

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{vib}} + \hat{H}_{\text{e-v}} + \hat{H}_{\text{e-e}} \quad (1)$$

where

$$\hat{H}_0 = \epsilon \sum_{\sigma m} \hat{c}_{\sigma m}^\dagger \hat{c}_{\sigma m} \quad (2)$$

$$\hat{H}_{\text{vib}} = \sum_{i\wedge\mu} \frac{\hbar\omega_{i\wedge}}{2} (\hat{P}_{i\wedge\mu}^2 + \hat{Q}_{i\wedge\mu}^2) \quad (3)$$

$$\hat{H}_{\text{e-v}} = \sum_{ri\wedge} \frac{k^\wedge g_{i\wedge}^r \hbar\omega_{i\wedge}}{2} \sum_{\sigma m m' \mu} C_{m m' \mu}^{r\wedge\mu} \hat{Q}_{i\wedge\mu} \hat{c}_{\sigma m}^\dagger \hat{c}_{\sigma m'} \quad (4)$$

$$\hat{H}_{\text{e-e}} = \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{m m' n n'} w_{\sigma, \sigma'}(m, m'; n, n') \hat{c}_{\sigma m}^\dagger \hat{c}_{\sigma' m'}^\dagger \hat{c}_{\sigma' n'} \hat{c}_{\sigma n} \quad (5)$$

are respectively the single-particle Hamiltonian, the vibron contribution (representing the phonon kinetic energy plus the restoring potential expanded to quadratic order around the equilibrium configuration of neutral C_{60}), the electron–vibron coupling (in the linear JT approximation) [4,6], and finally the mutual Coulomb repulsion between the electrons. The $\hat{c}_{\sigma, m}^\dagger$ denote the creation operators of a hole in the HOMO, described by the single-particle wave function $\varphi_{m\sigma}(\mathbf{r})$. σ indicates the spin projection; m and n label the component within the fivefold degenerate electronic HOMO multiplet, based on the C_5 quantum number m from the $I_h \supset D_5 \supset C_5$ group chain [4,7]. i counts the phonon modes of symmetry $\wedge$ ($2 A_g$, $6 G_g$ and $8 H_g$ modes). $C_{m m' \mu}^{r\wedge\mu}$ are Clebsch–Gordan coefficients [7] of the icosahedral group I_h , for coupling two h_u states to phonons of symmetry $\wedge$. r is a multiplicity label, relevant for modes of $\wedge = H_g$ symmetry only [6,7]. $\hat{Q}_{i\wedge\mu}$ are the molecular normal-mode vibration coordinates (measured from the adiabatic equilibrium configuration of C_{60}), and $\hat{P}_{i\wedge\mu}$ the corresponding conjugate momenta. Spin-orbit is exceedingly small in C_{60} [8] and it is therefore neglected.

The electron–vibron (e–v) couplings $g_{i\wedge}^r$ are conveniently expressed in units of the corresponding harmonic vibron quantum of energy $\hbar\omega_{i\wedge}$. In this calculation we adopt the numerical values of the e–v coupling parameters, listed in Table 1, from the density functional (DF) calculation of Ref. [6], and a second calculation [9] yields couplings in substantial accord with those of Table 1. The numerical factors $k^{A_g} = 5^{1/2}$, $k^{G_g} = (\frac{5}{4})^{1/2}$, $k^{H_g} = 1$ in $\hat{H}_{\text{e-v}}$ have been introduced for compatibility with the normalization of Ref. [6].

The Coulomb matrix elements are defined by:

$$w_{\sigma, \sigma'}(m, m'; n, n') = \int d^3 r \int d^3 r' \varphi_{m\sigma}^*(\mathbf{r}) \varphi_{m'\sigma'}^*(\mathbf{r}') u_{\sigma, \sigma'}(\mathbf{r}, \mathbf{r}') \varphi_{n\sigma}(\mathbf{r}) \varphi_{n'\sigma'}(\mathbf{r}') \quad (6)$$

Table 1. Computed mode eigenfrequencies and e–v linear coupling parameters of the h_u HOMO in C₆₀ [6]

	$\hbar\omega_{\pi_i}$ (cm ⁻¹)	$\hbar\omega_{\pi_i}$ (meV)	g_{π_i}	α_{π_i} (deg)	$E_s(D_5)$ (meV)	$E_s(D_3)$ (meV)
A_g	500	62.0	0.059		0.0	0.0
	1511	187.4	0.274		1.8	1.8
G_g	483	59.9	0.757		0.0	1.9
	567	70.3	0.102		0.0	0.0
	772	95.7	0.800		0.0	3.4
	1111	137.8	0.624		0.0	3.0
	1322	163.9	0.228		0.0	0.5
	1519	188.4	0.467		0.0	2.3
H_g	261	32.4	3.042	− 0.1	30.0	0.0
	429	53.2	1.223	30.1	6.0	1.1
	718	89.0	0.995	89.4	0.0	4.9
	785	97.3	0.784	− 2.3	6.0	0.0
	1119	138.7	0.221	76.6	0.0	0.4
	1275	158.0	0.519	28.0	3.3	0.5
	1456	180.5	0.962	28.1	13.0	2.1
	1588	196.9	0.869	− 31.1	10.9	2.2

The classical single-mode JT stabilization energies E_s are tabulated for both D_5 and D_3 distortions, for *one hole* in the HOMO

where $u_{\sigma,\sigma'}(\mathbf{r}, \mathbf{r}')$ is an effective Coulomb repulsion, screened by the other electrons of the molecule. Detailed symmetry analysis shows [1] that, assuming spin-independence of the orbitals, this set of coefficients can be expressed as

$$w_{\sigma,\sigma'}(m, m'n, n') = \sum_{r,r',\Lambda} F^{r,r',\Lambda} \left(\sum_{\mu} C_{mn}^{r\wedge\mu} C_{m'n'}^{r'\wedge\mu} \right) \quad (7)$$

in terms of a *minimal* set of independent parameters $F^{r,r',\Lambda}$. A DF calculation of these parameters was carried out in Ref. [1], and for our calculation we adopt those values of the Coulomb parameters, which we report for completeness in Table 2. For the Coulomb parameters, we use the shorthands

$$F_1 = F^{A_g}, \quad F_2 = F^{G_g}, \quad F_3 = F^{1,1,H_g}, \quad F_4 = F^{2,2,H_g}, \quad F_5 = F^{1,2,H_g} \quad (8)$$

and the combination

$$U = \left(\frac{F_1}{5} - \frac{4F_2}{45} - \frac{F_3}{9} - \frac{F_4}{9} \right) \quad (9)$$

U defines an average Coulomb repulsion within the n -holes multiplets, so that

$$E^{\text{ave}}(n) = \text{Tr}_n(\hat{H}_0 + \hat{H}_{e-e}) = \epsilon n + U \frac{n(n-1)}{2} \quad (10)$$

Table 2. The Coulomb parameters for C_{60}^{n+} , as obtained from the DF calculations of Ref. [1]

Parameter	Value (meV)
F_1	15646 ± 9
F_2	105 ± 10
F_3	155 ± 4
F_4	47 ± 5
F_5	0 ± 3
U	3097 ± 1

One of the tabulated parameters (e.g. F_1) is a linear combination of the five others

It should be noted that U differs from the usual definition of the Hubbard U , involving the lowest multiplet in each n -configuration: $U^{\min} = E^{\min}(n+1) + E^{\min}(n-1) - 2E^{\min}(n)$. This second definition is inconvenient here, since it depends wildly on n .

3. THE ADIABATIC CALCULATIONS

We approximate the vibron operators $\hat{Q}_{i\wedge\mu}$ with classical coordinates, in the spirit of the adiabatic approximation. In an orbitally degenerate situation (as for the C_{60}^{n+} ions at hand) the adiabatic approximation usually yields fairly accurate energetics in the limit of the large e–v couplings, so that tunneling between equivalent minima can safely be neglected [10]. The phonon kinetic term in equation (3) is neglected in the adiabatic approximation. In Section 5, we will partly restore this term by taking into account quantum zero-point energies. In any classical statically JT-distorted configuration, the icosahedral symmetry is broken: therefore, states of different icosahedral symmetry representations are inter-mixed. Only the total number of holes n , total spin S and its projection S_z are conserved upon distortion. Here, we neglect any change of the Coulomb Hamiltonian upon distortion, and we assume therefore that $\hat{H}_{e-e}$ is still determined according to equations (5)–(7) by the same parameters F_i of Table 2, as in icosahedral symmetry. Also, we assume no change of the phonon frequencies $\omega_{i\wedge}$ and couplings $g_{i\wedge}^r$ upon charging.

For each n , S and M_S , we allow the 64 (6×4 G_g plus 8×5 H_g) phonon coordinates to relax, and determine the optimal distortion, by full minimization of the lowest adiabatic potential sheet $V^{\text{ad}}(\mathbf{Q})$ in the space of all the phonons coordinates $\mathbf{Q}$. We leave the A_g modes out, since they contribute a trivial

$$E^{A_g}(n) = -\frac{1}{8}n^2 \sum_i g_{iA_g}^2 \hbar \omega_{iA_g} = -n^2 \cdot 1.79 \text{ meV} \quad (11)$$

spin- and symmetry-independent term to the energetics. Because of particle-hole symmetry, charges $n > 5$ can always be reduced to the computed charges $n < 5$. In Table 3, we report the resulting optimally distorted energy in each spin sector, based on the electron–electron (e–e) and e–v couplings of C_{60}^{n+} ions, as previously published in Ref. [1]. The main outcome of the adiabatic calculation is that positive C_{60} ions favor high-spin ground states (contrary to the analogous finding for negative ions).

In the present contribution, we extend the previous calculation to obtain the complete set of *all* the equivalent minima for each (n, S) sector. To this purpose, we generate about a hundred randomly distributed distortions away from the I_h high-symmetry point, and let the molecule relax to the closest minimum, by combined standard (simplex and conjugate-gradients) minimization algorithms. We then apply the symmetry operations of the icosahedral group to the each of the minima found, in order to locate any possibly missing minimum. Although the method employed is not deterministic, the symmetry analysis makes the probability that any set of minima is incomplete utterly negligible. Thus, for each n and S we obtain a complete set of equivalent global minima. In the few cases where the minimization leads to nonglobal minima, we have discarded them based on simple comparison of the adiabatic energies.

In Table 4 we summarize some global properties of the obtained JT minima for all charge and spin states. In these multi-mode JT systems, the local symmetry of an optimal distortion is described in terms of the subgroup G_{local} of symmetry operations which leave that minimum invariant. We remind that the minima in the

Table 3. The total adiabatic energy $V^{\text{ad}}(\mathbf{Q}_{\text{min}})$ (in meV) of the lowest electronic state for each n and S , including the e–e and e–v contributions from $\hat{H}_{\text{vib}} + \hat{H}_{\text{e-v}} + \hat{H}_{\text{e-e}}$ (but excluding the $[Un(n-1)/2]$ term), for C_{60}^{n+}

n	S	Adiabatic	Vibrational	Electronic
2	0	− 129	270	− 399
	1	− 142	99	− 241
3	1/2	− 168	267	− 435
	3/2	− 222	99	− 320
4	0	− 200	361	− 561
	1	− 211	229	− 440
	2	− 308	69	− 377
5	1/2	− 203	308	− 511
	3/2	− 256	169	− 425
	5/2	− 397	0	− 397

The last two columns distinguish the vibrational ($\hat{H}_{\text{vib}}$) and electronic ($\hat{H}_{\text{e-v}} + \hat{H}_{\text{e-e}}$) contributions

Table 4. The number and the local symmetries of the JT minima for given charge n and spin S

n	S	Number of minima	Local symmetry	Number of 1st, 2nd, 3rd... neighbors	Distortion $ \mathbf{Q}_{\min} $
2	0	6	D_{5d}	5	3.12
	1	15	D_{2h}	4 4 4 2	1.87
3	1/2	30	C_{2v}	2 1 2 4 4 2 2 2 4 4 2	3.08
	3/2	15	D_{2h}	4 4 4 2	1.87
4	0	10	D_{3d}	3 6	3.52
	1	30	C_{2v}	2 2 2 2 1 4 4 4 6 2	2.85
	2	6	D_{5d}	5	1.58
5	1/2	60	C_{2v}	1 2 2 4 4 4 2 2 2 4 2 2 4 2 2 2 4 4 4 2 2 1 1	3.27
	3/2	30	C_{2v}	8 12 8 1	2.46
	5/2	1	I_h	0	0

In the fifth column the number of neighbors of all orders are listed for a given minimum. The last column gives the total amount of dimensionless JT distortion at each minimum

$n = 1$, $S = \frac{1}{2}$ case, where e–e interaction is unimportant, were found to be 6, of local D_{5d} symmetry [3,4,6]. For $2 \leq n \leq 8$, where the role of e–e interaction is crucial, the number of JT minima follows from the local symmetry: it is generally given by the ratio $|I_h|/|G_{\text{local}}|$ of the orders of the icosahedral group (120) and of the invariant subgroup.

Special care has to be taken for $n = 5$ holes. Here, in addition to the icosahedral symmetry, the system is particle-hole symmetric, i.e., invariant under exchange of fermion creation and annihilation operators. This transformation leaves the Coulomb Hamiltonian $\hat{H}_{e-e}$ invariant, while the vibron interaction $\hat{H}_{e-v}$ is unchanged provided that a sign change of the vibron coordinates $\hat{Q}_{i,\Lambda,\mu}$ is also performed. Hence, for a given minimum $\mathbf{Q}_{\min}$, also its opposite $-\mathbf{Q}_{\min}$ is a minimum of the potential energy surface. In the case $n = 5$, $S = \frac{1}{2}$, this leads to a doubling of the minima: the local C_{2v} symmetry would lead to 30 minima, but 30 more equivalent minima are added in the opposite positions by particle-hole symmetry. For $n = 5$, $S = \frac{3}{2}$ instead, the number of minima remains 30, since for each minimum there is one of the I_h symmetry operations that transforms this minimum into its opposite point. Note that this operation is not the spatial inversion (since all vibrations considered here form even representations), which are invariant under inversion, but a twofold rotation. Finally, for $n = 5$, $S = \frac{5}{2}$, the electronic state is orbitally nondegenerate, thus no JT distortion takes place.

Table 5 collects some quantitative information about the contribution of each mode to the amount of JT distortion at each minimum. As expected, the largest distortion involves always the lowest H_g mode, which is the most strongly coupled

Table 5. The JT distortion at the minima, for each mode and value of the charge n and spin S . The distortions $|\hat{Q}_{i\Lambda}|$ are given in units of the length scale $x_0(\omega) = \sqrt{\hbar/(\omega m_C)}$ associated to each harmonic oscillator (m_C is the mass of the C atom)

n	S	Symmetry	Distortions of G_g and H_g modes (dimensionless)
2	0	D_{5d}	0.00 0.00 0.00 0.00 0.00 0.00 2.69 0.935 0.0095 0.692 0.0455 0.405 0.749 0.657
2	1	D_{2h}	0.0755 0.0102 0.0799 0.0623 0.0227 0.0466 1.58 0.611 0.138 0.404 0.0516 0.262 0.486 0.346
3	1/2	C_{2v}	0.0548 0.0074 0.0580 0.0452 0.0165 0.0339 2.62 1.01 0.185 0.669 0.0799 0.433 0.801 0.571
3	3/2	D_{3d}	0.0755 0.0102 0.0799 0.0623 0.0227 0.0466 1.58 0.611 0.138 0.404 0.0516 0.262 0.486 0.346
4	0	D_{3d}	0.0828 0.0112 0.0877 0.0683 0.0249 0.0512 2.88 1.30 0.494 0.728 0.153 0.553 1.02 0.486
4	1	C_{2v}	0.074 0.010 0.0782 0.061 0.0223 0.0457 2.39 0.968 0.228 0.609 0.0879 0.414 0.767 0.486
4	2	D_{5d}	0.00 0.00 0.00 0.00 0.00 0.00 1.36 0.473 0.0046 0.35 0.023 0.205 0.379 0.333
5	1/2	C_{2v}	0.101 0.0135 0.106 0.0827 0.0302 0.0619 2.70 1.17 0.401 0.683 0.129 0.50 0.926 0.492
5	3/2	C_{2v}	0.0384 0.0053 0.0411 0.032 0.0117 0.024 2.12 0.756 0.0391 0.544 0.0427 0.327 0.605 0.503
5	5/2	I_h	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00

The $x_0(\omega_{i\Lambda})$ for the G_g and H_g modes of C_{60} are: 76.3, 70.4, 60.3, 50.3, 46.1, 43.0; 103.7, 80.9, 62.6, 59.8, 50.1, 47.0, 43.9, 42.1 pm, respectively.

one (see Table 1). Also, the D_5 distortions receive no contribution of the G_g modes, which contribute to all the lower-symmetry minima instead.

Table 4 contains some information about the connectivity of the minima in $\mathbf{Q}$ space. In some cases, the specification of the number of first, second, etc. neighbors of a given minimum is sufficient to clarify completely the topology of the minima in the 64-dimensional space. In particular, the D_{5d} wells of both the $n = 2$, $S = 0$ and the $n = 4$, $S = 2$ surfaces both are located on the six vertices of the 5D regular simplex, the generalization of a tetrahedron, each minimum being equally distant from all the others: this is analogous to the previously determined minima of V^{ad} for $n = 1$, $S = \frac{1}{2}$ [4]. In analogy, the connectivity of the 10 D_{3d} minima for $n = 4$, $S = 0$ is the same of the one depicted in Fig. 1b of Ref. [4].

For the other cases of lower symmetry, the number of neighbors of any given order must be complemented by some extra connectivity information. First, we observe that the minima for $n = 2$, $S = 1$ and for $n = 3$, $S = \frac{3}{2}$ are exactly the same. Indeed, these two cases are related by a particle-hole symmetry applied only to one spin flavor. For all nonequivalent cases, the complete topological information about the wells is contained in the connectivity matrix $\mathcal{C}(n, S)$, whose matrix elements

indicate that minima i and j are $\mathcal{C}(n, S)_{ij}$ th neighbors. We report those matrices in the Appendix. Careful exam of $\mathcal{C}(n, S)$ for $n = 2$, $S = 1$ and $n = 3$, $S = \frac{3}{2}$ shows that each of the 15 minima is linked to four nearest neighbor minima, which, in turn, are linked to more minima, forming a completely connected regular polytope. The matrices $\mathcal{C}(3, \frac{1}{2})$, and $\mathcal{C}(4, 1)$, show that, for $n = 3$, $S = \frac{1}{2}$ and $n = 4$, $S = 1$, the 30 minima are divided into 6 pentagonal ‘clusters’ of 5 nearest-neighboring minima. In contrast, for $n = 5$, $S = \frac{1}{2}$, nearest-neighbor wells come in pairs. Finally, the 30 minima for $n = 5$, $S = \frac{3}{2}$, show the largest connectivity, and sit at the vertices of a highly symmetric polytope.

4. VERTICAL EXCITATION ENERGIES

In Table 6 we report the range of ‘vertical’ excitation energies ΔE for all final spin symmetries S' , in the frozen minimum configurations $\mathbf{Q}_{\min}(n, S)$, for all values of n and S . The complete spectrum (available upon request from the authors) is very dense and not much informative. The listed energies give a quantitative prevision of the spectral range where a fast (optical) spectroscopy is likely to locate the intra-band HOMO excitations of the C_{60}^{n+} ions. For the experimentally most accessible case $n = 2$, $S = 1$, here follows the complete list of the triplet–triplet excitation energies: 127, 149, 150, 178, 182, 218, 326, 337, and 346 meV.

5. NON-ADIABATIC CORRECTIONS

The leading quantum correction to the static JT energetics is given by the zero-point energy gain due to the softening of the vibrational frequency at the JT-distorted minima [5]. To obtain this information, by finite differences we compute the Hessian matrix of the second-order derivatives of the lowest adiabatic potential sheet, at one of the static JT minima $\mathbf{Q}_{\min}$

$$\mathcal{H}_{\{i\wedge\mu\}\{i'\wedge\mu'\}} = \left. \frac{\partial^2 V^{\text{ad}}(Q)}{\partial Q_{i\wedge\mu} \partial Q_{i'\wedge\mu'}} \right|_{\mathbf{Q}_{\min}} \quad (12)$$

The vibrational frequencies $\tilde{\omega}_j$ at the distorted point are the eigenvalues of the Hessian matrix. There is no square root involved in the $\tilde{\omega}_j$, as the coordinates are scaled with the harmonic length scale $x_0(\omega)$ defined in Table 5. In the harmonic approximation, these ‘new’ normal mode frequencies $\tilde{\omega}_j$ contribute a zero-point energy $\sum_j \frac{1}{2} \hbar \tilde{\omega}_j$ to that minimum configuration: the difference between this and the original zero-point energy $\sum_{i\wedge\mu} \frac{1}{2} \hbar \omega_{i\wedge}$ gives the leading quantum correction

$$E_{\text{zero}}(n, S) = \frac{1}{2} \left[\sum_j \hbar \tilde{\omega}_j(n, S) - \sum_{i\wedge\mu} \hbar \omega_{i\wedge} \right] \quad (13)$$

Table 6. The lowest and highest vertical excitation energies (in meV) calculated assuming that the C_{60}^{n+} ion remains frozen in one of the adiabatic minima when the electronic state is excited

Minimum		Exc. states (S')	$\Delta E^{\min}$ (meV)	$\Delta E^{\max}$ (meV)
n	S			
2	0	0	221	823
		1	140	507
	1	0	75	635
		1	127	346
3	1/2	1/2	132	918
		3/2	99	619
	3/2	1/2	125	784
		3/2	127	346
4	0	0	192	1464
		1	102	1141
		2	165	509
		1	82	1232
	1	1	120	881
		2	54	408
	2	0	234	981
		1	163	647
5	1/2	2	167	179
		1/2	128	1320
		3/2	74	805
		5/2	114	—
	3/2	1/2	120	997
		3/2	143	693
		5/2	28	—
	5/2	1/2	316	731
		3/2	203	377
		5/2	—	—

The first two columns fix the relevant distortion. The third column indicates the spin S' of the excited states considered. The excitation energies in the last two columns are referred to the adiabatic energy of each specific minimum, reported in [Table 3](#)

to the classical energy. We rewrite this correction as

$$\begin{aligned} E_{\text{zero}}(n, S) &= \frac{1}{2} \sum_{i \wedge \mu} \left[\mathcal{H}_{\{i \wedge \mu\} \{i \wedge \mu\}}(n, S) - \hbar \omega_{i \wedge} \right] \\ &= \frac{1}{2} \left[\nabla^2 V^{\text{ad}}(\mathbf{Q})|_{\mathbf{Q}_{\min}} - \sum_{i \wedge \mu} \hbar \omega_{i \wedge} \right] \end{aligned} \tag{14}$$

using the invariance of the trace under change of basis.

[Table 7](#) displays the lowest adiabatic energies for given charge and spin in various approximations. The first column reports the adiabatic energy, $E_{\text{class}} = V^{\text{ad}}(\mathbf{Q}_{\min})$, as

Table 7. The total adiabatic energy $E_{\text{class}} = V^{\text{ad}}(\mathbf{Q}_{\text{min}})$ (in meV) of the lowest electronic state for each n and S , including the e–v and e–e contributions from $\hat{H}_{\text{vib}} + \hat{H}_{\text{e-v}} + \hat{H}_{\text{e-e}}$ (but excluding the $[Un(n-1)/2]$ term), for C_{60}^{n+}

n	S	E_{class}	E_{zero}	$E_{\text{class}} + E_{\text{zero}}$
2	0	–129	–125	–254
	1	–142	–159	–301
3	1/2	–168	–207	–376
	3/2	–222	–159	–380
4	0	–200	–213	–412
	1	–211	–227	–437
	2	–308	–93	–400
5	1/2	–203	–247	–449
	3/2	–256	–175	–431
	5/2	–397	0	–397

The following column contains the leading nonadiabatic correction E_{zero} , the zero-point energy defined in equation (14). The last column reports the adiabatic energy E_{class} corrected by the zero-point term E_{zero} : for $n \geq 4$ it leads to a different ordering of the spin states

in Table 3. The zero-point energy corrections in the following column are comparable in magnitude to the leading adiabatic energies. In particular the very large values of zero-point energy gain for $n = 5$, $S = \frac{1}{2}$ is associated to very shallow minima, connected by low barriers. The lowest vibrational frequency is as small as $\tilde{\omega}_1 \approx 2.3$ meV. In the rather close competition between the Coulomb physics (Hund’s rules) and the JT physics (anti-Hund behavior) the zero-point correction is very important, and, as shown by the last column of Table 7, reduces drastically the spin-gap ($n = 3$), or even changes the ground-state symmetry in favor of an intermediate ($n = 4$) or low ($n = 5$) spin state.

The zero-point correction treated here represents the g_i^0 term of a large-coupling expansion, where the adiabatic energy E_{class} is the leading (g_i^2) term. The next corrections to be considered, of order (g_i^{-2}), are associated to tunneling among minima, possibly affected by Berry phases [4,11,12]. Tunneling is likely to be especially important between the pairs of neighboring minima of the $n = 5$, $S = \frac{1}{2}$ adiabatic surface. Tunneling will be dealt with in future work.

6. DISCUSSION AND CONCLUSIONS

In the present calculation both e–e and e–v interactions are included for the HOMO shell of C_{60} . E–e exchange terms are treated essentially exactly, in the assumptions that (i) inter-band couplings can be neglected, and only act as a renormalization of the Coulomb parameters and that (ii) the latter are independent of the charge n in the HOMO. In principle, due to both orbital and geometrical relaxation, the effective

Coulomb interaction (6) will depend on the instantaneous charge state of the fullerene ion. However, this effect, a very important one in single-atom calculations, is expected to be small in such a large molecule as C_{60} . In a JT system, the coupled phonons should in principle be treated fully quantum mechanically, as nonadiabatic effects may be important. However for strong electron–phonon coupling, the leading terms (of order g^2) are obtained in the adiabatic approximation, by studying the minima of the lowest adiabatic potential surface $V^{\text{ad}}(\mathbf{Q})$. Nonadiabatic effects are taken into account to the next order (g^0) by the calculation of the new harmonic oscillation frequencies close to the adiabatic JT minima. These zero-point corrections are significantly large, and they can even reverse the theoretical prevision for the symmetry of the ground state of the C_6^{n+} ion for $4 \leq n \leq 6$. Tunneling matrix elements which mix different minima to suitable dynamical combinations restore the original icosahedral symmetry and provide the next-order (g^{-2}) quantum correction to the energetics. These terms, which will be the subject of future work, are likely to be especially large for $n = 5$, $S = \frac{1}{2}$.

The present calculation was carried out in the *linear* e–v approximation. As the coupling and thus the distortions are fairly large, quadratic and higher-order (in $\mathbf{Q}$) couplings and vibrations anharmonicity could be important. Unfortunately, no estimate for those higher-order couplings is available yet.

The parameters used in this calculation, both for e–e and e–v interaction are most likely underestimated by the local density approximation used in their determination, as discussed in Ref. [1,6]. Consequently, both the Coulomb repulsion and the phonon-mediated attraction calculated within the local density approximation are likely to need a rescaling by a similar factor of order two. Indeed, the balance between the two opposing interactions is delicate in C_{60}^{n-} ions (as demonstrated by the presence of both high-spin and low-spin local ground states in different chemical environments [13–19]). In C_{60}^{n+} e–e interaction prevails at the adiabatic level: high-spin states are favored, as experiments confirm for $n = 2$ [2]. According to our calculation, however, more highly charged states, close to HOMO half filling should favor local low-spin.

An effective local exchange interaction favoring low spin is a crucial ingredient for superconductivity in a strongly correlated orbitally degenerate material such as a solid of doped C_{60} [20,21]. If screening and retardation effects could be neglected, the present single-molecule calculation suggests that superconductivity should be strongly suppressed in the hole-doped solid at doping $0 \leq n \leq 3$, but could be recovered close to half filling $4 < n < 6$. It is presently unclear if such a high level of hole doping is practically accessible, except possibly by field-induced charging [22].

ACKNOWLEDGEMENTS

We are indebted to M. Wierzbowska, G. Santoro, E. Tosatti for useful discussions. This work was supported by the European Union, contract ERBFMRXCT970155

$$c\left(5, \frac{1}{2}\right)^b =$$

-	-	2	2	-	-	-	9	5	-	-	-	-	4	5	-	5	4	-	-	-	-	5	9	-	-	-	-	4	4
-	-	-	2	2	-	4	5	-	5	-	-	-	-	9	-	-	4	5	-	-	-	-	-	-	-	-	9	5	-
2	-	-	-	2	5	4	-	-	4	4	-	-	-	-	-	-	-	9	5	-	-	-	-	-	-	-	4	5	-
2	2	-	-	-	9	-	-	5	-	5	9	-	-	4	-	-	-	4	5	-	-	-	-	-	-	-	-	-	-
-	2	2	-	-	-	-	-	4	4	-	-	5	4	-	5	9	-	-	-	-	-	-	-	-	-	-	-	-	5
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9	5	-	-	-	2	-	-	-	2	5	4	-	-	-	4	4	-	-	-	-	-	-	-	-	-	-	-	-	4
5	-	-	-	4	2	2	-	-	-	-	-	-	-	5	-	5	9	-	-	4	-	-	-	-	-	-	-	-	5
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-	9	5	-	-	-	-	4	4	-	-	-	5	9	4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	5	-	-	-	-	9	5	-	-	-	4	4	-	-	-	5	9	4	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	5	4	5	-	-	-	-	9	5	-	-	-	-	4	4	-	-	-	-	-	-	-	-	-	-	-

(A.6)

Finally,

$$c\left(5, \frac{3}{2}\right) =$$

-	2	2	2	2	3	3	3	3	2	3	3	3	3	3	2	2	1	1	1	1	1	1	1	1	1	1	2	2	2	4	
-	-	3	-	2	3	2	2	3	3	1	3	2	3	1	3	1	3	2	1	1	3	2	2	2	2	2	1	2	1	4	2
-	-	-	-	3	3	1	3	3	1	2	2	3	1	2	2	3	1	2	2	3	1	2	1	3	1	2	1	2	1	2	2
-	-	-	-	3	-	1	2	1	3	1	2	2	1	2	2	1	3	2	2	3	2	2	1	3	1	1	4	3	1	2	2
-	-	-	-	-	-	2	2	1	2	1	2	2	1	2	1	1	3	2	2	3	2	2	3	1	2	2	3	1	2	2	3
-	-	-	-	-	-	2	2	1	2	1	2	2	2	2	2	2	3	2	2	3	1	4	3	2	2	2	3	1	2	2	3
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-	-	-	-	-	-	3	1	1	2	2	2	2	2	2	2	2	3	2	2	3	1	3	1	2	2	2	2	3	1	2	1
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-	-	-	-	-	-	3	1	1	2	2	2	2	2	2	2	2	3	2	2	3	2	2	3	2	2	2	2	2	2	1	3
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-	-	-	-	-	-	3	1	1	2	2	2	2	2	2	2	2	3	2	2	3	2	2	3	2	2	2	2	2	2	1	3

- [5] N. Manini and E. Tosatti, *Phys. Rev. B*, 1998, **58**, 782.
- [6] N. Manini, A. Dal Corso, M. Fabrizio and E. Tosatti, *Philos. Mag. B*, 2001, **81**, 793.
- [7] P. H. Butler, *Point Group Symmetry Applications*, Plenum, New York, 1981.
- [8] E. Tosatti, N. Manini and O. Gunnarsson, *Phys. Rev. B*, 1996, **54**, 17184.
- [9] M. Saito, *Phys. Rev. B*, 2002, **65**, 220508.
- [10] R. Englman, *The Jahn Teller Effect in Molecules and Crystals*, Wiley, London, 1972.
- [11] A. Auerbach, N. Manini and E. Tosatti, *Phys. Rev. B*, 1994, **49**, 12998.
- [12] N. Manini and P. De Los Rios, *J. Phys.: Condens. Matter*, 1998, **10**, 8485.
- [13] V. Brouet, H. Alloul, T. N. Le, S. Garaj and L. Forro, *Phys. Rev. Lett.*, 2001, **86**, 4680.
- [14] R. F. Kie, T. L. Duty, J. W. Schneider, A. MacFarlane, K. Chow, J. W. Elzey, P. Mendels, G. D. Morris, J. H. Brewer, E. J. Ansaldo, C. Niedermayer, D. R. Noakes, C. E. Stronach, B. Hitti and J. E. Fischer, *Phys. Rev. Lett.*, 1992, **69**, 2005.
- [15] G. Zimmer, M. Mehring, C. Goze and F. Rachdi, in *Physics and Chemistry of Fullerenes and Derivatives* (eds H. Kuzmany, J. Fink, M. Mehring and S. Roth), World Scientific, Singapore, 1995, p. 452.
- [16] I. Lukyanchuk, N. Kirova, F. Rachdi, C. Goze, P. Molinie and M. Mehring, *Phys. Rev. B*, 1995, **51**, 3978.
- [17] K. Prassides, S. Margadonna, D. Arcon, A. Lappas, H. Shimoda and Y. Iwasa, *J. Am. Chem. Soc.*, 1999, **121**, 11227.
- [18] A. Schilder, H. Klos, I. Rystau, W. Schütz and B. Gotschy, *Phys. Rev. Lett.*, 1994, **73**, 1299.
- [19] D. P. Arovas and A. Auerbach, *Phys. Rev. B*, 1995, **52**, 10114.
- [20] M. Capone, M. Fabrizio and E. Tosatti, *Phys. Rev. Lett.*, 2001, **86**, 5361.
- [21] M. Capone, M. Fabrizio, C. Castellani and E. Tosatti, *Science*, 2002, **296**, 2364.
- [22] J. H. Schön, Ch. Kloc, R. C. Haddon and B. Batlogg, *Science*, 2000, **288**, 656.

Many Electron- and Hole Terms of Molecular Ions $C_{60}^{n\pm}$

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Abstract

Starting from a multipole expansion of intramolecular Coulomb interactions, we present an efficient configuration interaction calculation for the electron terms t_{1u}^n , $n = 2, 3, 4$, and the hole terms $(h_u^+)^n$, $n = 2-5$. We have studied magnetic moments for the electron and hole terms. The coupling of spin and orbital momenta differs from the Landé g -factor scheme of atoms. The magnetic moments do not depend on the orientation of the molecule with respect to an external magnetic field.

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C_{60} -fullerite and the alkali-intercalated fullerenes A_xC_{60} , where A is an alkali metal atom, are highly molecular solids in which the electronic and vibrational states are closely related to those of the free molecule or molecular ion [1]. The C_{60} molecule acts as an electron acceptor. The A_3C_{60} compounds, which exhibit superconductivity [2], fall in the class of strongly correlated electron systems where the Coulomb repulsion U between two electrons on a single molecule is larger than the intermolecular energy scale W [3]. Therefore, the consideration of intramolecular correlations should be a constituent part of a many electron theory aiming to describe superconductivity, magnetic properties, or a metal-insulator transition. In the present work, we have studied the terms scheme of the electron and hole doped molecular ions $C_{60}^{n\pm}$, $n = 2-5$. Beside the relevance for the understanding of the electronic or hole correlations in fullerenes or in hole-doped C_{60} -fullerite, such a study is immediately useful for the interpretation of molecular spectroscopy experiments in the gas phase and in electrolytic solutions. The term scheme is also a necessary ingredient for the calculation of Jahn–Teller distortions. To our knowledge, there are only a few earlier calculations of the term scheme of C_{60}^{n-} [4,5].

The problem is also a challenge from both group theoretical [6,7] and experimental [8] point of view. In the following we will use a method which is based on a multipole expansion of the Coulomb interaction between electrons on a same molecule [9,10]. Thereby we systematically include electronic transitions which go beyond the usual Hartree–Fock scheme and hence our approach is equivalent to a full configuration interaction calculation. The details of our technique are given in Ref. [10].

The neutral C_{60} molecule has fivefold degenerate highest occupied molecular orbitals (HOMO) of h_u symmetry and threefold degenerate lowest molecular orbital (LUMO) of t_{1u} symmetry [11], where h_u and t_{1u} are irreducible representations of the icosahedral group I_h . The angular parts of these molecular orbitals (MOs) are expressed as symmetry adapted linear combinations of spherical harmonics Y_l^m with angular momentum quantum number $l = 5$ [12]. In the following we will present a configuration interaction calculation of molecular energy terms due to the presence of several electrons t_{1u}^n in LUMO or several holes $(h_u^+)^n$ in HOMO configuration.

First, we consider the case of two t_{1u} electrons, later we will extend the results to more particles. Since the one electron spin-orbit coupling is negligible [13], we will work in the ‘ LS (Russel–Saunders)’ molecular approximation. Two electron basis ket vectors are denoted by a single index I :

$$|I\rangle = |i_1; i_2\rangle \quad (1)$$

where i_1 and i_2 are one-electron states. The corresponding wave functions are

$$\langle \vec{r}, \vec{r}' | I \rangle = \langle \vec{r} | i_1 \rangle \cdot \langle \vec{r}' | i_2 \rangle \quad (2)$$

where $\langle \vec{r} | i \rangle = \mathcal{R}(r) \langle \hat{n} | i \rangle$. The spin-orbitals $\langle \hat{n} | i \rangle$ are given by

$$\langle \hat{n} | i \rangle = \psi_k(\hat{n}) u_s(s_z), \quad i = 1-6 \quad (3)$$

Here ψ_k are the three t_{1u} MOs ($k = 1, 2, 3$), u_s is the spin function ($s = \pm$) for the spin projections $s_z = \pm 1/2$. $\mathcal{R}$ is the radial component of the MOs and $\hat{n}$ stands for the polar angles $\Omega = (\Theta, \phi)$. The order of indices in equations (1) and (2) is important if we associate the first electron with the state i_1 while the second with the state i_2 . From the dynamical equivalence of the electrons we can permute the spin-orbitals of the state $|i_2; i_1\rangle$ to the standard order, equation (1), by using

$$|i_2; i_1\rangle = -|i_1; i_2\rangle \quad (4)$$

The procedure is equivalent to the standard antisymmetrization of the two fermion wave functions and hence accounts for the Pauli’s exclusion principle.

We will use the basis vectors (1) where $i_1 > i_2$ and apply equation (4) when needed. For two t_{1u} electrons, our basis (1) consists of 15 different state vectors $|I\rangle$ (for two holes, the fivefold h_u degeneracy leads to 45 states). In the following we will study the intramolecular correlations of electrons (holes) within a multipole expansion of the two-body Coulomb potential $V(\vec{r}, \vec{r}') = 1/|\vec{r} - \vec{r}'|$ (charge $e = \text{unity}$). In terms of real spherical harmonics Y_l^τ , where τ stands for $m = 0$,

(m, c) or (m, s) [14], the expansion reads

$$V(\vec{r}, \vec{r}') = \sum_{l, \tau} v_l(r, r') Y_l^\tau(\hat{n}) Y_l^\tau(\hat{n}') \quad (5)$$

where

$$v_l(r, r') = \left(\frac{r_{<}^l}{r_{>}^{(l+1)}} \right) \frac{4\pi}{2l+1} \quad (6)$$

with $r_{>} = \max(r, r')$, $r_{<} = \min(r, r')$.

The direct matrix elements of the intramolecular Coulomb interaction for the transitions $i_1 \rightarrow j_1$ for the first electron and $i_2 \rightarrow j_2$ for the second (we recall that $i_1 > i_2$ and $j_1 > j_2$) are obtained as

$$\langle I | V(\vec{r}, \vec{r}') | J \rangle^{\text{dir}} = \sum_{l, \tau} v_l c_{l, \tau}(i_1 j_1) c_{l, \tau}(i_2 j_2) \quad (7)$$

Here

$$v_l = \int dr r^2 \int dr' r'^2 \mathcal{R}^2(r) \mathcal{R}^2(r') v_l(r, r') \quad (8)$$

accounts for the average radial dependence. The transition matrix elements $c_{l, \tau}$ are defined by

$$c_{l, \tau}(ij) = \int d\Omega \langle i | \hat{n} \rangle Y_l^\tau(\hat{n}) \langle \hat{n} | j \rangle \quad (9)$$

The exchange interaction is obtained by considering the transition $i_1 \rightarrow j_2$ for the first electron and the $i_2 \rightarrow j_1$ for the second and then by using equation (4) in order to return to the standard order of spin-orbitals. We find

$$\langle I | V(\vec{r}, \vec{r}') | J \rangle^{\text{exch}} = - \sum_{l, \tau} v_l c_{l, \tau}(i_1 j_2) c_{l, \tau}(i_2 j_1) \quad (10)$$

In evaluating the right hand side terms of equations (7) and (10) one uses the selection rules imposed by the coefficients $c_{l, \tau}$. One finds that only terms with even l occur: $l = 0, 2, 4, \dots, 10$. Adding the contributions from direct and exchange interactions, equations (7) and (10), and solving the secular problem for the 15×15 matrix of intramolecular interactions, we obtain the energy levels $E_p[t_{1u}^2]$, $p = 1-15$, which we write in form of the canonical expression (11) below. We have extended the method to the case of the three electron configuration t_{1u}^3 . There are 20 basis vectors $|I\rangle = |i_1 i_2 i_3\rangle$, where $i_1 > i_2 > i_3$. The transitions between these states are obtained by permutations of third order [10]. The Coulomb potential is now given by a sum of three two-body terms. Again we diagonalize the interaction matrix and write the energy levels $E_p[t_{1u}^3]$, $p = 1-20$, in the canonical form (11). Next, we have treated the case of four electrons. There we start from the completely filled t_{1u} shell (six electrons) and consider the interactions of two t_{1u} holes, $p = 1-15$.

Finally, the term scheme for $n = 2, 3, 4$ electrons is written as

$$E_p[t_{1u}^n] = \binom{n}{2} U_0 + \sum_{l=2}^{10} v_l \lambda_l^{(n)}(p) \quad (11)$$

for $p = 1-15, 1-20, 1-15$, respectively, and where only even values of l occur. Here $\binom{n}{2}$ is a binomial coefficient equal to the number of electron pairs, $U_0 = v_0/4\pi$ is the Hubbard repulsion, and $\lambda_l^{(n)}(p)$ are numerical constants that are polynomials of second degree in the transition matrix elements $c_{l,\tau}(ij)$. The symmetry between the four electrons and the two holes within the t_{1u} LUMO configuration implies $\lambda_l^{(4)}(p) = \lambda_l^{(2)}(p)$, $p = 1-15$.

Expression (11) has been written in a form which is analogous to the term scheme for the electronic energy levels of atoms [15]. Notice however that in the present case the quantities $\lambda_l^{(n)}(p)$ are obtained by taking into account the symmetry I_h of the molecule, in contradistinction with the spherical symmetry for the atomic case. The canonical form (11) suggests that the term scheme for a given n does only depend quantitatively but not qualitatively on the radial coefficients v_l . Irrespective of the values of v_l , the 15 states of the $n = 2$ case form three distinct terms, i.e., one ninefold degenerate $\{t_{1u}^2; 1\}$, one fivefold degenerate $\{t_{1u}^2; 2\}$ and one single-level term $\{t_{1u}^2; 3\}$. Similarly, the 20 states of the $n = 3$ case separate into one fourfold, one 10-fold and one sixfold degenerate terms. The orbital parts of the molecular many electron wave functions transform as irreducible representations Γ of I_h , while the spin functions as single (t_{1u}^2) or double valued (t_{1u}^3) representations of $SO(3)$ [1, 6, 7]. Therefore, we classify the molecular terms [6, 7] by the nomenclature $^{2S+1}\Gamma$, where $2S+1$ is the spin multiplicity. Notice that the t_{1u}^2 and t_{1u}^3 energy spectra are the analogue of p^2 ($^3P, ^1D, ^1S$) and p^3 ($^4S, ^2D, ^2P$) terms in atomic physics [15]. The number of states per term level (degeneracy) is given by $(2S+1)d_\Gamma$, where d_Γ is the dimension of the irreducible representation Γ . We recall that $d_\Gamma = 1, 3, 4, 5$ for A, T, G and H , respectively.

In order to study the splitting quantitatively, we have calculated the integrals v_l using as a model the radial dependence

$$\mathcal{R}(r) = C' \mathcal{R}_{p_z}(|r - r_{C_{60}}|) \quad (12)$$

where C' is a normalization constant and $\mathcal{R}_{p_z}$ is the radial dependence of the carbon p_z orbital in LDA. The results for v_l and U_0 are quoted in Table 1. Notice that U_0 is close to the estimated value of a free molecule [3]. (We have also performed calculations using different models for $\mathcal{R}$, but the results were found almost the

Table 1. Calculated U_0 and v_l ($l = 2, 4, 6, 8, 10$), in eV

U_0	$l = 2$	4	6	8	10
3.622	6.798	2.965	1.673	1.074	0.747

Table 2. Calculated molecular terms, in eV; $({}^n_2)U_0$ is zero of energy

$(t_{1u})^2$			$(t_{1u})^3$		
${}^3T_{1g}$	${}^1H_g$	${}^1A_g$	${}^4A_u$	${}^2H_u$	${}^2T_{1u}$
-0.117	0.073	0.359	-0.351	-0.066	0.125

same [10].) Taking into account the calculated values of $\lambda_l(p)$, we finally obtain for the molecular terms $E_p[r^n_{1u}]$ the values quoted in Table 2.

From Table 2 we see that the ground state of C_{60}^{2-} is the ${}^3T_{1g}$ triplet, in agreement with Hund’s rule but at variance with earlier configuration interaction calculations [4]. We have thoroughly investigated the discrepancy by studying the mixing between molecular terms of the $(t_{1u})^2$ and $(t_{1g})^2$ configurations as a function of the energy separation $\Delta\epsilon_1 = \epsilon(t_{1g}) - \epsilon(t_{1u})$ between one electron states. (The configuration $t_{1u}t_{1g}$ has different parity and does not mix with $(t_{1u})^2$ and $(t_{1g})^2$.) From Fig. 1 we see that the ground state changes from the singlet ${}^1A_g$ to the triplet ${}^3T_{1g}$ with increasing $\Delta\epsilon_1$. The experimental value $\Delta\epsilon_1 = 1.153$ eV [8,16] implies that the ground state is a triplet, as obtained by our calculations. The smaller value $\Delta\epsilon_1 = 0.64$ eV used in [4] leads probably to the overestimate of configuration mixing.

Next we have investigated the configurations of holes $(h_u^+)^n$, $n = 2-5$, which are equivalent to the configurations $(h_u)^{10-n}$ of electrons in the molecular HOMO levels.

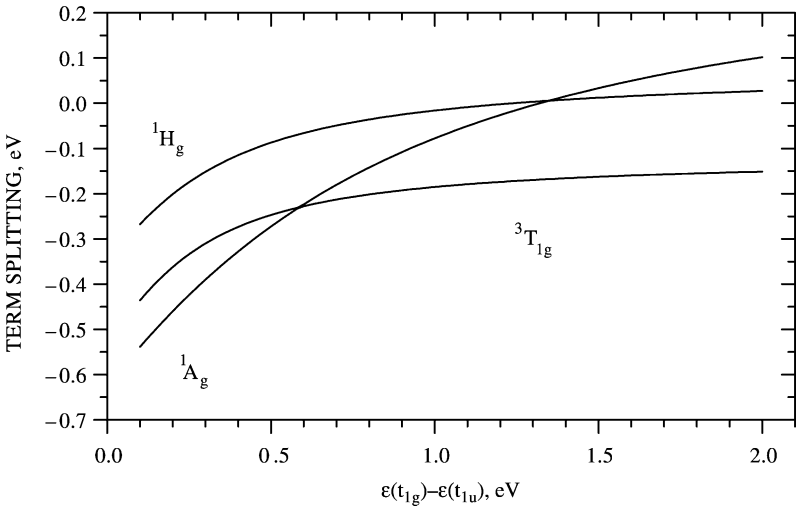


Fig. 1. Three lowest levels of the coupled $(t_{1u})^2 + (t_{1g})^2$ configurations as a function of $\Delta\epsilon_1 = \epsilon(t_{1g}) - \epsilon(t_{1u})$. The ground state is a singlet ${}^1A_g$ for $\Delta\epsilon_1 < 0.58$ eV, and the triplet ${}^3T_{1g}$ for $\Delta\epsilon_1 > 0.58$ eV.

As a result, we obtain the term scheme

$$E_p[h_u^{+n}] = \binom{10-n}{2} U_0 + \sum_{l=2}^{10} v_l \mu_l^{(n)}(p) \quad (13)$$

where only even values of l occur. The coefficients $\mu_l^{(n)}(p)$ are again molecular invariants. The number of states is $p_{\max}(n) = 45, 120, 210, 252$ and the number of different energy terms is 7, 12, 27, 27 for $n = 2, 3, 4, 5$, respectively. In Table 3 we have quoted the four lowest terms and the highest one for each of these cases. By using $(2S+1)d_f$ we see that the number of states in a small energy interval $\Delta\epsilon \sim 0.03$ eV near the ground state is 30, 40, 25, 6 for $n = 2, 3, 4, 5$, respectively. This suggests that the configuration of $n = 3$ holes is most susceptible for Jahn–Teller distortions of the C_{60} molecule.

As a direct application of electric molecular terms we calculate the corresponding magnetic moments by studying the polarization of electronic (hole) states in a small external magnetic field. For a field H in z -direction we add to the potential (5) a magnetic term

$$V_H = -\mathcal{M}_z \cdot H \quad (14)$$

Here the magnetization for n electrons (or holes) $\mathcal{M}_z = \sum_i^n M_z(n)$ is a sum of one-electron (-hole) terms with

$$M_z(n) = \mu_B(L_z(n) + 2S_z(n)) \quad (15)$$

where L_z and S_z are the z -component of the angular momentum and the spin, respectively; μ_B is the Bohr magneton. We consider matrix elements $\langle I|V_H|J\rangle$ where $|I\rangle$ and $|J\rangle$ are again n -electron basis vectors. For the case of two t_{1u} electrons we have explicitly

$$\begin{aligned} \langle I|V_H|J\rangle = & [\langle i_1|M_z|j_1\rangle\delta(i_2j_2) + \langle i_2|M_z|j_2\rangle\delta(i_1j_1) - \langle i_1|M_z|j_2\rangle\delta(i_2j_1) \\ & - \langle i_2|M_z|j_1\rangle\delta(i_1j_2)] \cdot H \end{aligned} \quad (16)$$

Table 3. Calculated molecular terms of the configurations $(h_u^+)^m$, $m = 2-5$, in eV; $\binom{10-n}{2}U_0$ is zero of energy

$(h_u)^2$		$(h_u)^3$		$(h_u)^4$		$(h_u)^5$	
$^3T_{1g}$	-0.242	$^4T_{1u}$	-0.687	^5H_g	-1.337	^6A_u	-2.228
^3G_g	-0.216	^4G_u	-0.662	^3G_g	-0.982	^4H_u	-1.672
$^3T_{2g}$	-0.213	$^4T_{2u}$	-0.658	^3H_g	-0.981	^2H_u	-1.294
^1G_g	-0.049	$^2T_{2u}$	-0.423	^1G_g	-0.805	^2G_u	-1.293
...	...	...	...	...	...	...	...
^1A_g	0.958	^2H_u	0.514	^1A_g	1.027	^2H_u	0.135

The elements $\langle i|M_z|j\rangle$ describe transitions between one-electron spin-orbitals and are readily evaluated. Next we diagonalize $\langle I|V + V_H|J\rangle$, where V is the Coulomb operator. Due to the presence of the magnetic term V_H , the degeneracies of the Coulomb contributions in Table 2 are lifted and the magnetic moment of each sublevel p is given by $\mathcal{M}(p) = \langle p|M_z|p\rangle$, where $|p\rangle$ is the corresponding eigenvector. For the two electron case the ninefold degenerate ground state ${}^3T_{1g}$ gives rise to the magnetic moments $\mathcal{M}_z = (\pm 4.5, \pm 2.5, \pm 2, \pm 0.5, 0)$, in units μ_B , while ${}^1H_g$ leads to $\mathcal{M}_z = (\pm 5, \pm 2.5, 0)$. In the ${}^1A_g$ state $\mathcal{M}_z = 0$, since the spin and the orbital moments are quenched. For the case of three t_{1u} electrons we have $\mathcal{M}_z = (\pm 3, \pm 1)$ for the ${}^4A_u$ ground term and $\mathcal{M}_z = (\pm 6, \pm 4, \pm 3.5, \pm 1.5, \pm 1)$ and $\mathcal{M}_z = (\pm 3.5, \pm 1.5, \pm 1)$ for the terms ${}^2H_u$ and ${}^2T_{1u}$, respectively. We conclude that the values of the magnetic moments of ${}^3T_{1g}$, ${}^2H_u$ and ${}^2T_{1u}$ terms are not equidistant, in contrast with the atomic case, and hence they cannot be described by the Landé g factor. We have also calculated magnetic moments for the hole configurations $(h_u^+)^n$, $n = 2-4$ and the same remark applies.

In order to study the magnetic moment for an arbitrary orientation of the molecule with respect to the magnetic field, we have rotated the molecule away from the standard position of [12] by using the transformation laws of spinors and spherical harmonics [14]. For both t_{1u}^n and $(h_u^+)^n$ cases we have found that the magnetic moment is independent of the molecular orientation. While such a result is known for the atomic case, where spherical symmetry applies [15], it is unexpected here, since the C_{60} molecule has icosahedral symmetry. (For example, the magnetic moment of a π or δ MO of diatomic molecule is anisotropic in respect to the direction of the magnetic field [17].) In order to clarify this issue, we have studied the polarization of spin and orbital momenta separately. While for spins the orientation invariance is rather obvious, it also holds for the orbital momenta. For the cases of one t_{1u} electron or one h_u^+ hole we have demonstrated the orientation invariance in a fully analytical calculation [10]. On a more general scale, this problem calls for a group theoretical solution.

Finally, we have calculated optical absorption lines for the dipolar electronic transitions $(t_{1u})^2 \rightarrow (t_{1u}t_{1g})$ of C_{60}^{2-} . We find three lines for the ground state ${}^3T_{1g}$ level [10]. Two transitions, ${}^3T_{1g} \rightarrow {}^3H_u$ and ${}^3T_{1g} \rightarrow {}^3T_{1u}$ can be tentatively ascribed to the two near-infrared dominant bands at 950 and 830 nm, obtained by infrared spectroscopy of C_{60}^{2-} in solutions [8]. In addition, we find a third band ${}^3T_{1g} \rightarrow {}^3A_u$ at higher energy (~ 0.9 eV). We suggest to perform optical experiments on C_{60}^{n-} in the gas phase, possibly with the method of Ref. [18].

In the present paper we assume that the molecule has the icosahedral symmetry. If one wants to consider a distortion of C_{60}^{m+} or C_{60}^{n-} , the energy levels and their eigenvectors obtained here can be used as a starting point for the description of the Jahn–Teller effect in these systems. Indeed, the electron–phonon (or vibronic) coupling occurs if $[\Gamma_{el}]^2$ contains Γ_{vib} [19]. (Here Γ_{el} is the symmetry of an electronic molecular term, while Γ_{vib} is the symmetry of a vibrational normal mode.) Calculations using the terms in scheme of Ref. [4] have been performed in Ref. [20].

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REFERENCES

- [1] M. S. Dresselhaus, J. Dresselhaus and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, London, 1995.
- [2] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, 1991, **350**, 600.
- [3] O. Gunnarsson, *Rev. Mod. Phys.*, 1997, **69**, 575.
- [4] F. Negri, G. Orlandi and F. Zerbetto, *J. Am. Chem. Soc.*, 1992, **114**, 2909.
- [5] R. Saito, G. Dresselhaus and M. S. Dresselhaus, *Chem. Phys. Lett.*, 1993, **210**, 159.
- [6] B. N. Plakhutin, *Chem. Phys. Lett.*, 1994, **227**, 396; B. N. Plakhutin and R. Carbo-Dorca, *Phys. Lett. A*, 2000, **267**, 370.
- [7] E. Lo and B. R. Judd, *Phys. Rev. Lett.*, 1999, **82**, 3224; B. R. Judd and E. Lo, *J. Chem. Phys.*, 1999, **111**, 5706.
- [8] C. A. Reed and R. D. Bolskar, *Chem. Rev.*, 2000, **100**, 1075.
- [9] A. V. Nikolaev and K. H. Michel, *Eur. Phys. J. B*, 1999, **9**, 619; A. V. Nikolaev and K. H. Michel, *Phys. Rev. B*, 2002, **66**, 054103.
- [10] A. V. Nikolaev and K. H. Michel, *J. Chem. Phys.*, 2002, **117**, 4761.
- [11] R. C. Haddon, *et al.*, *Chem. Phys. Lett.*, 1986, **125**, 459; R. C. Haddon, *Science*, 1993, **261**, 1545.
- [12] N. V. Cohan, *Proc. Camb. Phil. Soc. Math. Phys. Sci.*, 1958, **54**, 28.
- [13] E. Tosatti, N. Manini and O. Gunnarsson, *Phys. Rev. B*, 1996, **54**, 17184.
- [14] C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids*, Clarendon Press, Oxford, 1972.
- [15] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, University Press, Cambridge, 1967.
- [16] T. Kato, T. Kodma, T. Shida, T. Nakagawa, Y. Matsui, S. Suzuki, H. Shiromaru, K. Yamauchi and Y. Achiba, *Chem. Phys. Lett.*, 1991, **180**, 446; M. A. Greaney and S. M. Gorun, *J. Phys. Chem.*, 1991, **95**, 7142.
- [17] P. W. Atkins, *Molecular Quantum Mechanics*, University Press, Oxford, 1988.
- [18] M. Boyle, K. Hoffmann, I. V. Hertel, R. D. Levine and E. E. B. Campbell, *Phys. Rev. Lett.*, 2001, **87**, 273401.
- [19] L. D. Landau, E. M. Lifshitz, *Quantum Mechanics – Non-relativistic Theory*, Pergamon Press, Oxford, 1965, Vol. 3, Chap. 102.
- [20] M. C. M. O'Brien, *Phys. Rev. B*, 1996, **53**, 3775.

Cage Structure Distortion of Fullerenes

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Abstract

We report an electron spin resonance (ESR) study on a C_{60}^- anion and a metal (M) encapsulated in fullerene (C_n) (a metallofullerene: $M@C_n$). The anisotropy components of the g -factor of C_{60}^- were determined accurately from the analysis of angular-dependent ESR spectra of single crystal C_{60}^- salt. The evaluation of the g -factor was performed according to the classification of symmetry of the C_{60}^- geometry. It was found out from the evaluation that the molecular structure of C_{60}^- should be distorted to lower symmetry, C_{2h} or C_i . The variety of ESR spectra of metallofullerenes of $La@C_n$ s was obtained in terms of a g -factor, a hyperfine coupling constant, and a line width. In the case of the isomer I of $La@C_{80}$ and the isomer II of $La@C_{84}$, an abnormally large line width was measured. The molecular structure with high symmetry would reflect on the specific spin dynamics.

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Some fullerenes have a molecular structure with high symmetry [1]. It is well known that the I_h structure of C_{60} was experimentally proved by ^{13}C -NMR measurements [2]. Spectroscopic study on fullerenes offers a likely playground for the discussion of molecular symmetry in 3D fashion [3–10]. Two examples of the study on the cage structure distortion of fullerenes are given in this report.

The first example is the analysis of the anisotropy components of the g -factor, which could give detailed information of the molecular and electronic structure of C_{60}^- . The electron spin resonance (ESR) spectrum with g -factor of 1.9991 was reported for a radical ionic salt of C_{60}^- in microcrystals [11]. It is expected that the well-aligned orientation of the C_{60}^- molecule in a single crystal gives a sharper line to the ESR spectrum, and allows the determination of the accurate values of the g -factor. Pénicaud *et al.* [12] have reported on the synthesis of high-quality single crystals of salts of $[(C_6H_5)_4P]_2[C_{60}][I]_x$. They demonstrated the production of C_{60}^- in the crystal by NIR absorption and ESR measurements. Gotschy *et al.* [13] have measured the ESR spectra of the same system at frequencies of 9.7 GHz (X-band) and 34 GHz (Q-band) in the temperature range between 3.5 and 300 K, and pointed out the dynamic process of the temperature-dependent jumping between the Jahn–Teller distorted structures of C_{60}^- . We synthesized a series of salts of

$[(C_6H_5)_4P]_2[C_{60}][X]_x$ ($X = Cl, Br, I$) and investigated not only the crystal structures by X-ray analysis but also the g -tensors of C_{60}^- in the crystals by angular-dependent ESR measurements [6]. We clarify the relationship between the orientations of C_{60}^- defined in the crystal and the g -tensors. The space group is determined to be $I_{4/m}$ for all the crystals from the X-ray analysis, as reported by other groups [12–14]. There are no distinct differences of crystal structures between the salts with different halogen anions, in which C_{60}^- are located on $4/m$ centers. However, the icosahedral point group has no element of 4-fold symmetry. So, it was assumed in the analysis of the X-ray data that the orientational disorder about C_{60}^- remains in the crystal. The two sites of C_{60}^- correspond to different orientations at right angles relative to each other on the a – b plane, and they are distributed with equal statistical weight in the crystal. They are degenerate and have equivalent crystal fields because of the equivalence of the a and b axes in the crystal. The doublet lines were obtained in the ESR measurement at 4 K. It was deduced that these two lines came from two different g -tensors. Thus we performed the angular-dependent ESR measurements by rotating the crystal about two axes at right angles in the magnetic field to determine the principal values and the principal axes of the two g -tensors. The principal values of the two g -tensors were almost the same within experimental error ($g_{\parallel} = 1.9995$, $g_{\perp} = 1.9968$) and the long axes of the two g -tensors crossed at right angles. Then the components of the deviation relative to that of free electron (g_e) were both negative, ($\Delta g_{\parallel} = -0.0028$, $\Delta g_{\perp} = -0.0055$). There was no definite difference among the results of three kinds of crystals containing different halogen anions. An analysis which treats the observed g -factor with the ordinary second-order perturbation theory was applied here. It was assumed that the triply degenerate T_{1u} states were split by the Jahn–Teller effect and the angular momentum was quenched accordingly. Then the anisotropic components of the deviation (Δg_{ij}) relative to the value of g_e were given by the following expression,

$$\Delta g_{ij} = -2\lambda \sum_n \frac{\langle g | L_i | n \rangle \langle n | L_j | g \rangle}{E_n - E_g}$$

where λ is the spin–orbit coupling constant of carbon atom, $|g\rangle$ and $|n\rangle$ are the ground and the n th excited electronic states, E_g and E_n are the energy levels of the ground and n th excited electronic states, L_i is the i th component of the angular momentum operator. Only the three lowest lying electronic states which were belonging to the T_{1u} degenerate states prior to the splitting were considered here. These three electronic states can be classified according to symmetry. For example the three states are denoted as B_{1u} , B_{2u} , and B_{3u} states in D_{2h} symmetry, A_u and two B_u states in C_{2h} symmetry, or three A_u states in C_i symmetry. It is deduced from the character table that the three angular momentum operators L_x , L_y , L_z provide a basis for each representation. The integral $\langle g | L_i | n \rangle$ will vanish unless the direct product of three representations $\Gamma(g) \times \Gamma(L_i) \times \Gamma(n)$ contains the totally symmetric representation. Then we can evaluate the anisotropic components of the deviation Δg_{ij} according to the classification of symmetry. Consequently, the analysis deduced that

only the case of the B_u ground state in C_{2h} symmetry, or the A_u state in C_i symmetry, can give non-vanishing deviation, Δg_{xx} , Δg_{yy} , and Δg_{zz} . On the other hand, the non-zero values of the deviation, $\Delta g_{\parallel} = -0.0028$ and $\Delta g_{\perp} = -0.0055$, were experimentally obtained as mentioned before; this means that the molecular structure of C_{60}^- in $[(C_6H_5)_4P]_2[C_{60}][X]_x$ ($X = Cl, Br, I$) should be distorted to the lower symmetries C_{2h} or C_i .

Our other example is the temperature-dependent ESR study of the series of $La@C_n$ isomers in CS_2 solution [9,10], which revealed the influence of the cage structure on the electronic structure of endohedral La ions. The anisotropic ESR parameters, such as Δg , Δa , and the quadrupole interaction, were determined. The quantitative discussion of these parameters indicated that the electronic structure of all $La@C_n$ could be described as $La^{3+}@C_n^{3-}$. The various values of g close to g_e reflected the relative position of the low-lying orbital to that of the π orbital of the cage. Interesting features such as extra spin dynamics other than those induced by molecular tumbling in solution were suggested for $La@C_{80}$ -I and $La@C_{84}$ -II. The line width at maximum slope ω_{msl} of the ESR spectrum was fitted to an expression of the form [15].

$$\Delta\omega_{msl} = K_0 + K_1M_I + K_2M_I^2 + K_4M_I^4$$

where coefficient K_i means

$$\begin{aligned} K_0 &= \frac{\hbar}{g_e\mu_B} \left\langle \frac{1}{45} \left[\Delta g \frac{\mu_B B_0}{\hbar} \right]^2 \left\{ 4\tau_r + 3 \frac{\tau_r}{1 + (\omega_z \tau_r)^2} \right\} \right. \\ &\quad + \frac{1}{40} \left(\frac{2}{3} \Delta a \right)^2 I(I+1) \left\{ 3\tau_r + 7 \frac{\tau_r}{1 + (\omega_z \tau_r)^2} \right\} \\ &\quad \left. + \frac{3}{40} \left[\frac{eQV_{zz}}{I(2I-1)} \right]^2 I(I+1)[I(I+1)-1]\tau_r \right\rangle \\ K_1 &= \frac{\hbar}{g_e\mu_B} \frac{1}{15} \left[\Delta g \frac{\mu_B B_0}{\hbar} \right] \left(\frac{2}{3} \Delta a \right) \left\{ 4\tau_r + 3 \frac{\tau_r}{1 + (\omega_z \tau_r)^2} \right\} \\ K_2 &= \frac{\hbar}{g_e\mu_B} \left\langle \frac{1}{40} \left(\frac{2}{3} \Delta a \right)^2 \left\{ 5\tau_r - \frac{\tau_r}{1 + (\omega_z \tau_r)^2} \right\} + \frac{3}{20} \left[\frac{eQV_{zz}}{I(2I-1)} \right]^2 I(I+1)\tau_r \right\rangle \\ K_4 &= -\frac{\hbar}{g_e\mu_B} \frac{9}{40} \left[\frac{eQV_{zz}}{I(2I-1)} \right]^2 \tau_r \end{aligned}$$

Here the parameters g_e , μ_B , ω_z , I , M_I , and τ_r were the g -factor of the free electron, the Bohr magneton, the microwave frequency of measurement, the nuclear spin quantum number, its projection, and the molecular rotational correlation time in solution. The anisotropic parameters, Δg , Δa and $eQV_{zz}/I(2I-1)$ were estimated from line width coefficients, K_1 , K_2 and K_4 , respectively. Thus the analysis of the temperature dependences of coefficients K_1 , K_2 and K_4 gave the anisotropic parameters, Δg , Δa and $eQV_{zz}/I(2I-1)$ for all molecules. On the other hand,

the coefficient K_0 in the line width formula includes nuclear spin-independent contributions from spin–rotation, exchange and electron dipole–dipole interaction in addition to terms from anisotropic g , a , and quadrupole interactions. The K_0 for all cases of La@C_n showed a parabolic temperature dependence due to spin–rotation interaction, which is proportional to $(\Delta g)^2$. For a quantitative analysis, a constant value of about 0.027 G should be subtracted first in the whole temperature range. This constant contribution might result from unresolved ^{13}C -hyperfine couplings and field inhomogeneity of the spectrometer. A deviation from “standard behaviors” was observed for $\text{La@C}_{80}\text{-I}$ and $\text{La@C}_{84}\text{-II}$. A much larger contribution to K_0 was observed at higher temperatures. The contribution increased with increase of temperature. It is worthwhile mentioning that the satellite structure due to the ^{13}C -hyperfine on the fullerene cage disappeared in the case of $\text{La@C}_{80}\text{-I}$ and $\text{La@C}_{84}\text{-II}$ even at the temperature of 215 K for which the minimum line width was observed. The origin of this thermally activated process for two metallofullerenes is attributed to the following mechanisms. One might be related to a multi-minimum potential of the metal ion. Spin relaxation would be induced by thermally agitated latchet motion between various minima. The energy barriers in $\text{La@C}_{80}\text{-I}$ and $\text{La@C}_{84}\text{-II}$ are small enough to be overcome. Internal motion of the ion was suggested by the NMR study of $\text{La}_2\text{@C}_{80}$. Another mechanism would be transitions between Jahn–Teller distorted structures of the cage. According to the isolated pentagon rule, the formation of 7 ($2C_{2v}$, D_2 , D_3 , D_{5d} , D_{5h} , and I_h) cages of C_{80} , and 24 (C_1 , $5C_s$, $5C_2$, $4C_{2v}$, $4D_2$, $2D_{2d}$, D_{3d} , D_{6h} , and T_d) cages of C_{84} are possible [1]. Among them the cages of D_3 , D_{5d} , D_{5h} , and I_h -symmetry for $\text{La@C}_{80}\text{-I}$ and of D_{2d} , D_{3d} , D_{6h} , and T_d -symmetry for $\text{La@C}_{84}\text{-II}$ would be highly symmetric structures which are Jahn–Teller active. Simple MO diagrams of C_{84} with D_{2d} and T_d symmetries were obtained by MO calculations. The LUMO of the D_{2d} structure is doubly degenerate, and the resultant electronic state after an intermolecular triple charge transfer in La@C_{84} leads to degeneracy and an open shell nature. A similar behavior can be expected for the T_d case. We have to note here that the off-center position of the metal will break the high symmetry of the total system. However, the pseudo-Jahn–Teller effect could still be expected. The estimated values of the activated energies for $\text{La@C}_{80}\text{-I}$ and $\text{La@C}_{84}\text{-II}$ should be compared with that predicted by the theoretical calculation of the energy potential.

REFERENCES

- [1] P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Oxford University Press, Oxford, 1995.
- [2] H. Ajie, M. M. Alvarez, S. J. Anz, R. D. Beck, F. Diederich, K. Fostiropoulos, D. R. Huffman, W. Kratschmer, Y. Rubin, K. E. Schriver, D. Sensharma, and R. L. Whetten, *J. Phys. Chem.*, 1990, **94**, 8630.
- [3] C. A. Reed and R. D. Bolskar, *Chem. Rev.*, 2000, **100**, 1075.
- [4] T. Kato, T. Kodama, M. Oyama, S. Okazaki, T. Shida, T. Nakagawa, Y. Matsui, S. Suzuki, H. Shiromaru, K. Yamauchi, and Y. Achiba, *Chem. Phys. Lett.*, 1991, **186**, 35.

- [5] T. Kato, T. Kodama, and T. Shida, *Chem. Phys. Lett.*, 1993, **205**, 405.
- [6] T. Kodama, M. Kato, K. Mogi, M. Aoyagi, and T. Kato, *Mol. Phys. Rep.*, 1997, **18/19**, 121.
- [7] T. Kato, S. Suzuki, K. Kikuchi, and Y. Achiba, *J. Phys. Chem.*, 1993, **97**, 13425.
- [8] T. Kato, S. Bandow, M. Inakuma, and H. Shinohara, *J. Phys. Chem.*, 1995, **99**, 856.
- [9] S. Okubo, T. Kato, M. Inakuma, and H. Shinohara, *New Diamond Front. Carbon Technol.*, 2001, **11**, 285.
- [10] S. Okubo and T. Kato, *Appl. Magn. Reson.*, 2002, **23**, 481.
- [11] P.-M. Allemand, G. Srdanov, A. Koch, K. Khemani, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, and R. L. Whetten, *J. Am. Chem. Soc.*, 1991, **113**, 2780.
- [12] A. Pénicaud, A. Perez-bernitez, V. R. Gleason, P. E. Munoz, R. Escudero, *J. Am. Chem. Soc.*, 1993, **115**, 10392.
- [13] B. Gotschy, M. Keil, H. Klos, I. Rystau, *Solid State Commun.*, 1994, **92**, 935.
- [14] U. Bilow and M. Jansen, *J. Chem. Soc., Chem. Commun.*, 1994, 403.
- [15] R. Wilson and D. Kivelson, *J. Chem. Phys.*, 1966, **44**, 154.

Multiple Occupancy of Triply Degenerate States in Icosahedral Symmetry

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Abstract

In fullerene anions C_{60}^{n-} , the n electrons outside closed shells occupy t_{1u} triplet electronic states. Jahn–Teller (JT) coupling between these states and 5-fold h -type vibrations has important consequences for many properties of the fullerene anions. It is therefore important to understand the JT effect experienced by these ions from a theoretical point of view. We will study the cases of $n = 2$ and 4, where the lowest adiabatic potential energy surface is found to consist of a two-dimensional trough in linear coupling. The motion of the system therefore consists of vibrations in three directions ‘across’ the trough and pseudo-rotations in two directions around the trough. Analytical expressions for states of the system that reflect this motion are obtained and the resultant energies determined.

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1. INTRODUCTION

Since the discovery of fullerenes [1], many scientists have been investigating the chemical and physical properties of this interesting class of materials. In particular, the alkali-metal-doped fullerides A_xC_{60} ($A = K, Rb$, etc. and $x = 1-6$) have been found to show a variety of interesting phenomena. For example, it has been found that K_3C_{60} and related materials can be metals [2] or they can be superconducting [3–5]. However, A_4C_{60} and A_2C_{60} have been found to be non-magnetic insulators [6–8]. This is somewhat surprising because the electrons occupy a LUMO band of t_{1u} symmetry [9,10] which is only partly filled. These materials would therefore be expected to be metals from band theory [11,12]. A number of theoretical explanations for these anomalies have been put forward [13–15]. Many of these explanations require the presence of a strong electron–phonon interaction, known as Jahn–Teller (JT) coupling in this context. It has been proposed that A_4C_{60} and A_2C_{60} are insulating because electron–electron and electron–phonon interactions open band gaps cooperatively, and that they are non-magnetic because the JT coupling overcomes the usual Hund’s rule ordering. It is therefore important to understand the JT effect in doped C_{60}^{n-} molecules from a theoretical point of view. Although a range of different analytical and numerical approaches have been used to examine various JT problems [16–18], little work has been undertaken on JT effects applicable to these systems.

In this paper, we will study in particular the cases of doping with $n = 2$ or 4 electrons. The electrons occupy t_{1u} orbitals, and couple vibronically to 5-fold h vibrational modes in what has been called $p^2 \otimes h$ and $p^4 \otimes h$ JT effects because of the convenience of labelling the resultant states using angular momentum notation [19]. The approach adopted is based on a method used previously for $E \otimes e$ and $T \otimes h$ JT systems [20,21]. However, the extension is far from trivial as it involves 5-fold vibrations and a 6-fold electronic basis. We will consider coupling to a single h mode only. Although it is very straightforward to incorporate coupling to multiple modes by including summations in the appropriate formula, it complicates the results by introducing many more parameters (i.e., vibronic coupling strengths and frequencies) and does not significantly alter the underlying physics. Also, it is sometimes possible to reformulate multimode problems in terms of a single effective mode, depending upon what properties are required.

In the approach adopted, the lowest adiabatic potential energy surface (APES) of the JT system in question is analysed in linear coupling. Although five-dimensions are needed to describe the h_g mode in general, in the cases of $p^2 \otimes h$ and $p^4 \otimes h$ the lowest APES is found to form a trough that can be mapped onto the surface of a two-dimensional (2D) sphere [19]. The motion of the system can then be visualized in terms of rotations around the trough (called pseudo-rotations to avoid confusion with real rotations of the molecule [22]) combined with the simultaneous motion of the system across the trough involving the nuclear vibrations. It should be noted that if quadratic or other higher-order coupling terms are also included, the bottom of the trough will warp into distinct wells (i.e., low-symmetry minima). If the warping

terms are sufficiently large, the motion of the system is frozen into one of the wells. When the warping is less strong, the system will tunnel between equivalent wells. When the warping is even weaker, the pseudo-rotation will persist as a hindered rotation. This situation is very difficult to account for theoretically. As a first step it is important to understand the simple case of linear coupling only. Hence warping will not be considered further in this paper.

2. JT INTERACTION MATRICES

The Hamiltonian for the $p^2 \otimes h$ and $p^4 \otimes h$ systems can be written as

$$\mathcal{H} = -\frac{1}{2} \sum_{i=1}^5 \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_{i=1}^5 Q_i^2 + M(h) \quad (1)$$

in units in which the mass and frequency of the h mode along with $\hbar$, are set to one. The first two terms represent the kinetic and potential energies of five simple harmonic oscillators, which together transform as the H irreducible representation. They are written using normal-mode coordinates $\{Q_1, Q_2, Q_3, Q_4, Q_5\}$ as defined in Ref. [19]. Note that these corresponds to the set $\{Q_0, Q_5, Q_6, Q_e, Q_4\}$ used by Dunn *et al.* for the $T \otimes h$ system [20]. The last term represents the JT coupling between the vibrational modes and the electronic states of either the $p^2 \otimes h$ or $p^4 \otimes h$ system.

The terms from the two configurations p^2 and p^4 are ^3P , ^1D , and ^1S [23]. The high spin state ^3P is simply a P state coupled to the h vibrations. This corresponds to the system studied previously by Dunn *et al.* [20]. Therefore, we will concentrate on the low spin states in this paper. The S state does not have any diagonal JT coupling, but it is coupled to the D states. This results in a 6-fold basis.

It is now necessary to construct the JT interaction matrix. In icosahedral symmetry, the terms ^3P , ^1D , and ^1S correspond to the T_1 , H and A irreducible representations, respectively. Using the Clebsch–Gordon coefficients from Ref. [24], the orbital part of all these three terms can be written down in terms of one-electron states. The spin part can also be written as a singlet and a triplet. Next, the total states are obtained by multiplying the orbital states with the spin states. However, our total wavefunctions must be antisymmetrical in order to obey the Pauli's exclusion principle and thus an antisymmetric operator is acted upon the total wavefunctions. Eventually, the final form of the wavefunctions can be expressed in the form of a Slater determinant [23]. It is then a simple matter to construct the JT interaction matrices. The matrix elements are expanded using the Wigner–Eckart theorem [25]. The reduced matrix elements in all the cases are in fact the respective JT coupling constants and it was found that coupling constants for the D to D JT interaction is equal to that for the S to D JT interaction but is equal to the negative value of that for the P JT interaction. It is worth noting that the latter case is equivalent to the single-electron JT system. Hence the vibronic coupling constant will be defined in terms of the single-electron coupling constant k . The resulting

interaction matrix is the same as that which was given in Ref. [19] without proof, namely

$$M_{SD} = -k$$

$$\times \begin{pmatrix} 0 & -\sqrt{2}Q_1 & -\sqrt{2}Q_2 & -\sqrt{2}Q_3 & -\sqrt{2}Q_4 & -\sqrt{2}Q_5 \\ -\sqrt{2}Q_1 & Q_1 & (1/2)Q_2 & -Q_3 & -Q_4 & (1/2)Q_5 \\ -\sqrt{2}Q_2 & (1/2)Q_2 & (1/2)Q_1 + (\sqrt{3}/2)Q_4 & (\sqrt{3}/2)Q_5 & (\sqrt{3}/2)Q_2 & (\sqrt{3}/2)Q_3 \\ -\sqrt{2}Q_3 & -Q_3 & (\sqrt{3}/2)Q_5 & -Q_1 & 0 & (\sqrt{3}/2)Q_2 \\ -\sqrt{2}Q_4 & -Q_4 & (\sqrt{3}/2)Q_2 & 0 & -Q_1 & -(\sqrt{3}/2)Q_5 \\ -\sqrt{2}Q_5 & (1/2)Q_5 & (\sqrt{3}/2)Q_3 & (\sqrt{3}/2)Q_2 & -(\sqrt{3}/2)Q_5 & (1/2)Q_1 - (\sqrt{3}/2)Q_4 \end{pmatrix} \quad (2)$$

3. ADIABATIC POTENTIAL ENERGY SURFACES (APES)

We now wish to analyse the potential part of the Hamiltonian in equation (1) in order to understand the combination of vibrational and (pseudo)rotational motion of the system. To do this, it is very convenient to follow O'Brien [26,27] and use the angular parametrization

$$\begin{aligned} Q_1 &= Q \left(\frac{1}{2} (3 \cos^2 \theta - 1) \cos \alpha + \frac{\sqrt{3}}{2} \sin^2 \theta \sin \alpha \cos 2\gamma \right), \\ Q_2 &= Q \left(\frac{1}{2} \sqrt{3} \sin 2\theta \cos \phi \cos \alpha - \frac{1}{2} \sin 2\theta \cos \phi \sin \alpha \cos 2\gamma \right. \\ &\quad \left. + \sin \theta \sin \phi \sin \alpha \sin 2\gamma \right), \\ Q_3 &= Q \left(\frac{1}{2} \sqrt{3} \sin^2 \theta \cos 2\phi \cos \alpha + \frac{1}{2} (1 + \cos^2 \theta) \sin 2\phi \sin \alpha \cos 2\gamma \right. \\ &\quad \left. + \cos \theta \cos 2\phi \sin \alpha \sin 2\gamma \right), \\ Q_4 &= Q \left(\frac{1}{2} \sqrt{3} \sin^2 \theta \cos 2\phi \cos \alpha + \frac{1}{2} (1 + \cos^2 \theta) \cos 2\phi \sin \alpha \cos 2\gamma \right. \\ &\quad \left. - \cos \theta \sin 2\phi \sin \alpha \sin 2\gamma \right), \\ Q_5 &= Q \left(\frac{1}{2} \sqrt{3} \sin 2\theta \sin \phi \cos \alpha - \frac{1}{2} \sin 2\theta \sin \phi \sin \alpha \cos 2\gamma \right. \\ &\quad \left. - \sin \theta \cos \phi \sin \alpha \sin 2\gamma \right) \end{aligned} \quad (3)$$

derived in Appendix F of Ref. [19]. Conditions $0 \leq Q < \infty$, $0 \leq \alpha < \pi/3$, $0 \leq \gamma < \pi$, $0 \leq \pi/2$ and $0 \leq \phi < 2\pi$ are required to ensure that all possible distortions

in the 5D phase space are covered without repetition. Using these parametric equations, the JT interaction matrix can be transformed to a nearly diagonal form by a sequence of orthogonal transformations as given in Ref. [19]. It is possible at this stage to include a term splitting between the ${}^1D$ and ${}^1S$ states. In the remainder of this paper, we will set the term splitting to zero to avoid the complication of introducing an additional variable and also as it does not alter the principle of the calculations. However, we should bear in mind that the ${}^1S$ and ${}^1D$ terms are unlikely to be degenerate in a real system. With this simplification, one final transformation can be used to yield the six energy eigenvalues

$$kQ\left\{2\cos\left(\alpha \pm \frac{\pi}{3}\right), -\cos\left(\alpha \pm \frac{\pi}{3}\right), -2\cos\alpha, \cos\alpha\right\} \quad (4)$$

It is clearly seen that the lowest APES can occur for values $\alpha = 0, \pm \frac{2\pi}{3}$. The physics will be the same for any of these choices. For the sake of simplicity, we choose to consider $\alpha = 0$.

3.1. The Hamiltonian in the adiabatic approximation

O'Brien has applied a full adiabatic approximation [19] to the Hamiltonian (1) for the motion on the lowest APES. Using the parametrization (3), the kinetic energy part of equation (1) becomes

$$\begin{aligned} \mathcal{H}_{KE} = & -\frac{1}{2}\left[\frac{1}{Q^4}\frac{\partial}{\partial Q}\left(Q^4\frac{\partial}{\partial Q}\right) + \frac{1}{Q^2\sin 3\alpha}\frac{\partial}{\partial \alpha}\left(\sin 3\alpha\frac{\partial}{\partial \alpha}\right)\right] + \frac{1}{8Q^2} \\ & \times \left[\frac{\lambda_x^2}{\sin^2(\alpha - 2\pi/3)} + \frac{\lambda_y^2}{\sin^2(\alpha + 2\pi/3)} + \frac{\lambda_z^2}{\sin^2(\alpha)}\right] \end{aligned} \quad (5)$$

where $\lambda_x, \lambda_y, \lambda_z$ are the three components of an angular momentum operator, λ within the phonon space. Explicitly,

$$\begin{aligned} \lambda_x &= i \cos \gamma \left(\cot \theta \frac{\partial}{\partial \gamma} - \csc \theta \frac{\partial}{\partial \phi} \right) + i \sin \gamma \frac{\partial}{\partial \theta}, \\ \lambda_y &= -i \sin \gamma \left(\cot \theta \frac{\partial}{\partial \gamma} - \csc \theta \frac{\partial}{\partial \phi} \right) + i \cos \gamma \frac{\partial}{\partial \theta}, \\ \lambda_z &= i \frac{\partial}{\partial \gamma} \end{aligned} \quad (6)$$

Under the adiabatic approximation, the lowest energy eigenvalue from equation (4) at $\alpha = 0$ is used in equation (1) and together with equation (5), it can be shown that

the kinetic energy operator is eventually transformed into

$$\begin{aligned}
 & -\frac{1}{2} \left[\frac{1}{Q^2} \frac{\partial}{\partial Q} \left(Q^2 \frac{\partial}{\partial Q} \right) + \frac{1}{Q^2 \sin \alpha} \frac{\partial}{\partial \alpha} \left(\sin \alpha \frac{\partial}{\partial \alpha} \right) + \frac{1}{Q^2 \sin^2 \alpha} \frac{\partial^2}{\partial \gamma^2} \right] \\
 & + \frac{1}{2} Q^2 - 2kQ + \frac{1}{3Q^2} - \frac{1}{6Q^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (7)
 \end{aligned}$$

A complete treatment of this derivation can be found in Ref. [19]. The first three terms in the kinetic energy operator indicates the presence of a 3D harmonic oscillator, and the final two terms indicate the presence of a 2D rotator (as for the hydrogen atom). A similar conclusion was made by Auberbach *et al.* [22] where they use a semi-classical quantisation method and the molecule is said to undergo a unimodal distortion and then the semi-classical Hamiltonian is found to be separated into two parts - a harmonic oscillator part with three vibrational coordinates and a rotational part with two rotational coordinates. However, more progress in terms of specifying the wavefunctions of the system can be made by following a different approach.

4. ROTATIONAL COORDINATES

Although the parametrization of coordinates in equation (3) is useful to indicate the separation into vibrations and rotations, it does not clearly separate the five nuclear modes into vibrational and rotational parts. However, it must always be possible to move to a set of ‘rotating’ coordinates Q'_λ , formed from a linear combination of the general coordinates Q_λ that do separate into rotational and vibrational coordinates, so that the Hamiltonian in equation (5) can be written as a sum of $\mathcal{H}_{\text{rot}}$ and $\mathcal{H}_{\text{vib}}$ over the rotational coordinates and vibrational coordinates, respectively. The vibrational problem in particular is then easier to solve as the number of variables is reduced.

For the relatively simple 2D trough of the $E \otimes e$ JT system, the form of the rotating coordinates was found by inspection [21]. For the 5D space of the h -modes, this is not so obvious but can still be found with the help of the rotation matrices in Ref. [19]. We define a rotation matrix with elements $D_{\nu\lambda}$ such that

$$Q'_\nu = \sum_\lambda D_{\nu\lambda}(\phi, \theta, \gamma, \alpha) Q_\lambda \quad (8)$$

where λ and ν can take values 1–5. Setting $Q'_1 = Q$ and inverting equation (8), the parametrization (3) is recovered and therefore this makes Q'_1 the radius of the trough.

4.1. Öpik–Pryce method and shift transformation

The positions of the minimum points on the APES can be determined by applying a shift transformation

$$U = \exp\left(i \sum_{\lambda} \alpha_{\lambda} P_{\lambda}\right) \equiv \exp\left(i \sum_{\lambda} \alpha'_{\lambda} P'_{\lambda}\right) \quad (9)$$

to the original Hamiltonian and finding optimum values for the parameters α_{λ} using the Öpik–Pryce method [28], as used previously for other JT systems, by solving the equations

$$\left\langle \psi \left| \frac{\partial \tilde{\mathcal{H}}}{\partial \alpha_{\lambda}} \right| \psi \right\rangle = 0 \quad (10)$$

where $\tilde{\mathcal{H}}$ is the transformed Hamiltonian and $|\psi\rangle$ is the electronic state at the bottom of the trough, which is the eigenvector corresponding to that eigenvalue of the matrix (4) which gives the lowest value when $\alpha = 0$.

The calculation can be carried out in either the rotating or the non-rotating basis. However, as all points on the trough of minimum-energy points will be the same distance from the origin, the shift transformation parameters for the vibrational modes will be constants in the rotating system whereas they will be functions of the angles defining the trough in the non-rotating system. This makes the results in the rotating system somewhat easier to interpret. Also, if we knew which of the coordinates correspond to vibrations, we could apply the transformation to these coordinates only. However, as this is not yet known, we must apply the transformation to all coordinates. If a shift parameter is found to be zero, this means that either the coordinate corresponds to a rotation or it corresponds to a vibration about the origin of that coordinate.

Solution of equation (10) is very complicated, but the calculation can be simplified considerably because the energies of the lowest APESs are already known from equation (4) above. The results in the rotating coordinate system are

$$\alpha'_{\lambda} = \begin{cases} \rho/\hbar, & \text{for } \lambda = 1 \\ 0, & \text{for } \lambda = 2 \text{ to } 5 \end{cases} \quad (11)$$

where

$$\rho = \sqrt{\frac{2}{5}} \frac{V_H}{\mu \omega_H^2} \quad (12)$$

is the radius of the trough. This confirms the conclusion at the end of the last section that Q'_1 corresponds to a vibrational coordinate. However, at this stage the nature of the remaining coordinates is still undetermined.

4.2. Conjugate momenta

The kinetic energy part of the Hamiltonian can be written in the primed system as

$$\mathcal{H}_{\text{KE}} = \frac{1}{2} \sum_{\lambda} P'_{\lambda}{}^2 \quad (13)$$

The conjugate momenta obey the relations

$$P'_{\lambda} = -i\hbar \frac{\partial}{\partial Q'_{\lambda}} = -i\hbar \left[\sum_{\nu} D_{\lambda\nu} \frac{\partial}{\partial Q_{\nu}} \right] \quad (14)$$

After much algebra and when the appropriate limits are taken as α tends to zero, we find that

$$\begin{aligned} P'_1 &= \frac{\partial}{\partial Q} \\ P'_2 &= \frac{\lambda_y}{2Q \sin(\alpha + 2\pi/3)} \\ P'_3 &= \frac{\lambda_z}{2Q \sin \alpha} \\ P'_4 &= \frac{1}{Q} \frac{\partial}{\partial \alpha} \\ P'_5 &= \frac{\lambda_x}{2Q \sin(\alpha - 2\pi/3)} \end{aligned} \quad (15)$$

The overall result is the same as that in equation (5) following the transformation carried out by O'Brien [19]. However, this approach tells us the additional information that P'_1 , P'_3 and P'_4 contribute to the 3D harmonic oscillator part and P'_2 and P'_5 , to the rotator part.

5. THE STATES

Now that we have divided the primed coordinates into rotations and vibrations, we are in a position to be able to construct expressions for the states of the system.

5.1. Vibronic states

The shift transformation method yields expressions for the vibronic state at a point on the trough of minimum-energy points (see Ref. [29] and references therein). We know that Q'_1 , Q'_3 and Q'_4 are vibrations and therefore, the unitary shift transformation operator U will only act on these three phonon coordinates. The generalised vibronic states allowing for phonon excitations can be written in

the form of

$$U \left| \psi_{\text{vibronic}}; n_1 n_3 n_4 \right\rangle = U \left(b_1'^{\dagger} \right)^{n_1} \left(b_3'^{\dagger} \right)^{n_3} \left(b_4'^{\dagger} \right)^{n_4} \left| \psi; 0 \right\rangle \quad (16)$$

n_1 , n_3 and n_4 represent phonon excitations of $1'$, $3'$ and $4'$ symmetry, respectively. These can be obtained by applying the corresponding phonon creation operators $b_{\lambda}'^{\dagger}$ to the phonon vacuum state. Note that these must be specified in the rotating coordinate system. It is not meaningful to specify a phonon excitation in the fixed system as it would incorrectly include part of the rotation as a vibration.

5.2. Rotational states

The rotational coordinates are Q_2' and Q_5' . The rotational motion can be visualized by mapping the trough onto the surface of a 2D sphere; the rotation is governed by the usual polar coordinate definitions, θ and ϕ . This is also shown in equation (7) which has the usual form for a rotator with spherical harmonic solutions Y_{lm} . The solutions will be written in the form $|\psi_{\text{rot}}; lm\rangle$. For the high spin states case, it was found that l must be odd in order to obey the Pauli's exclusion principle and preserve the antisymmetric nature of the total wavefunctions at any point on the trough under symmetric operations [26]. In the current case, similar arguments show that l must be even. This is because the electronic basis is even under inversion and the whole vibronic wavefunction must also be even under inversion. A general mathematical proof can be found in Ref. [23].

5.3. Total states

The above procedures yield expressions for the states at a single point on the trough of minimum-energy points. As all of these points are equivalent, the total states of the system must be an integral

$$|\psi_{\text{total}}\rangle = \int U |\psi_{\text{vibronic}}\rangle |\psi_{\text{rotation}}\rangle d\Omega \quad (17)$$

over all of these points, weighted by appropriate volume elements $d\Omega$. As the trough can be mapped onto the surface of a sphere in which θ and ϕ have their usual polar coordinate definitions, it follows that $d\Omega = \sin \theta d\theta d\phi$.

In some JT systems, the lowest APES contains a set of minimum-energy wells. In these cases, tunnelling between the wells must be allowed for by taking appropriate linear combinations of the well states. Suitable combinations can be found using projection operator techniques [29]. The form of the state in equation (17) can be derived more formally using a continuous projection method as developed by Judd [31], Chancey [32] and Judd and Vogel [33], where the summation is replaced by a multi-dimensional integration to ensure that all points on the trough are considered.

6. ENERGY EVALUATIONS

It is now a simple matter to use the second quantised form of the Hamiltonian to derive expressions for the energies of the states in terms of multi-dimensional integrals. The expressions can then be evaluated computationally for any required value of coupling strength. The calculations follow the method used by Dunn *et al.* [20] for the $T \otimes h$ JT system, using general results from Ref. [34]. Overlaps and matrix elements must be evaluated between any point a on the trough and all other points b on the trough and the results integrated over all possible points a and b . In general, each point on the trough is specified by the angles θ , ϕ and γ . Therefore the calculations will involve 6D integrals over θ , ϕ and γ for point a and θ' , ϕ' and γ' for point b . The energies of the rotational states are independent of the value of m .

6.1. Zero phonon excitation states

The calculations and results for the states with no phonon excitations are carried out first. In these and subsequent calculations, the integrals that arise are all of the form

$$J(G) = \int G e^{(3/4)k^2(Z^2-1)} Y_{lm}^*(\theta', \phi') Y_{lm}(\theta, \phi) d\Omega d\Omega' \quad (18)$$

where G is a function of θ' , ϕ' , γ' , θ , ϕ , and γ . The overlap integral is found to be

$$O_{lm} = J(Z^2) \quad (19)$$

where Z^2 is the electronic overlap between the states at points θ , ϕ , and θ' , ϕ' , given by

$$Z = \cos \theta \cos \theta' + \sin \theta \sin \theta' (\cos \phi \cos \phi' + \sin \phi \sin \phi') \quad (20)$$

In order to evaluate the matrix elements, it is useful to write the Hamiltonian in the second quantised form

$$\mathcal{H} = -\frac{k}{2\sqrt{2}} \sum_{\lambda} r_{\lambda} (b_{\lambda} + b_{\lambda}^{\dagger}) + \sum_{\lambda} \left(b_{\lambda}^{\dagger} b_{\lambda} + \frac{1}{2} \right) \quad (21)$$

where the r_{λ} , are electronic operators and the sum is taken over the five components of the h mode. It is then possible to use equation (19) of Ref. [34], giving the matrix element

$$M_{lm} = J \left(Z^2 \left[\frac{5}{2} + \sum_{\lambda} k_{\lambda}(\theta', \phi') k_{\lambda}(\theta, \phi) \right] - \frac{k}{2\sqrt{2}} \sum_{\lambda} R_{\lambda} (k_{\lambda}(\theta', \phi') + k_{\lambda}(\theta, \phi)) \right) \quad (22)$$

where $R_{\lambda} = \langle \psi(\theta', \phi', \gamma') | r_{\lambda} | \psi(\theta, \phi, \gamma) \rangle$.

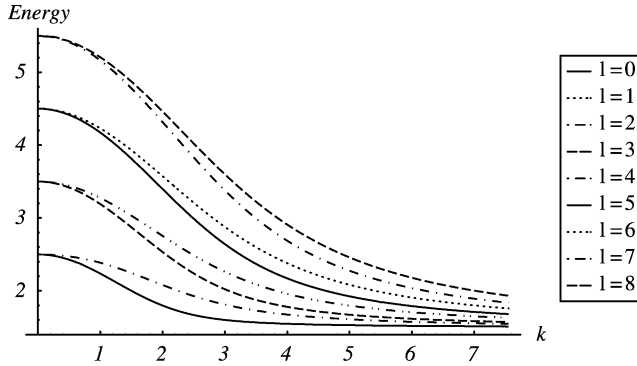


Fig. 1. The energies of the states relative to the JT energy with $L = \text{odd}$ (due to high spin term) and $L = \text{even}$ (due to low spin terms) with no phonon excitations and in units of $\hbar\omega$.

The total energy is obtained by dividing M_{lm} by O_{lm} as given in equation (19). It can be seen that for these no-phonon states, the integrals are independent of γ so are 4D. Also, the results do not depend upon the quantum number m , so we can choose to work with any m of the spherical harmonics. Nevertheless, the calculation still involves 4D integrals, which cannot be evaluated analytically and hence numerical calculations are carried out. The results are plotted against the coupling strength and relative to the JT energy in Fig. 1. The figure also shows the results for the high spin case calculated in Ref. [20].

6.2. States with phonon excitations

The calculation of the energies of the states with phonon excitations proceeds in a similar manner to that for the no-phonon states, except that the integrals are no longer independent of γ and γ' and are therefore 6D. This means that they are more complicated to evaluate both analytically and numerically. Results will be given here for one-phonon excitation only, although the procedures used can be extended to higher states if required. In general terms, the overlap factor for the state with one-phonon excitation of an arbitrary symmetry τ is given by

$$O_{lm}(\tau) = J(Z^2[X_1 - k^2 X_2]) \quad (23)$$

where

$$\begin{aligned} X_1 &= \sum_{\lambda} D_{\tau\lambda}(\theta', \phi', \gamma') D_{\tau\lambda}(\theta, \phi, \gamma) \\ X_2 &= \sum_{\lambda\mu} D_{\tau\lambda}(\theta', \phi', \gamma') D_{\tau\lambda}(\theta, \phi, \gamma) D_{\lambda} D_{\mu} \end{aligned} \quad (24)$$

with $D_\lambda = D_{1\lambda}(\theta', \phi', \gamma') - D_{1\lambda}(\theta, \phi, \gamma)$. After some algebra, we find that the energy matrix elements are

$$\begin{aligned}
 M_{lm}(\tau) = & \left(\frac{7}{2} - \frac{5}{4}k^2 \right) O_{lm}(\tau) \\
 & + J \left(\frac{3}{4}k^2 \sum_{\lambda} D_{\tau\lambda}(\theta', \phi', \gamma') D_{\tau\lambda}(\theta, \phi, \gamma) Z^4 \right. \\
 & + \sum_{\lambda\mu} D_{\tau\lambda}(\theta', \phi', \gamma') D_{\tau\mu}(\theta, \phi, \gamma) \\
 & \times \left[-\frac{3}{4} D_{\lambda} D_{\mu} Z^4 + Z^2 [k_{\lambda}(\theta', \phi') D_{\mu} - k_{\mu}(\theta', \phi') D_{\lambda}] \right. \\
 & \left. \left. - \frac{k}{2\sqrt{2}} (R_{\lambda} D_{\mu} - R_{\mu} D_{\lambda}) \right] \right] \quad (25)
 \end{aligned}$$

We are now in a position to compute the integrals involved in the overlaps and matrix elements, using the same method as described above for states with no phonon excitations. The results are also displayed for both the high spin and low spin states systems in Fig. 2 relative to the JT energy. It can be noticed that incorrect weak coupling limits occur and this is because the one-phonon state with given values of l and m is not orthogonal to the no-phonon state with the same values of l and m . It is therefore necessary to orthogonalise the one-phonon states to the equivalent no-phonon states. Although this introduces a number of extra integrals to be evaluated connecting the no-phonon states to the one phonon states, the method remains the same.

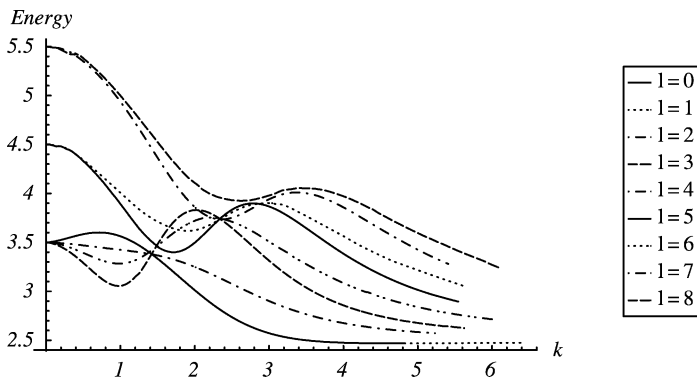


Fig. 2. The energies of the states relative to the JT energy with $L = \text{odd}$ (due to high spin term) and $L = \text{even}$ (due to low spin terms) with one phonon excitation of n_1 -symmetry, neglecting orthogonalisation to the states with no phonon excitations. See text for details.

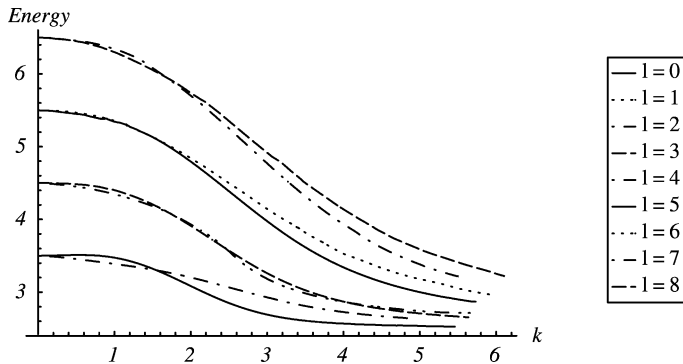


Fig. 3. As Fig. 2 but including orthogonalisation to the states with no phonon excitations.

Figure 3 shows the energies of the new orthogonalised states. As is expected, the energies in weak coupling are all $\hbar\omega$ larger than those in strong coupling, consistent with two vibrations being converted to rotations as the coupling strength increases. The excited states are all $\hbar\omega$ larger than the corresponding states with no phonon excitations in both strong and weak coupling. Also, the states now tend to their strong-coupling values from above, unlike with the non-orthogonalised states. Finally, it is also worthwhile to note that in both strong and weak coupling limits, the different excited states plots are approximately separated by the vibrational quanta $\hbar\omega$.

7. DISCUSSION

Little previous work has been done to determine the energies of the linear $p^2 \otimes h$ and $p^4 \otimes h$ JT systems as a function of the vibronic coupling constant, in spite of the rising interest in the peculiarities of the C_{60} compounds. O'Brien [30] tackled the problem with a numerical approach. The low-lying energies were presented as a function of g^2 in the strong coupling limit, where g is her definition of the vibronic coupling constant. Our results are consistent with hers in this limit. Auberbach *et al.* [22] have also studied multiple occupancy in charged fullerenes. They used a semi-classical scheme with fractional parentage method in the strong-coupling limit and calculated results numerically. As their method has a very different basis, direct comparisons are very hard to make. Nevertheless, we can infer from their work that both of our results agree satisfactorily in the weak and strong coupling limits. It is very noticeable from the Figs 1 and 3 that the weak coupling limits and strong coupling limit are as expected, i.e., they account for five vibrations being reduced to two rotations as predicted by Auberbach *et al.* [22].

As mentioned previously, the energies of states in the linear $T_{1u} \otimes h_g$ JT system, which applies to our high spin states, have been calculated previously using a similar analytical approach to that presented in this paper [20]. More quantitative comparisons with other approaches are available for this system, with the agreement between analytical and numerical approaches being found to be good [20]. This therefore indicates that our method is a valid one.

The ground states are usually those most discussed, as in Fig. 1. It is seen that the high spin states are always lower in energy than the low spin states. However, the JT interaction will always reduce the energy of the low spin states more effectively than the high spin states. In the $p^2 \otimes h$ system, the configuration interaction already makes the ^1S states lowest and the JT interaction will probably encourage it to remain so. There is experimental evidence that this is indeed so [35]. In the $p^2 \otimes h$ system, the near degeneracy of ^1S and ^3P will allow a linear coupling within the triplet state to make it the ground state if the coupling is really weak but at the intermediate coupling strength, the coupling in ^1S and ^1D can be expected to bring ^1S below ^1D .

8. CONCLUSION

The model described and the results presented illustrate the physics underlying the role of the vibronic coupling in $p^2 \otimes h$ and $p^4 \otimes h$ JT systems. However, the theory needs to be developed further in the future to allow comparisons with experiment. Indeed, our main motivation for this work was to provide information to help understand some of the anomalies that exist for the A_xC_{60} compounds. In particular, we may help explain why A_3C_{60} shows metallic and superconductive properties whilst A_2C_{60} and A_4C_{60} show insulating and non-magnetic [36,37] properties though band theory predicts otherwise. It is interesting to note that recently Chida *et al.* [38] studied similar systems theoretically and predicted the formation of C_{60}^{3-} compounds from initial states of C_{60}^{2-} and C_{60}^{4-} via photoemission and inverse photoemission processes.

It is known that the C_{60} molecules can undergo a static distortion in intercalated compounds. It is believed that the JT distortion of C_{60} molecules results in the breakdown of the band picture in A_4C_{60} , making A_4C_{60} an insulating non-magnetic compound [39]. The origin of the problem, therefore, as proposed by Suzuki *et al.* [40] and many other authors is cooperation between the electron–electron and electron–phonon interactions in opening the band gaps in A_2C_{60} and A_4C_{60} . A strong vibronic coupling results in a static distortion which favours the non-magnetic and insulating properties in A_2C_{60} and A_4C_{60} . Our graphs indeed show that the energies start saturating for rather lower vibronic coupling values than expected for other similar systems, e.g. A_1C_{60} . Although it is too premature for quantitative predictions for C_{60} to be made, our work contains interesting physics which will be continued in future work.

REFERENCES

- [1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.
- [2] R. C. Haddon, A. F. Hebbard, M. J. Rosseinsky, D. W. Murphy, S. J. Duclos, K. B. Lyons, B. Miller, J. M. Rosamilia, R. M. Fleming, A. R. Kortan, S. H. Glarum, A. V. Makhija, A. J. Muller, R. H. Eick, S. M. Zahurak, R. Tycko, G. Dabbagh and F. A. Thiel, *Nature*, 1991, **350**, 320.
- [3] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, 1991, **350**, 600.
- [4] M. J. Rosseinsky, A. P. Ramirez, S. H. Glarum, D. W. Murphy, R. C. Haddon, A. F. Hebard, T. T. M. Palstra, A. R. Kortan, S. M. Zakurak and A. V. Makhija, *Phys. Rev. Lett.*, 1991, **66**, 2830.
- [5] K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo and S. Kuroshima, *Nature*, 1991, **352**, 222.
- [6] R. F. Kiefl, T. L. Duty, J. W. Schneider, A. MacFarlane, K. Chow, J. W. Elzey, P. Mendels, G. D. Morris, J. H. Brewer, E. J. Ansaldo, C. Niedermayer, D. R. Noakes, C. E. Stronach, B. Hitti and J. E. Fischer, *Phys. Rev. Lett.*, 1992, **69**, 2005.
- [7] D. W. Murphy, M. J. Rosseinsky, R. M. Fleming, R. Tycko, A. P. Ramirez, R. C. Haddon, T. Siegrist, G. Dabbagh, J. C. Tully and E. Walstedt, *J. Phys. Chem. Solids*, 1992, **53**, 1321.
- [8] P. J. Benning, F. Stepniak, D. M. Poirier, J. L. Martins, J. H. Weaver, L. P. F. Chibante and R. E. Smalley, *Phys. Rev. B*, 1993, **47**, 13843.
- [9] S. C. Erwin and M. R. Pederson, *Phys. Rev. Lett.*, 1991, **67**, 1610.
- [10] S. Saito and A. Oshiyama, *Phys. Rev.*, 1991, **44**, 11536.
- [11] S. C. Erwin, in *Buckminsterfullerenes* (eds W. E. Billups and M. A. Ciufolini), VCH, New York, 1993, p. 217.
- [12] S. C. Erwin and C. Bruder, *Physica B*, 1994, **199/200**, 600.
- [13] J. E. Ham, E. Koch and O. Gummarsson, *Phys. Rev. Lett.*, 2000, **84**, 1276.
- [14] S. Suzuki and K. Nakao, *Phys. Rev. B*, 1995, **52**, 206.
- [15] M. Fabrizio and E. Tosatti, *Phys. Rev. B*, 1997, **55**, 13465.
- [16] I. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, Berlin, 1989.
- [17] F. S. Ham, in *Electron Paramagnetic Resonance* (ed. S. Geschwind), Plenum, New York, 1972, pp. 1–119.
- [18] Y. E. Perlin and M. H. L. Wagner, *The Dynamical Jahn–Teller Effect in Localised Systems*, North Holland, Amsterdam, 1984.
- [19] C. C. Chancey and M. C. M. O'Brien, *The Jahn–Teller Effect in C₆₀ and Other Icosahedral Complexes*, Princeton University Press, Princeton, 1997.
- [20] J. L. Dunn, M. R. Eccles, Y. Liu and C. A. Bates, *Phys. Rev. B*, 2001, **65**, 115107.
- [21] J. L. Dunn and M. R. Eccles, *Phys. Rev. B*, 2001, **64**, 195104.
- [22] A. Auerbach, N. Manini and E. Tosatti, *Phys. Rev. B*, 1994, **49**, 12998.
- [23] M. Weissbluth, *Atoms and Molecules*, Academic Press, New York, 1978.
- [24] P. W. Fowler and A. Ceulemans, *Mol. Phys.*, 1985, **54**, 767.
- [25] E. P. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*, Academic Press, New York, 1959.
- [26] M. C. M. O'Brien, *Phys. Rev.*, 1969, **187**, 407.
- [27] M. C. M. O'Brien, *J. Phys. C*, 1971, **4**, 2524.
- [28] U. Öpik and M. H. L. Pryce, *Proc. R. Soc.*, 1957, **238**, 425.
- [29] J. L. Dunn and C. A. Bates, *Phys. Rev. B*, 1995, **52**, 5996.
- [30] M. C. M. O'Brien, *Phys. Rev. B*, 1996, **53**, 3775.
- [31] B. R. Judd, *Can. J. Phys.*, 1974, **52**, 999.
- [32] C. C. Chancey, *J. Phys. A: Math. Gen.*, 1987, **20**, 2753.
- [33] B. R. Judd and E. E. Vogel, *Phys. Rev.*, 1975, **11**, 2427.
- [34] J. L. Dunn, *J. Phys. C: Solid State Phys.*, 1988, **21**, 383.
- [35] P. C. Trulove, R. T. Carlin, G. R. Eaton and S. S. Eaton, *J. Am. Chem. Soc.*, 1995, **117**, 6265.

- [36] R. Tycko, G. Dabbagh, M. J. Rosseinsky, D. W. Murphy, A. P. Ramirez and R. M. Fleming, *Phys. Rev. Lett.*, 1992, **68**, 1912.
- [37] I. Lukyanchuk, N. Kirova, F. Rachdi, C. Goze, P. Moline and M. Mehring, *Phys. Rev. B*, 1995, **51**, 3978.
- [38] T. Chida, S. Suzuki and K. Nakao, *J. Phys. Soc. Jpn*, 2002, **71**, 525.
- [39] Y. Iwasa and T. Kaneyasu, *Phys. Rev. B*, 1995, **51**, 3678.
- [40] S. Suzuki, S. Okada and K. Nakao, *J. Phys. Soc. Jpn*, 2000, **69**, 2615.

Vibronic-induced Shifts in the Optical Spectra of Doped Fullerenes

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Abstract

The discovery that doped derivatives of C_{60} are capable of exhibiting superconductivity has led to intense interest in these so-called fullerides resulting in the preparation and characterisation of a large variety of such compounds. However, the mechanism for superconductivity in the fullerides is still not well understood, although it is thought that electron–phonon (e–p) coupling within the fullerene cage, namely intramolecular Jahn–Teller (JT) effects, play a significant role in the process. JT coupling in the C_{60}^- ion is described theoretically by a $T_{1u} \otimes 8h_g$ JT problem, in which eight h_g modes are coupled to the T_{1u} ground electronic state of the ion. Thus, there is a need to ascertain quantitatively the extent of the coupling to each of the eight modes. To date, the best method of achieving this experimentally is by photoemission spectroscopy. However, this technique suffers from a relatively low resolution and is not routinely carried out in the preparative laboratory. On the other hand, optical spectroscopies have excellent resolution and have been used extensively to characterise the fullerides. The purpose of this work is to attempt to use this body of experimental data to determine quantitatively the e–p coupling in the doped derivatives of C_{60} , focussing in particular on shifts in the optical spectra of doped fullerenes induced by the vibronic coupling.

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1. INTRODUCTION

Since its discovery in 1985 [1], Buckminsterfullerene has been the subject of tremendous interest. One of the reasons for this interest lies in its icosahedral symmetry, which gives rise to highly degenerate electronic and vibrational states, making its derivatives highly susceptible to intramolecular vibronic interactions of the Jahn–Teller (JT) type. Another reason lies in the discovery in 1991 that doped derivatives (fullerides) of C_{60} are capable of exhibiting superconductivity [2,3]. The interplay between superconductivity and electron–phonon (e–p) coupling in the fullerides is a subject of high current interest but is not one that features to any great extent in the current work. An informative review may, however, be found in the paper by Gunnarsson [4].

For C_{60}^- , group theory indicates that vibronic coupling will occur for the Raman-active a_g and h_g vibrational modes, and consequently much theoretical effort has been devoted to the so-called $T_{1u} \otimes h_g$ problem [5,6]. However, coupling theories necessarily contain parameters to represent the interaction between electronic and vibrational motions, the exact predictions resulting from the theory depending critically upon the magnitude of the coupling strength. Thus, there is a need to determine quantitative values for the e–p coupling parameters in these systems. In the case of C_{60}^- , experimental values for vibronic coupling constants have been obtained by Gunnarsson *et al.* using photoemission spectroscopy (PES). Unfortunately, the PES experiment has a rather low resolution making it difficult to unequivocally assign the data to individual a_g and h_g vibrational modes.

In contrast, vibrational spectroscopies have a much higher resolution, so that it is easy to make accurate assignments of individual normal modes. Also, since e–p coupling provides an additional mechanism for relaxation of excited vibrational states, vibronic-induced changes may be expected in the optical spectra of the doped fullerenes. Typically, the modes of C_{60} are found to split and shift in frequency upon doping (a comprehensive list of papers relating to spectra of the fullerides may be found in Ref. [7]). In principle, therefore, it should be possible to derive values for coupling constants from the IR and Raman spectra of the fullerides. The results of such an attempt have been recently published by the current authors [7]. In Ref. [7], the shifts in the vibrational frequencies of the modes were attributed to two sources. Firstly, the addition of electrons to C_{60} will clearly affect the bonding within the molecule, changing bond strengths and force constants and, consequently, vibrational frequencies. Secondly, for C_{60}^{n-} where $1 \leq n \leq 5$ or $7 \leq n \leq 11$, a shift may be present due to the JT effect. Ions with a 6- and 12-fold negative charge have completely filled molecular orbitals (*vide infra*) and so cannot exhibit the JT effect. In these cases the shifts in the vibrational frequencies (from the frequencies observed for the neutral molecule) are solely due to bonding changes.

Using a simple method of separating the two different contributions to the mode shifts, coupling constants were derived in Ref. [7] that are in good general agreement with those measured using PES. However, the simple interpretation used there has no firm theoretical foundation and so it remains uncertain as to whether

there really are any JT-induced mode shifts in the spectra. In the present work, we hope to show that such JT-related mode shifts are indeed present. We start by developing an improved force constant model for C_{60} . Then we deduce the values of the force constants for C_{60} and C_{60}^{6-} that are consistent with our model. Then we attempt to interpolate between these two extremes to predict how the mode frequencies should vary in the absence of the JT effect. A comparison of these predictions with the experimentally observed trends is then made. Preliminary results indicate that the experimental trends cannot be attributed solely to bonding changes, so that JT-induced shifts are genuinely present. Furthermore, the discrepancy between the predicted behaviour and the observed behaviour for the h_g modes appears to give qualitative agreement with the coupling constants deduced from PES measurements.

2. VIBRONIC COUPLING IN C_{60}

The structure of C_{60} is that of a truncated icosahedron, as shown in Fig. 1. Each pentagonal face of the molecule is regular and constructed from nominally single bonds whose bond length is $l_s \approx 1.46 \text{ \AA}$. The hexagonal faces show a degree of bond alternation, consisting of alternating single and double bonds, the latter of length $l_d \approx 1.39 \text{ \AA}$. The double bonds are therefore expected to be very similar in character to those in benzene ($l_{\text{benzene}} \approx 1.40 \text{ \AA}$), whereas the single bonds have a correspondingly greater degree of single bond character (typical length $\approx 1.54 \text{ \AA}$). Each carbon atom is nominally sp^2 hybridised, so that there are 60 radially-oriented p orbitals that must be combined to produce the π molecular orbitals for the molecule. Simple Hückel theory [8] may be used to deduce the energies of the resulting orbitals, as shown partially in Fig. 2.

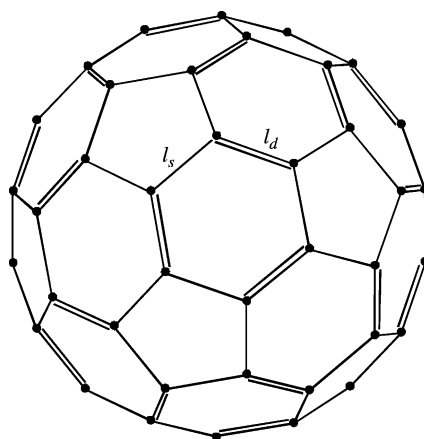


Fig. 1. The structure of C_{60} .

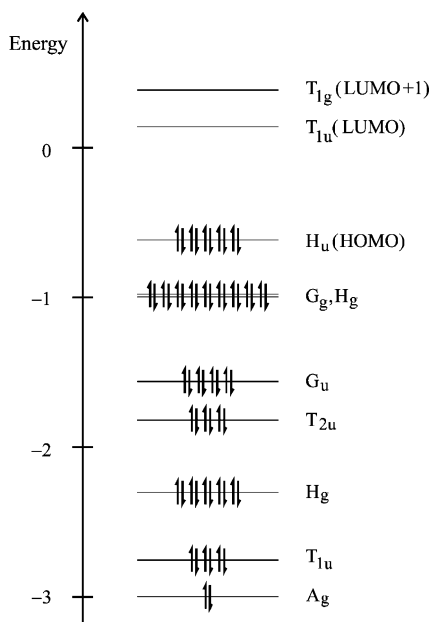


Fig. 2. Hückel molecular orbital diagram for C_{60} .

Doping C_{60} initially introduces electrons into the triply degenerate T_{1u} lowest unoccupied molecular orbital (LUMO). The addition of six electrons will fill these levels so that the JT effect is expected to be absent in the C_{60}^{6-} ion. Additional doping involves adding electrons to the triply degenerate T_{1g} LUMO + 1 levels, so that C_{60}^{12-} will also be JT inactive. The orbital picture shown in Fig. 2 does not change significantly if curvature of the molecule is accounted for [9], with perhaps the most obvious change being the loss of the accidental degeneracy of the G_g and H_g levels.

The vibrational modes of the molecule also show a high degree of degeneracy so that only three of the $3N - 6 = 174$ modes of vibration are non-degenerate, the normal modes transforming as:

$$2a_g + 3t_{1g} + 4t_{2g} + 6g_g + 8h_g + a_u + 4t_{1u} + 5t_{2u} + 6g_u + 7h_u \quad (1)$$

This high degeneracy results in particularly simple vibrational spectra so that only the four t_{1u} modes appear in the IR spectrum of C_{60} . Similarly, the Raman spectrum is surprisingly simple for such a large molecule as only 10 peaks feature in it due to the a_g and h_g modes. The totally symmetric modes are easy to visualise and constitute the so-called breathing ($\sim 495 \text{ cm}^{-1}$) and pentagonal pinch modes ($\sim 1470 \text{ cm}^{-1}$). Henceforth these modes will be referred to as the $a_g(1)$ and $a_g(2)$ modes, respectively, following the notation that modes are enumerated consecutively starting with the one with lowest energy. The $a_g(1)$ mode involves each carbon atom undergoing purely radial motion (relative to the centre of the C_{60}

molecule). On the other hand, the $a_g(2)$ mode involves contraction/expansion of the pentagonal faces and thus involves a considerable degree of tangential motion. As can be seen from the frequencies of these modes, radial modes generally occur at lower frequencies compared to tangential modes, as these modes cause less change to the interatomic distances between adjacent carbon atoms. This is, of course, consistent with there being strong forces between adjacent carbon atoms.

The addition of a single electron to the neutral molecule results in an ion of T_{1u} symmetry. Group theory indicates that such an electronic level can only couple to the a_g and h_g modes and so we shall be mainly concerned with the doping shifts induced in the Raman spectra of the fullerenes. The $T_{1u} \otimes h_g$ JT problem has been well studied [5] and will not be discussed in any great detail here. In their treatment [6], Dunn and Bates used a Hamiltonian of the form

$$H = H_{\text{vib}} + V_1 H'_1 + V_2 H'_2 + V_3 H'_3 \quad (2)$$

where H_{vib} is the uncoupled Hamiltonian, $V_1 H'_1$ is the linear interaction Hamiltonian, written so as to emphasise its dependence on the linear vibronic coupling constant V_1 and the last two terms are the Hamiltonians for the two types of quadratic coupling that occurs in this system. These terms are, once again, moderated by V_2 and V_3 , the quadratic coupling constants.

In the absence of quadratic coupling, linear coupling produces a continuous, spherical adiabatic potential energy surface (APES). When quadratic terms are included this surface is warped to produce discrete minima and maxima. Depending on the values of the coupling constants, the otherwise icosahedral ion may become distorted into ions of either D_{3d} or D_{5d} symmetry. The type of distortion that occurs in the discrete C_{60}^- ion is still not known to any degree of certainty. Whichever distortion occurs, it is clear that the overall theoretical picture that most closely describes the monoanion is that of a JT-distorted system that may interconvert between any of several equivalent configurations *via* quantum mechanical tunneling. This dynamic picture implies that there is a characteristic timescale τ for the interconversion or pseudorotation. Observation of the ion over a time span much longer than τ will lead to the impression of an ion of icosahedral symmetry. Similarly, observation on a timescale much shorter than τ will result in the impression that the ion is permanently distorted (i.e., there is a static JT effect). In principle, the timescale τ can be related to the coupling constants V_i and so knowledge of the actual values of these parameters is imperative if we are to ascertain the type of distortion and the pseudorotational dynamics that occur in C_{60}^- . It is to this problem that we now turn our attention.

3. EXPERIMENTAL COUPLING CONSTANTS

To date, the best experimental data in the literature pertaining to vibronic coupling constants in the free C_{60}^- ion are the (PES) results of Gunnarsson *et al.* [10]. Figure 3 shows the spectrum obtained by these workers together with a graphical

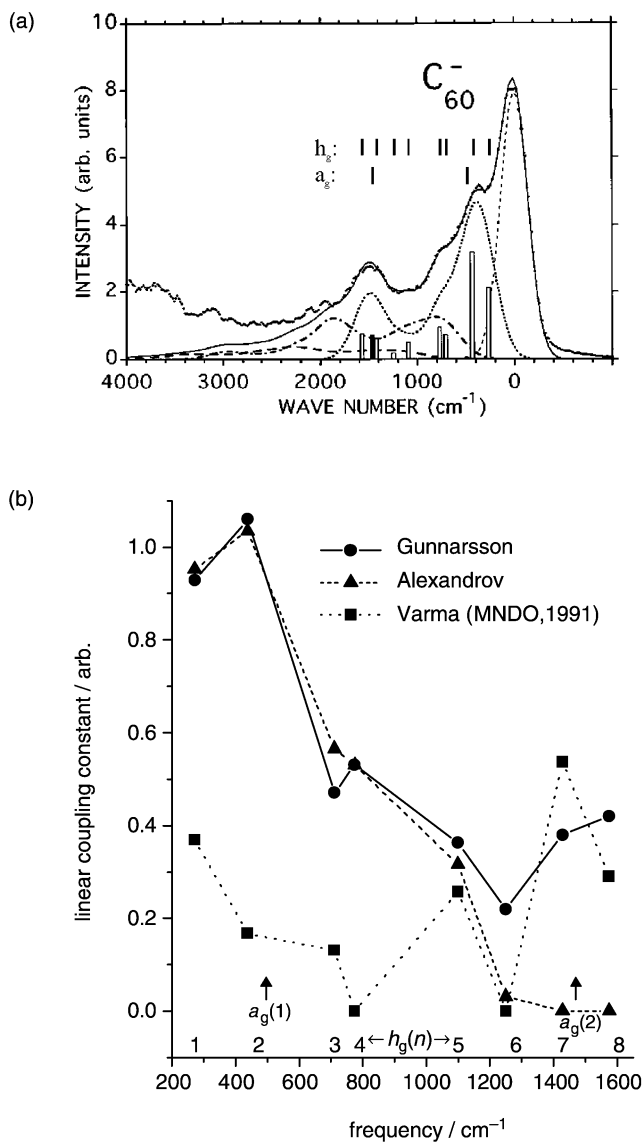


Fig. 3. PES results for C_{60}^- . (a) shows the data obtained by Gunnarsson *et al.* [10], and (b) shows the coupling constants subsequently derived for the h_g modes ($\text{---}\bullet\text{---}$). Also shown in (b) is the results of a reassessment of the data by Alexandrov *et al.* ($\text{---}\blacktriangle\text{---}$) [11] and a MNDO calculation by Varma *et al.* ($\text{---}\blacksquare\text{---}$) [12].

representation of their inferred linear coupling constants. The results constitute clear evidence for vibronic coupling in C_{60}^- . However, the peaks in Fig. 3(a) are not clearly resolved (instrument resolution $\sim 320 \text{ cm}^{-1}$) and so it is not easy to

unequivocally assign the data to individual modes. Of particular trouble is the $a_g(2)$ mode at $\sim 1470 \text{ cm}^{-1}$. In fact, Gunnarsson's data has been reassessed by Alexandrov and Kabanov [11] who included polaron–exciton coupling and also attributed greater weight to the $a_g(2)$ mode in their analysis. Their results are also shown in Fig. 3(b). However, the overall conclusion is very similar: it is the lower energy, radial modes that couple more strongly to the T_{1u} level. This is to be contrasted with the semi-empirical calculations made by Varma *et al.* [12] using modified neglect of diatomic overlap (MNDO) methodology. In these calculations, it is the tangential modes that appear to couple most strongly.

The above discussions indicate that the situation with regards the linear coupling constants still remains open to debate. However, numerical values for them have been obtained both experimentally and theoretically. Unfortunately, the same cannot be said of the quadratic constants whose values appear to be completely unknown. Interestingly, it is these latter constants that are responsible for the warping of the APES and so would be expected to have a dramatic effect on the rate at which tunneling occurs between energy minima. Values for these quantities may therefore follow from dynamical studies that are capable of directly measuring tunneling rates in the C_{60}^- ion.

4. DOPING EFFECTS IN THE OPTICAL SPECTRA OF FULLERIDES

The presence of e–p coupling provides an additional channel for the relaxation of phonon states leading to an increase in phonon linewidths [13]. In addition, the modes shift in frequency due to the coupling. The magnitude of the induced shift $\Delta\omega^{(e-p)}$ has been given by the approximate formula [14,15]

$$\Delta\omega^{(e-p)} \approx -\lambda\omega/5 \quad (3)$$

where λ is the partial e–p coupling constant. Therefore, for a mode with a partial coupling parameter $\lambda \sim 0.1$, a shift of $\sim 2\%$ is to be expected as a result of vibronic coupling. This change should be readily measurable. Doping-induced mode shifts should, therefore, be capable of giving good estimates for the partial coupling parameters, and hence linear coupling constants. One advantage of this proposal is that vibrational spectroscopies have a high resolution ($\sim 1 \text{ cm}^{-1}$) and so, unlike in PES experiments, individual modes are easy to identify. Another advantage is that Raman and IR analyses are routinely undertaken in the preparative laboratory and so there is much vibrational data in the literature pertaining to the fullerenes. By collating this data, it is possible to acquire a good picture of how doping C_{60} with electrons affects its normal modes of vibration [7]. As an example of the kind of behaviour observed, Fig. 4 shows the trends observed in the totally symmetric modes of vibration (similar plots for the h_g modes are given in Fig. 11). The data illustrated is taken from Ref. [7], each point representing an experimental observation of the mode for the particular fullerene indicated. To avoid systematic errors, the observations are

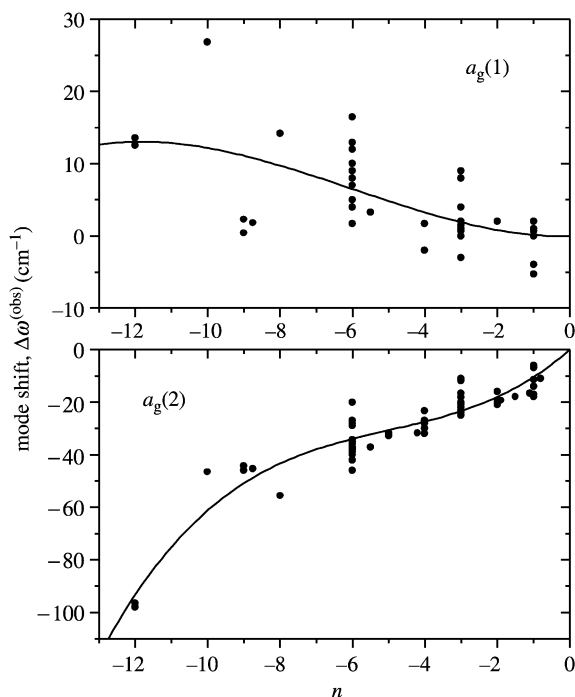


Fig. 4. Doping-induced changes to the totally symmetric modes of vibration of C_{60} . The graphs illustrate the shift in frequency, measured relative to the uncharged molecule, caused by the addition of $|n|$ electrons. The data points correspond to experimental data collated in Ref. [7] and the lines are least squares fits to the theoretical expression in equation (8).

expressed, wherever possible, in terms of shifts from the vibrational frequencies measured for neutral C_{60} by the same experimentalists. Thus, we have defined

$$\Delta\omega^{(\text{obs})} = \omega^{(\text{obs})} - \omega^{(\text{undoped})} \quad (4)$$

where $\omega^{(\text{obs})}$ is the observed vibrational frequency for a particular mode and $\omega^{(\text{undoped})}$ is the frequency of the mode in the experimentalist's spectrum of neutral C_{60} .

We see from Fig. 4 that doping C_{60} causes a slight hardening of the $a_g(1)$ mode and a very strong softening of the $a_g(2)$ mode. However, this change cannot be due solely due to vibronic effects. This is because C_{60}^{6-} and C_{60}^{12-} are not JT active and yet these ions show a non-zero shift in frequency. The shifts for these ions are, of course, explained by the fact that doping affects the bonds in the molecule and this will affect the vibrational frequencies. This is entirely consistent with the observation that the $a_g(2)$ mode shifts more than the $a_g(1)$ mode upon doping: the $a_g(2)$ mode is a tangential mode and therefore more sensitive to changes in the bonds than the $a_g(1)$ mode which involves radial motion.

4.1. A simple model for doping effects

The foregoing discussion implies that in order to understand the doping behaviour observed in the optical spectra of the fullerenes, we must consider both bonding and vibronic effects. A simple method of separating these two contributions has been given in Ref. [7] and is outlined here for the sake of completeness. The shift in mode frequency is expressed as sum of two contributions:

$$\Delta\omega^{(\text{obs})} = \Delta\omega^{(\text{CT})} + \Delta\omega^{(\text{e-p})} \quad (5)$$

where $\Delta\omega^{(\text{e-p})}$ is the shift due to vibronic effects and $\Delta\omega^{(\text{CT})}$ is that due to bonding changes. The superscript CT is used in equation (5) in acknowledgement of the use of the term ‘charge transfer’ in the literature for such changes.

For the e–p contribution, we wish to find a simple dependence on molecular charge that reflects the fact that there is no e–p coupling in C_{60} , C_{60}^{6-} and C_{60}^{12-} . Thus, we write

$$\Delta\omega^{(\text{e-p})} = cn(n+6)(n+12) \quad (6)$$

where n is the charge on the doped ion and c is a constant that is directly related to the linear vibronic coupling constant. For the CT contribution, we wish to reflect the often-observed fact that the addition of a few electrons to the molecule is expected to cause only small changes to the bonding. Thus, we seek a simple linear, or at most, quadratic relation to describe the dependence on charge:

$$\Delta\omega^{(\text{CT})} = an + bn^2 \quad (7)$$

Combining equations (5)–(7), we arrive at the simple doping expression

$$\Delta\omega^{(\text{obs})} = an + bn^2 + cn(n+6)(n+12) \quad (8)$$

By fitting the doping behaviour to this expression, values for the c constants may be extracted and used to deduce values for the linear coupling constants. As c has been assumed to be directly proportional to V_1 for a particular h_g mode, only relative measures may be made. However, this does allow the trend in the coupling constants to be deduced. In order to make a more direct comparison with the PES results, however, we may scale the inferred coupling constants to make them comparable. Figure 5 shows the result of such a procedure in which the two sets of data have been scaled so that they coincide at the $h_g(2)$ mode. We see that the trend predicted by the mode-shift data is remarkably similar to that deduced from the PES data. Interestingly, the coupling strength predicted for the $h_g(7)$ mode lies somewhere in between that derived by Gunnarsson *et al.* and Alexandrov *et al.*, consistent with one work assigning too little importance to the nearby $a_g(2)$ mode, and the other too much.

The good agreement shown in Fig. 5 is encouraging. However, the simple method of separating vibronic- and CT-induced contributions to the mode shifts is somewhat intuitive. It is clear that the observed mode shifts are not due to vibronic interactions alone. However, we may ask if it possible that the observed trends can be explained by bonding changes alone. In order to answer this question we shall try to model the changes that occur in C_{60} as doping progresses and thus make

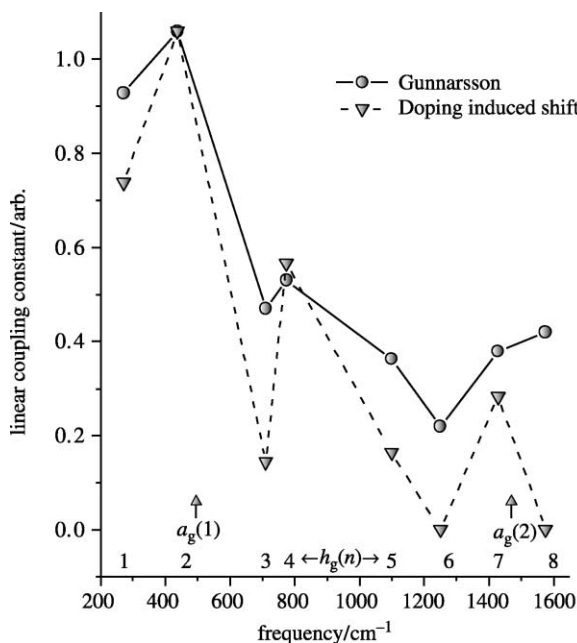


Fig. 5. Comparison of the h_g coupling constants extracted from PES (—●—) data with those deduced from the doping-induced mode shifts (—▼—).

a prediction of the $\Delta\omega^{(CT)}$ part of equation (5). To this end, we first seek to create force constant models for C_{60} and C_{60}^{6-} . As already intimated, these systems are important because they cannot exhibit the JT effect and so their mode shifts are entirely due to bonding changes. Then, we may interpolate between these models and use the results to investigate the doping behaviour to be expected in the absence of vibronic coupling. Any discrepancy with the observed behaviour may then be taken as a clear indication that vibronic effects are present.

5. FORCE CONSTANT MODELS FOR C_{60}

The early force constant models for C_{60} were based on just four force constants, which may loosely be referred to as two stretching and two bending constants. In this work, we shall refer to such models as 4k models. The stretching constants, labelled here as k_s and k_d , correspond to the single and double bonds within the molecule, respectively. The bending constants correspond to energy changes associated with changes in bond angles. Here, we label them as k_p and k_h , as they relate to changes in pentagonal and hexagonal angles, respectively.

Figure 6 gives a diagrammatic representation of the 4k model and illustrates the results obtained by two sets of workers [16,17]. It is interesting that the two groups of

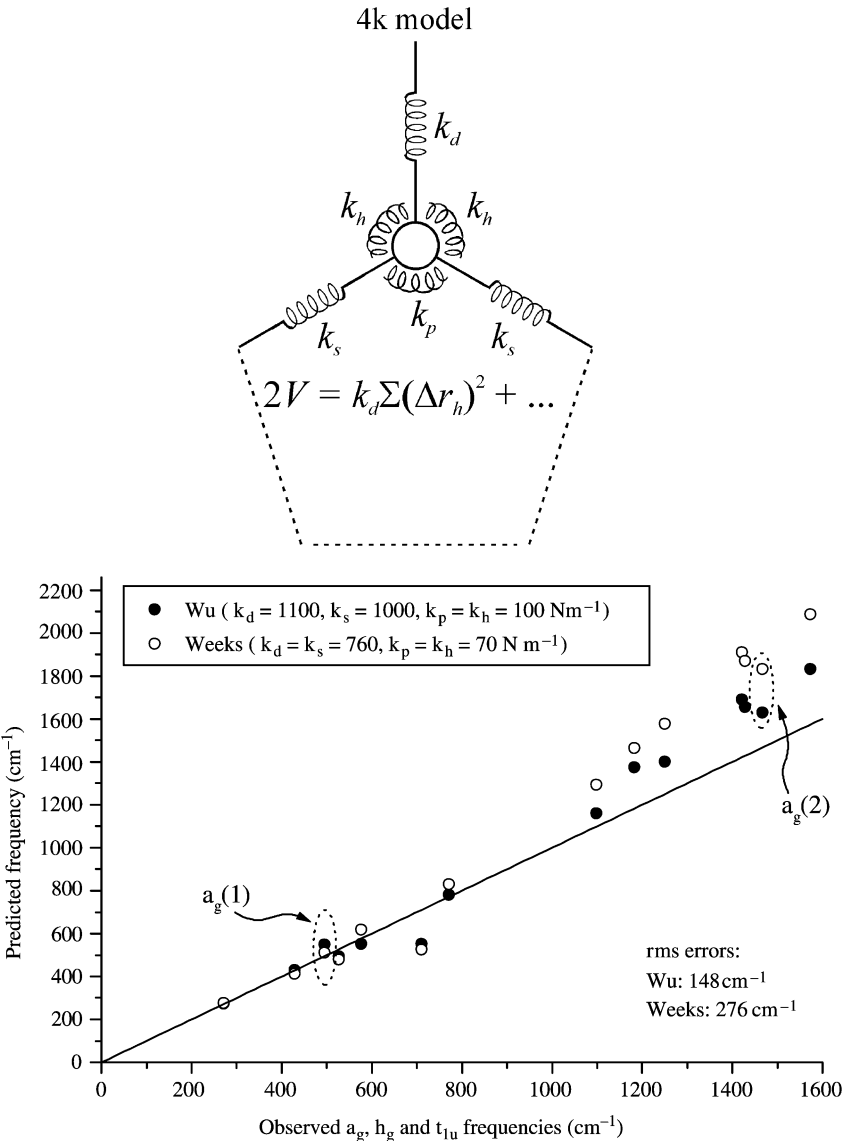


Fig. 6. The 4k model and a graphical illustration of the predictions made by Wu *et al.* [16] and Weeks and Harter [17]. The solid line plots out the scenario where predicted behaviour equals that observed.

workers used very different sets of numerical values for the force constants but both have very similar predictions. Indeed, the 4k model seems to give an adequate representation of the lower energy (radial) modes, but progressively over estimate

higher energy (tangential) modes. In fact, one of the failings of the 4k model is that it cannot simultaneously predict the correct frequencies for the two totally symmetric modes of vibration (highlighted in Fig. 6).

This situation was later remedied by Ceulemans *et al.* [18] who used an extended-Wu potential employing six force constants. For consistency, we shall refer to this model as the 6k model. The model builds upon the 4k model by adding in two extra force constants corresponding to two interaction constants k_5 and k_6 , as shown in Fig. 7. Such a model can correctly predict the frequencies of the a_g modes. Using the model, the authors obtained values for the six force constants by minimising the error between predicted and observed mode frequencies. As can be seen in Fig. 7, a much better fit to the data is obtained in this way.

The inclusion of the interaction constants k_5 and k_6 is a logical step to take as a way of improving the basic 4k model. Intuitively, one would expect these interaction constants to be the most important as they represent interactions between the two numerically largest force constants, namely k_s and k_d . To improve the situation further, other interaction constants need to be included.

If only interactions with nearest neighbours are important, the local environment surrounding a particular atom may be specified using six variables. Thus, in Fig. 8, atom i is surrounded by three nearest neighbours labeled $i_1, \dots, i_3$ and specification of $r_h, r_p, r'_p, \alpha_h, \alpha'_h$ and α_p , defined relative to an appropriate set of coordinates, determines the local potential experienced by atom i .

Considering all quadratic combinations of these variables, the potential energy associated with atom i is found to be

$$\begin{aligned}
 2V_i = & \frac{1}{2}k_d(\Delta r_h)^2 + \frac{1}{2}k_s[(\Delta r_p)^2 + (\Delta r'_p)^2] + k_h r_h^{(0)} r_p^{(0)} [(\Delta \alpha_h)^2 + (\Delta \alpha'_h)^2] \\
 & + k_p (r_p^{(0)})^2 (\Delta \alpha_p)^2 + 2k_5 \Delta r_h [\Delta r_p + \Delta r'_p] + 2k_6 \Delta r_p \Delta r'_p \\
 & + 2k_7 r_p^{(0)} (r_h^{(0)} r_p^{(0)})^{1/2} \Delta \alpha_p [\Delta \alpha_h + \Delta \alpha'_h] + 2k_8 r_h^{(0)} r_p^{(0)} \Delta \alpha_h \Delta \alpha'_h \\
 & + 2k_9 (r_h^{(0)} r_p^{(0)})^{1/2} \Delta r_h [\Delta \alpha_h + \Delta \alpha'_h] + 2k_{10} r_p^{(0)} \Delta r_h \Delta \alpha_p \\
 & + 2k_{11} (r_h^{(0)} r_p^{(0)})^{1/2} [\Delta r_p \Delta \alpha_h + \Delta r'_p \Delta \alpha'_h] \\
 & + 2k_{12} (r_h^{(0)} r_p^{(0)})^{1/2} [\Delta r_p \Delta \alpha'_h + \Delta r'_p \Delta \alpha_h] + 2k_{13} r_p^{(0)} \Delta \alpha_p [\Delta r_p + \Delta r'_p] \quad (9)
 \end{aligned}$$

where a zero subscript indicates the value of a variable at equilibrium. In all, we see that there are 13 force constants that need to be included to give a complete description of the problem in the nearest neighbour approximation. Again, for consistency we shall refer to this model as the 13k model. Only a brief description of the method used to obtain the normal mode frequencies can be given here. A full description of the procedure will be given elsewhere [19].

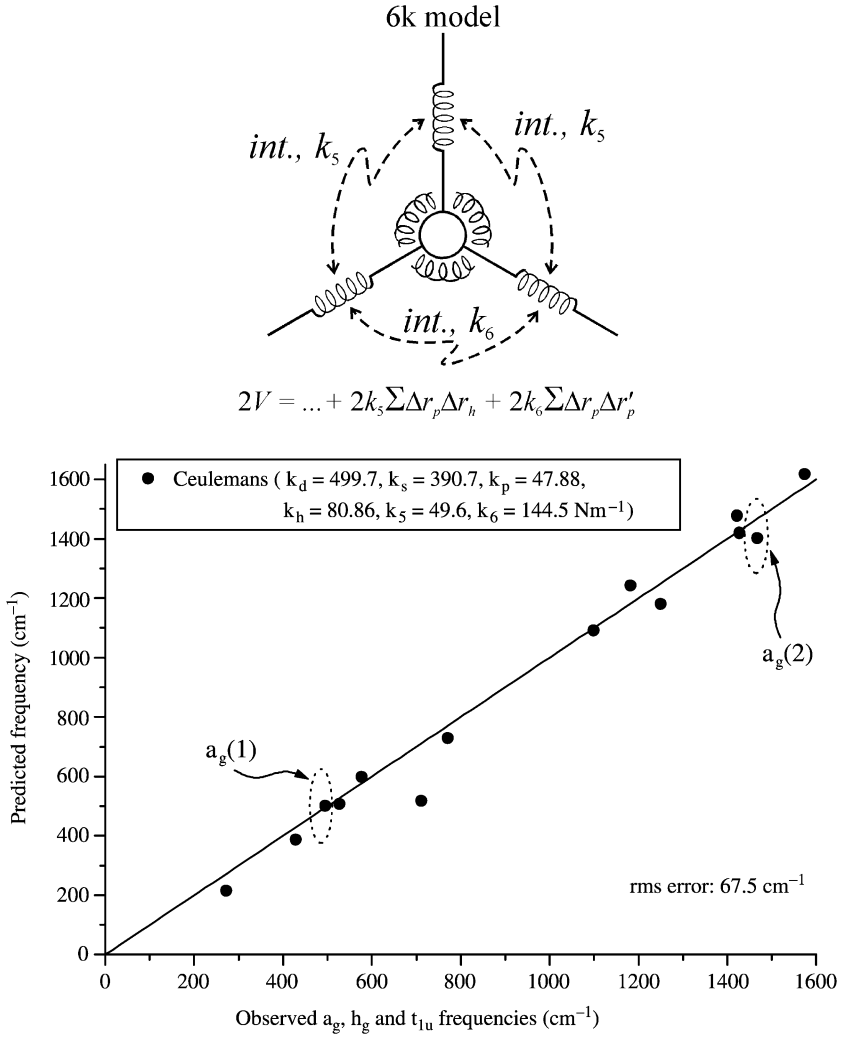


Fig. 7. The 6k model and numerical predictions of Ceulemans *et al.* [18]. The solid line once again represents perfect agreement between theory and experiment.

The total molecular potential is given by

$$V = \sum_{i=1}^{60} V_i \quad (10)$$

and is thus cast in terms of displacements $\Delta r_h, \dots, \Delta \alpha_p, \dots$. We now define unit vectors along the bonds (taken at equilibrium), so that, for example, $\hat{\mathbf{d}}_{i,i_1}$ points from atom i

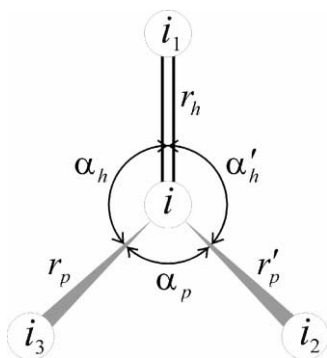


Fig. 8. Local variables for atom i .

to atom i_1 . The displacement of i may then be written in the form

$$\mathbf{x}_i = \sum_{k=1}^3 x_{i,i_k} \hat{\mathbf{d}}_{i,i_k} \quad (11)$$

The displacements of all the atoms in the molecule will be represented by the vector $\mathbf{x} = (\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_{60})$. Similarly, the forces acting on the atoms in the molecule may be formulated, $\mathbf{F} = m_C \ddot{\mathbf{x}}$. As usual, the displacements from equilibrium are assumed small so that the forces may be derived in the form

$$\mathbf{F} = \mathbf{A}\mathbf{x} \quad (12)$$

where $\mathbf{A}$ is a 180×180 matrix whose coefficients are functions of the 13 force constants. If the displacements $\mathbf{x}$ represent a normal mode of frequency ω , then $\ddot{\mathbf{x}} = -\omega^2 \mathbf{x}$ and the frequency follows after solving the eigenvalue problem

$$\mathbf{A}\mathbf{x} = -m_C \omega^2 \mathbf{x} \quad (13)$$

In solving this eigenvalue problem, the presence of symmetry is often used to block diagonalise the 180×180 matrix and hence simplify matters. In this work, however, we use an alternative approach.

Using representation theory, James obtained bases for the normal modes of vibration of C_{60} appropriate to the nearest neighbour approximation [20]. Using these bases and equation (13) it is a simple matter to derive expressions for the frequencies of the normal modes of vibration in terms of the 13 force constants. The expressions are quite cumbersome and are not reproduced here. For a given set of force constants, the frequencies of all of the modes of vibration may be found using a modest desktop computer in ~ 1 s.

5.1. Force constants for C_{60} and C_{60}^{6-}

As usual, the actual values for the force constants themselves must be derived by fitting the predicted frequencies of the visible modes to the experimental values.

Figure 9 shows the result of such a fit made by minimising the squares of the errors between predicted and observed frequencies. A problem here is that there are 13 constants to determine and only 14 experimental frequencies known accurately. It is clear that a good fit to the visible modes can be obtained. However, we can never be sure that the fit obtained represents a *global* minimum in the error function. The data in Fig. 9 must therefore be viewed upon as the best fit currently available. The values of the force constants themselves must be viewed with some scepticism. However, as more data becomes available, i.e., accurate frequencies of some of the silent modes are obtained, the model may be refined to improve these initial estimates.

For the hexa-anion, we first examine the changes in bond lengths caused by doping [21]. Figure 10 shows that doping lengthens the double bond, i.e., weakens it, and that the converse is true for the single bond (although the effect is less dramatic). Simple polynomial fits yield values for the bond lengths to use when fitting the C_{60}^{6-} data ($l_s = 1.433 \text{ \AA}$ and $l_d = 1.451 \text{ \AA}$). The fit to the vibrational data is also shown in Fig. 10. The fit is not as good as for the neutral molecule but this may just reflect the fact that the data is less reliable for the doped systems. One interesting find is that the force constant for the double bond appears to be decreased by 15% in C_{60}^{6-} compared to C_{60} , and that for the single bond appears to increase by 6.2%. These changes are consistent with the changes in bonding discussed above and illustrated in Fig. 10(a).

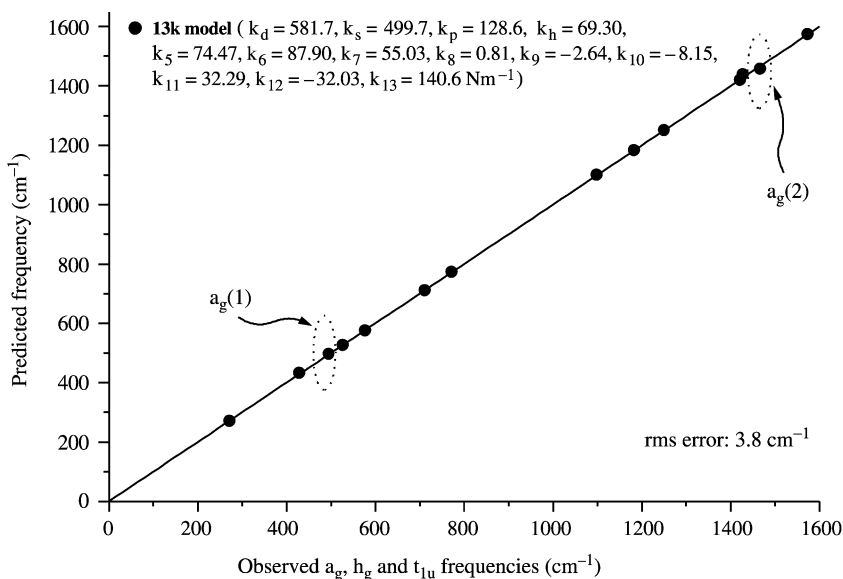


Fig. 9. Determination of the force constants in C_{60} using the 13 k model.

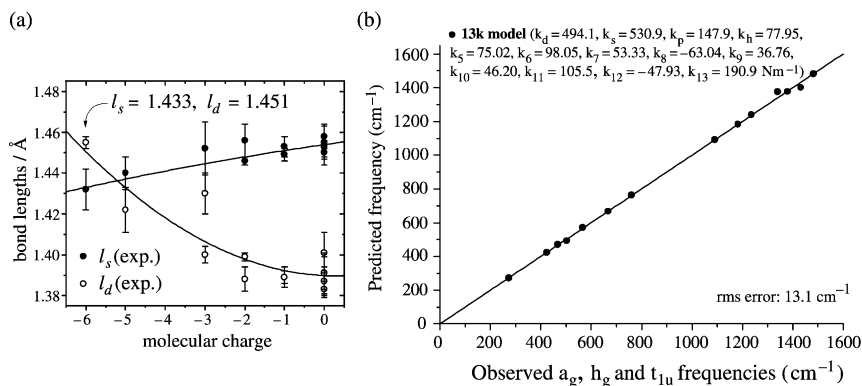


Fig. 10. (a) Shows the changes in bond lengths that occur as C_{60} is doped. In (b) the 13k model is used to extract force constants for the hexa-anion.

6. CHARGE TRANSFER-INDUCED MODE SHIFTS

Having found the force constants for C_{60} and C_{60}^{6-} we can now interpolate between these two extremes to find the manner in which the vibrational frequencies should change due to doping-induced bonding changes only.

We assume that the force constants change in a linear fashion between the neutral molecule and the hexa-anion. We also take bond lengths for each ion from the polynomial fit in Fig. 10(a). The CT-induced doping behaviour of the h_g modes thus predicted is shown in Fig. 11 (dashed lines), together with the experimentally observed shifts (full line). The behaviour predicted for three of the modes [$h_g(3)$, $h_g(7)$ and $h_g(8)$] seems to follow the observed behaviour quite closely. These modes are thus expected to show little e–p coupling, as is roughly the case (Fig. 5). Also, some of the modes, most notably $h_g(1)$, $h_g(2)$, $h_g(4)$ and $h_g(5)$ show strong differences between predicted and observed behaviour. Once again, there is a rough correlation with those modes thought to be most strongly coupled to the T_{1u} level.

It would appear that the changes predicted using the 13k model cannot explain the observed doping behaviour. Furthermore, the biggest discrepancies appear to occur in the modes that have the strongest vibronic coupling, i.e., the radial modes (Fig. 5). All in all, this gives a strong indication that the doping data does indeed contain information pertaining to e–p coupling.

7. CONCLUSIONS AND DISCUSSION

It is quite apparent that the addition of electrons to C_{60} causes changes in the frequencies of the normal modes of vibration. Clearly, one reason for the changes is that the bonding within the molecule undergoes transformations as electrons are

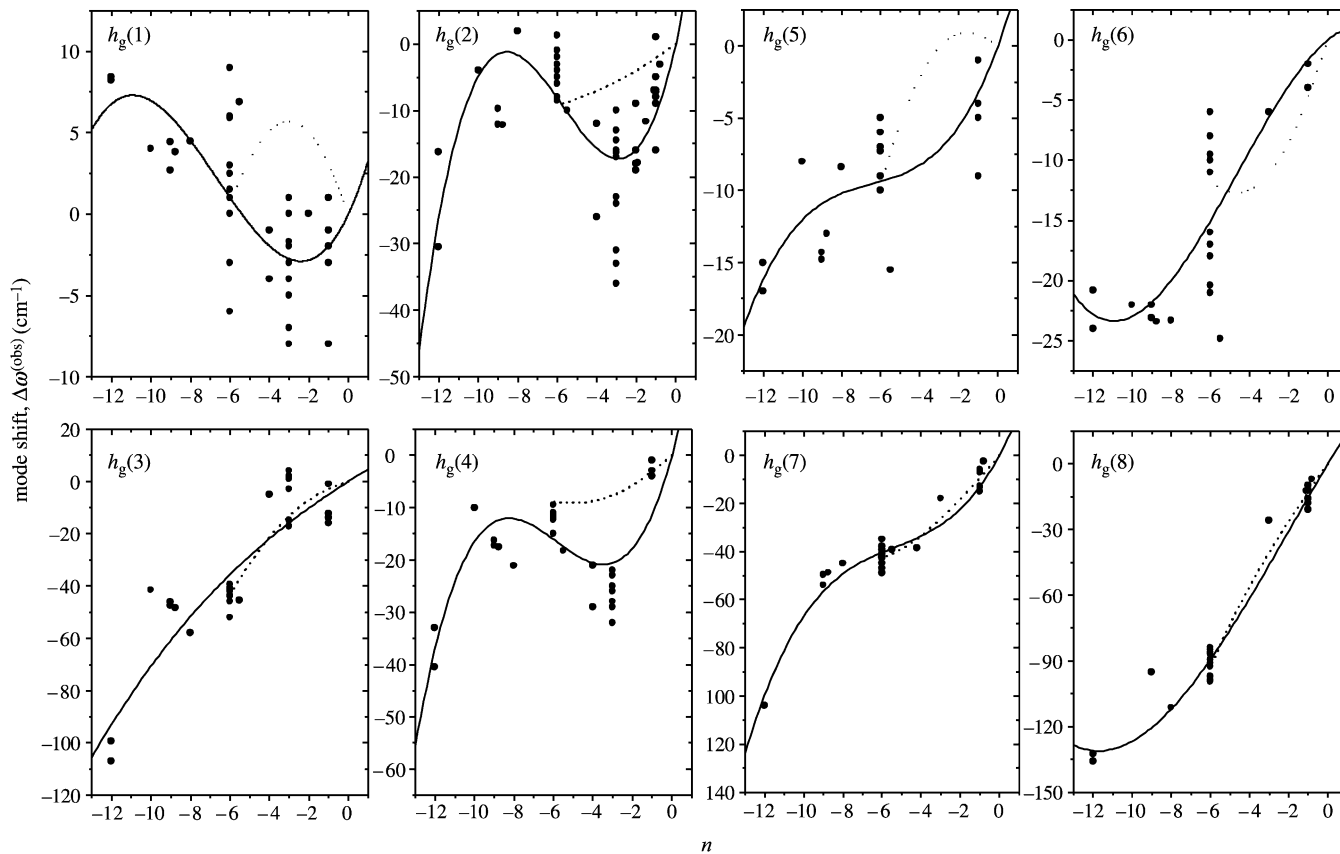


Fig. 11. Doping behaviour of the h_g modes. The full lines represent fits of the experimental data [7] to equation (8). The dashed lines indicate the doping behaviour predicted using the 13 k model.

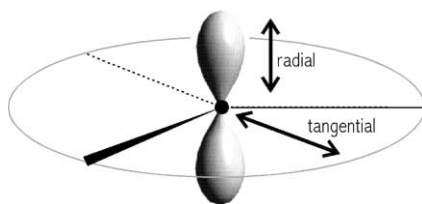


Fig. 12. A simple representation of a single carbon atom in C_{60} , illustrating the π orbital used to create the T_{1u} and other molecular orbitals and its radial nature.

added to the system. In this paper we have attempted to model these changes using a force constant model that is complete within the nearest neighbour approximation.

Our preliminary results indicate that the doping-induced behaviour cannot be explained using the force constant model alone. We have also seen that the modes whose doping characteristics diverge most strongly from the force constant model are those that have the largest vibronic coupling constants. Thus, it would seem that the observation of doping-induced shifts in the vibrational spectra of the fullerenes is a viable and valuable route to vibronic constants.

The agreement between the coupling constants deduced using photoemission spectroscopy and those from a study of doping-induced mode shifts is remarkable (Fig. 5) and indicates that in general it is the radial modes of vibration that couple most strongly to the T_{1u} level in C_{60} . This may not be too surprising a result. Figure 12 shows the local electronic structure for a single carbon atom in C_{60} prior to delocalisation of the π atomic orbital to form, amongst other things, the T_{1u} LUMO. A radial motion of the carbon nucleus clearly takes it directly into the region of space where the T_{1u} orbital is localised. A tangential mode, however, keeps the nucleus in the nodal plane of the orbital and offers little opportunity for interaction.

It may be possible to test this supposition by looking for a correlation between the magnitudes of the coupling constants and the radial components of the vibrational modes involved. This, of course, requires knowledge of the eigenfunctions associated with the normal modes. These may be obtained using the 13k model and so we leave this as an exercise for a later date when a clearer indication of the true force constants within the molecule has been found.

ACKNOWLEDGEMENTS

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REFERENCES

- [1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and E. Smalley, *Nature*, 1985, **318**, 162.
- [2] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, 1991, **350**, 600.

- [3] M. J. Rosseinsky, A. P. Ramirez, S. H. Glarum, D. W. Murphy, R. C. Haddon, A. F. Hebard, T. T. M. Palstra, A. R. Kortan, S. M. Zahurak and A. V. Makhija, *Phys. Rev. Lett.*, 1991, **66**, 2830.
- [4] O. Gunnarsson, *Rev. Mod. Phys.*, 1997, **69**, 575.
- [5] C. C. Chancey and M. C. M. O'Brien, *The Jahn–Teller Effect in C_{60} and Other Icosahedral Complexes*, Princeton University Press, New Jersey, 1997.
- [6] J. L. Dunn and A. Bates, *Phys. Rev. B*, 1995, **52**, 5996.
- [7] I. D. Hands, J. L. Dunn and A. Bates, *Phys. Rev. B*, 2001, **63**, 245414.
- [8] R. C. Haddon, L. E. Brus and K. Raghavachari, *Chem. Phys. Lett.*, 1986, **125**, 459.
- [9] I. D. Hands, J. L. Dunn, C. A. Bates and Z. Polinger, *Chem. Phys.*, 2002, **278**, 41.
- [10] O. Gunnarsson, H. Handschuh, P. S. Bechthold, B. Kessler, G. Ganteför and W. Eberhardt, *Phys. Rev. Lett.*, 1995, **74**, 1875.
- [11] A. S. Alexandrov and V. V. Kabanov, *JETP Lett.*, 1995, **62**, 937.
- [12] C. M. Varma, J. Zaanen and K. Raghavachari, *Science*, 1991, **254**, 989.
- [13] (a) P. B. Allen (eds G. K. Horton and A. A. Maradudin), North-Holland, New York, 1980; (b) P. B. Allen, *Solid State Commun.*, 1974, **14**, 937.
- [14] C. O. Rodriguez, A. I. Liechtenstein, I. I. Mazin, O. Jepsen, O. K. Anderson and M. Methfessel, *Phys. Rev. B*, 1990, **42**, 2692.
- [15] J. Winter and H. Kuzmany, *Phys. Rev. B*, 1996, **53**, 655.
- [16] Z. C. Wu, D. A. Jelski and T. F. George, *Chem. Phys. Lett.*, 1987, **137**, 291.
- [17] D. E. Weeks and W. G. Harter, *Chem. Phys. Lett.*, 1988, **144**, 366.
- [18] A. Ceulemans, P. W. Fowler and I. Vos, *J. Chem. Phys.*, 1994, **100**, 5491.
- [19] I. D. Hands, J. L. Dunn and C. A. Bates, to be published.
- [20] G. James, *J. Algebra*, 1994, **167**, 803.
- [21] C. A. Reed and R. D. Bolskar, *Chem. Rev.*, 2000, **100**, 1075.

A DFT Based Parameterization of the Vibronic Mixing between Two Non-degenerate Electronic States and the Application to s^2 -lone Pairs

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Dedicated to Professor I. B. Bersuker on the occasion of his 75th birthday

Abstract

A parameterization method of the Hamiltonian for two electronic states which couple *via* nuclear distortions (vibronic coupling), based on density functional theory (DFT) and Slaters' transition state method, is presented and applied to the pseudo-Jahn–Teller coupling problem in molecules with an s^2 -lone pair. The diagonal and off-diagonal energies of the 2×2 Hamiltonian matrix have been calculated as a function of the symmetry breaking angular distortion modes [$\alpha_2''(D_{3h})$ and $\tau_2^b(T_d)$] of molecules with the coordination number CN = 3 (model examples: $\text{As}^{\text{III}}\text{F}_3$, $\text{As}^{\text{III}}\text{Br}_3$) and 4 (model example: $\text{Se}^{\text{IV}}\text{F}_4$); they have been used as a data base to express the matrix elements in terms of polynomial series using a single interacting mode. It is concluded that vibronic coupling expressions, in which only linear and quadratic terms are taken into account, do not adequately describe the diagonal matrix elements, while the off-diagonal matrix elements are well approximated by linear functions on the distortion coordinate. The parameters of the 2×2 Hamiltonian, calculated at the geometry of the ground state energy minimum, allow to judge the relative importance of the bending [CN = 3, D_{3h} : α_2'' ; CN = 4, T_d : $\tau_2^b(\zeta)$, $\varepsilon(\theta)$] and stretching [CN = 3, D_{3h} : α_1' ; CN = 4, T_d : $\tau_2^s(\zeta)$, α_1] vibrations for the mentioned molecules with an s^2 -lone-pair.

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1. INTRODUCTION

Vibronic coupling is a common phenomenon in inorganic molecules and solids. Thus, polyhedra with the constitution $AX_n^{-(g-2-n)}$ – with central ions in subvalent oxidation states such as A^{III} , A^{IV} , A^V and A^{VI} from the $g = 5, 6, 7$ and 8 main groups, and with $X = \text{halogen}$ – frequently possess geometries which deviate from the high-symmetry expectation: planar D_{3h} (coordination number CN = 3), tetrahedral T_d (CN = 4), trigonal bipyramidal D_{3h} (CN = 5) and octahedral O_h (CN = 6). Observed low-symmetry structures can be predicted by the VSEPR model [1] and its recent extension (ligand close packing) [2, 3], but more precisely by a vibronic coupling approach [4,5] – both concepts based on a stereochemically active lone pair. In the latter model, one starts from the highest symmetry for the respective CN and considers the interaction of the ground state (g) with certain excited states (e) *via* specific normal vibrational modes (pseudo Jahn–Teller (PJT) coupling [6,7]). Group theory specifies these modes by the condition that the direct product between the irreducible representations of the ground state, the excited state and of the vibration has to be totally symmetric. Thus, for CN = 3 (D_{3h}) the totally symmetric A'_1 (s^2 -type) ground state can couple with the $A''_2(s^1p_z^1)$ -type excited state *via* the α''_2 normal mode which drives the system from the planar (D_{3h}) toward a pyramidal (C_{3v}) nuclear configuration (Fig. 1). For CN = 4 (T_d) we have an A_1 (s^2) ground state and a T_2 (s^1p^1) excited state which couple *via* the τ_2 bending and stretching modes (Fig. 2). A good approximation in many cases is to restrict to a two-state model and to consider matrix equation (1), where E_g , E_e and N denote the energies of the ground and excited states and their coupling, respectively.

$$\begin{bmatrix} E_g & N \\ N & E_e \end{bmatrix} \quad (1)$$

PJT coupling for CN = 4 is described in a general form by a 4×4 matrix [8]; however, if we restrict the treatment to specific τ_2 -type distortion pathways

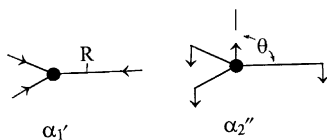


Fig. 1. The bending and stretching vibrations of a planar molecule with the CN = 3, involved in the PJT-type $D_{3h} \rightarrow C_{3v}$ process due to the presence of a lone pair.

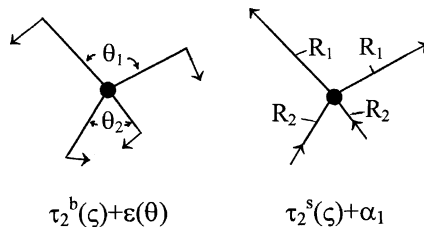


Fig. 2. The bending (τ_{bc}) and stretching (τ_{sc}) vibrations of a tetrahedral molecule or complex, involved in the PJT-type $T_d \rightarrow C_{2v}$ vibronic process due to the presence of a lone pair – τ_{bc} and τ_{sc} are the displacements according to combinations of the symmetry breaking ζ components of the τ_2 modes with the angular $\epsilon(\theta)$ component and the totally symmetric α_1 stretching vibration respectively.

leading from T_d to the minima of C_{2v} (or C_{3v}) symmetry, we may use equation (1) as well. The latter is written in the basis of the ground (ψ_g) and excited (ψ_e) state wavefunctions of the parent high-symmetry coordination, where $E_g = 0$, $E_e = \delta$, and $N = 0$. Diagonalization leads to the eigenvalues and the eigenfunctions for the ground (–) and excited (+) states in equations (2) and (3), respectively [9]. It is common to refer to equations (1) and (2) as representations of the Hamiltonian, written in a non-diagonal (diabatic) and diagonal (adiabatic) basis.

$$E_{\pm} = (1/2)(E_g + E_e) \pm [(\delta E_{g,e}/2)^2 + N^2]^{1/2}, \quad \delta E_{g,e} = E_e - E_g \quad (2)$$

$$\Psi_- = c_1 \Psi_g + c_2 \Psi_e, \quad \Psi_+ = -c_2 \Psi_g + c_1 \Psi_e \quad (3)$$

The particular dependence of $E_g(q)$, $E_e(q)$ and $N(q)$ on the nuclear coordinates (q) is of crucial importance for setting up the matrix of the coupled motions between nuclei and electrons (vibronic problem); here, harmonic vibrational wavefunctions centered at the undistorted geometry for the ground $\chi_{g,i}(q)$ and for the excited $\chi_{e,j}(q)$ state, are coupled *via* the $E_g(q)$, $E_e(q)$ and $N(q)$ functions, which thus serve as potential energy operators for the nuclear motions, in addition to the kinetic energy operator. $N(q)$ is just the operator, which leads to (non-adiabatic) coupling between the ground (g) and excited state (e) vibrational functions, $\langle \chi_{g,i}(q) | N(q) | \chi_{e,j}(q) \rangle$. The solution of the resulting equations yields vibronic eigenfunctions, which describe in a detailed way the nuclear dynamics (dynamic PJT effect). The energies E_g^m , E_e^m and N^m , when calculated for the geometry of the absolute minimum (m) of the ground state potential surface, allow to analyze the ground state stabilization energy E_-^m – the driving force for the distortion from high to low symmetry – with respect to the various underlying vibronic interactions (static PJT effect). In earlier studies we utilized DFT data of s^2 -lone pair $A^{III}X_n^{-(3-n)}$ molecules in a vibronic coupling model with a linear and quadratic dependence on the distortion coordinate [9,10]. Some insight into the mechanism of the lone pair activity has been achieved in this way.

In this contribution fitting procedures to the DFT calculated E_g , E_e , N , E_- and E_+ energy curves (Figs 3 and 5) have been performed, which avoid assumptions about

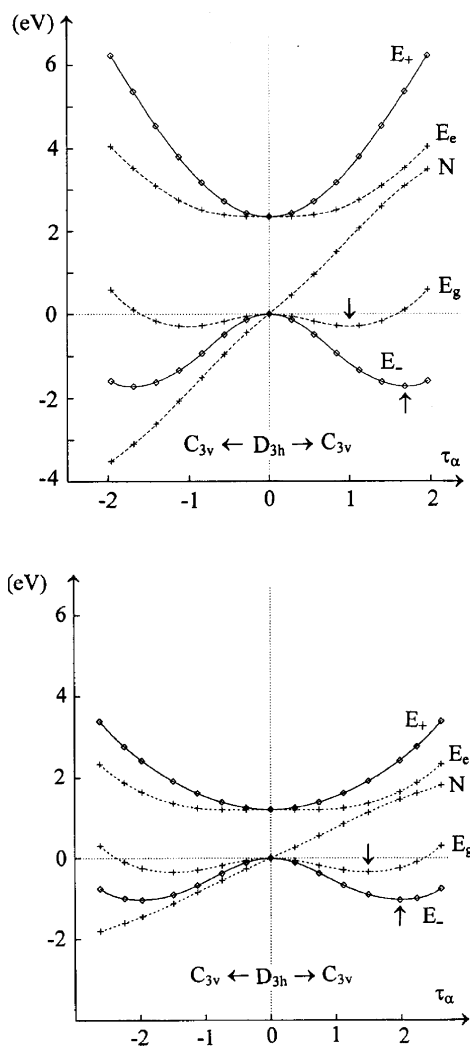


Fig. 3. The dependence of energies, characterizing the vibronic process, on nuclear displacements according to the α_2'' bending mode τ_α (Å) (see equation (12)), for AsF_3 (above) and $AsBr_3$ (below) at the As–F(Br) spacing 1.85(2.47) Å in D_{3h} . Point-markings and solid lines refer to DFT data and their fitting (equation (8)), respectively.

the leading terms of the Herzberg–Teller expansion of the electronic energy into a series along nuclear coordinates. We present a method, which is based on DFT and adopts the concept of a ‘transition state’ (TS) and partial occupation numbers, introduced by Slater [11] and utilized by others to describe atomic states [12] and avoided crossing situations [13]. In Section 4 we apply this new recipe for

calculating E_g, E_e and N to AsF_3 , AsBr_3 (Section 4.1) and SeF_4 (Section 4.2), characterizing E_g, E_e and N in regard to their dependence on a single interacting mode – here the bending vibration – and utilizing a polynomial expansion series; furthermore, we study the relative significance of the bending and of the stretching vibrational modes in regard of their respective contributions to the energy stabilization from high to low symmetry.

2. A NEW RECIPE FOR CALCULATING E_g, E_e AND N USING DFT

In DFT the energy of a given many electron state stems from a calculation in which the electron density is approximated by considering the occupied spin-orbitals resulting from a self-consistent solution of the Kohn–Sham (KS) equations; thus, ground and excited states imply different sets of KS orbitals. However, there is a unique case in which the ground state and *one* excited state can be described in terms of one common set of KS orbitals, namely within the TS concept introduced by Slater [11]. Choosing an s^2 -lone pair system ($\text{CN} = 3$) in distorted D_{3h} geometry (equation (1)) with the ground state configuration $\cdots(\varepsilon_-)^2$ and an $\cdots(\varepsilon_-)^1(\varepsilon_+)^1$ excited state configuration – ε_- and ε_+ are the energies of the HOMO and LUMO – the TS corresponds to $\cdots(\varepsilon_-)^{1.5}(\varepsilon_+)^{0.5}$. Hence one SCF–DFT calculation using orbital occupations according to the latter configuration (the upper index t denotes the TS character of the MOs) characterizes both, the ground and excited state. The electronic transition energy between two electron states $E_{\text{FC}} = E_+ - E_-$ is approximated in a remarkably accurate way by the orbital energy difference (equation (4)) [11].

$$E_{\text{FC}}^{\text{m}} = \varepsilon_+^{\text{t}} - \varepsilon_-^{\text{t}} \quad (4)$$

A brief outline of the formalism bridging the many-electron and the one-electron energies is given in Appendix A.1. DFT also yields the data needed to express the corresponding KS orbital wave functions φ_+^{t} and φ_-^{t} in terms of the KS HOMO and LUMO wave functions $\varphi(a_1')$ and $\varphi(a_2'')$ of the parent D_{3h} geometry (equation (5)). The underlying formalism, based on the Löwdin orthogonalization procedure [14] and effective Hamiltonian theory [15], has been described in detail elsewhere [16] (see also Appendix A.2). Matrix (1) – at the C_{3v} energy minimum (index m) – can now be reformulated according to equation (6), yielding the energies N^{m} , E_g^{m} and E_e^{m} (equations (7)). The new procedure can be equally well applied to any point of the ground state potential surface, allowing to study explicitly the dependence of E_g, E_e and N on one or several vibrational modes. The presented approach is only applicable if just two non-degenerate electronic states – the ground and one excited state – are involved in the vibronic mixing process. Though in the case of $\text{CNs} = 4\text{--}6$ the excited p-type states are degenerate in the high-symmetry parent geometries – 3-fold (T_d), 2-fold (D_{3h}), 3-fold (O_h) – this is not the case in the distorted polyhedra anymore, where the analysis is performed; here one specific p_z orbital is selected by symmetry. Studies on s^2 -type lone pair $\text{AX}_n^{(g-2-n)-}$ molecules, with A belonging to

the fifth and sixth main group, have shown that the described procedure is a rather good approximation in most cases [23].

$$\varphi_-^m = c_1 \varphi(a'_1) + c_2 \varphi(a''_2), \quad \varphi_+^m = -c_2 \varphi(a'_1) + c_1 \varphi(a''_2), \quad c_1^2 + c_2^2 = 1 \quad (5)$$

$$\begin{aligned} \begin{bmatrix} E_g^m & N^m \\ N^m & E_e^m \end{bmatrix} &= \begin{bmatrix} c_1 & c_2 \\ -c_2 & c_1 \end{bmatrix} \begin{bmatrix} E_-^m & 0 \\ 0 & E_+^m \end{bmatrix} \begin{bmatrix} c_1 & -c_2 \\ c_2 & c_1 \end{bmatrix} \\ &= \begin{bmatrix} (c_1)^2 E_-^m + (c_2)^2 E_+^m & c_1 c_2 (E_+^m - E_-^m) \\ c_1 c_2 (E_+^m - E_-^m) & (c_2)^2 E_-^m + (c_1)^2 E_+^m \end{bmatrix} \end{aligned} \quad (6)$$

$$\begin{aligned} E_g^m &= E_-^m + (c_2)^2 E_{FC}^m, \quad E_e^m = E_-^m + (c_1)^2 E_{FC}^m, \quad N^m = c_1 c_2 E_{FC}^m, \\ E_{FC}^m &= E_+^m - E_-^m \end{aligned} \quad (7)$$

3. COMPUTATIONAL DETAILS

The calculations have been performed using the Amsterdam Density Functional (ADF) program package [17–21] with the choice of the functionals described in Ref. [10]. We used a triple zeta basis in all geometry optimizations. For the chosen examples the two-state approximation is valid; though using an extended basis set the LUMO is well separated from higher excited MOs of the same symmetry.

4. APPLICATIONS

4.1. AsF₃ and AsBr₃

The pyramidalization of AsF(Br)₃ is accompanied by a contraction of the As–F(Br) bond length by about 0.09(0.08) Å proceeding from the D_{3h} saddle point to the C_{3v} minimum; this implies contributions from α_2'' and α_1' modes to the distortion process (Fig. 1) – both vibrations transform as α_1 in the lower C_{3v} symmetry and thus can mix. Neglecting this mixing by freezing α_1 at the As–ligand spacing in D_{3h} yields the one-dimensional plots for $E = E_g, E_e, N, E_-$ and E_+ vs. the τ_α (α_2'') nuclear displacements (see also equation (12)) in Fig. 3. Here, E_g, E_e and E_-, E_+ are energies *without* ($N = 0$) and *with* taking the PJT coupling into account, respectively. The $E(\tau_\alpha)$ dependencies can be rather well fitted using a τ_α polynomial series (equation (8)) with coefficients listed in Table 1. The PJT process can be accounted for by the simple expressions (9–12), where t_α denotes the linear coupling constant and K_α and K'_α are the harmonic force constants for the ground state $A'_1(s^2)$ and the excited state $A''_2(s^1 p_z^1)$ in D_{3h} , respectively; δ is the initial splitting between the latter states. While the data in Table 1 and Fig. 3 indicate that

N is an almost linear function of τ_α , the assumption of an harmonic approximation for $E_g(\tau_\alpha)$ and $E_e(\tau_\alpha)$ fails – here at least an additional $a_4\tau_\alpha^4$ term is needed for a proper fit. Though according to equation (10) and $K_\alpha > 0$ E_g should be always positive, implying that the PJT mixing is the only cause for the distortion, Fig. 3 reflects a contrasting result. The $a_2\tau_\alpha^2$ term in the $E_g(\tau_\alpha)$ expansion is negative, leading to a minimum at a small angular distortion. This result does not essentially change when variations of the As–F(Br) bond distances (R) are taken into account. One deduces from Table 2 and further calculations at $\tau_\alpha < \tau_\alpha^m$ and $\tau_r \leq \tau_r^m$ however, that the $E_g(\tau_\alpha)$ curves slightly shift to higher energy values in such cases, but that the minima remain. The upper index m characterizes the full optimization for the angular and/or stretching-type nuclear motions. Apparently the existence of a finite PJT mixing term N seems to be only a sufficient, but not a necessary condition for a geometric $D_{3h} \rightarrow C_{3v}$ transition. AsF₃ and AsBr₃ might spontaneously distort already without PJT coupling, though the extent of distortion (see the minimum positions of $E_g(\tau_\alpha)$ at $\theta = 107.8$ and 110.0° for AsF₃ and AsBr₃, respectively) and in particular the stabilization energy E_- is much smaller than the one induced by N . The origin of the shallow minima in the $E_g(\tau_\alpha)$ curves is not clear; it might result from the approximations, when using a 2×2 model and applying Slaters’ TS method. A possible physical reason could be the change in overlap within the bonding $2a_2''$ MO during the $D_{3h} \rightarrow C_{3v}$ transition, which occurs even without the PJT admixing of $4s(\text{As})(N = 0)$. The pure π -bonds in D_{3h} adopt partly σ character on distortion, presumably connected with a small energy gain – as may be deduced from Fig. 4.

$$E = \sum_i a_i \tau_\alpha^i$$

(8)

Table 1. Coefficients a_i in the polynomial series expansions (equation (8)) of $E_g(\tau_\alpha)$, $E_e(\tau_\alpha)$, $N(\tau_\alpha)$, $E_-(\tau_\alpha)$ and $E_+(\tau_\alpha)$ along the α_2'' normal mode distortion path for AsF₃ and AsBr₃; values of $|a_i|$ with $i > 6$ are smaller than 0.015

Parameter	a_0	a_1	a_2	a_3	a_4	a_5	a_6
<i>AsF₃</i>							
E_g	0	0	−0.670	0	0.474	0	−0.110
E_e	2.362	0	0.078	0	0.264	0	−0.069
N	0	1.636	0	0.283	0	−0.105	0
E_-	0	0	−0.749	0	0.209	0	−0.028
E_+	1.200	0	0.334	0	−0.008	0	0.001
<i>AsBr₃</i>							
E_g	0	0	−0.374	0	0.134	0	−0.018
E_e	1.197	0	−0.040	0	0.066	0	−0.009
N	0	0.718	0	0.037	0	−0.012	0
E_-	0	0	−1.757	0	0.723	0	−0.152
E_+	2.362	0	1.164	0	0.016	0	−0.028

Table 2. Energies (eV) and geometrical ($R(\text{\AA})$, $\theta(^{\circ})$) parameters for the $D_{3h} \rightarrow C_{3v}$ transition of AsF_3 and AsBr_3 (in parentheses), calculated when taking only variations of τ_r and τ_{α} , respectively, into account, and when optimizing both, the radial *and* angular geometry (upper index m)

Parameter	$\tau_{\alpha} = 0; \tau_r = \tau_r^m$	$\tau_{\alpha} = \tau_{\alpha}^m; \tau_r = 0$	$\tau_{\alpha} = \tau_{\alpha}^m; \tau_r = \tau_r^m$
R	1.76 (2.39)	1.85 (2.47)	1.76 (2.39)
θ	90.0 (90.0)	120.0 (116.5)	120.0 (116.5)
N	0 (0)	3.10 (1.45)	3.64 (1.66)
E_g^a	0.30 (0.12)	0.10 (−0.25)	0.31 (−0.14)
E_e	2.46 (1.18)	3.54 (1.64)	3.69 (1.58)
E_-	0.30 (0.12)	−1.72 (−1.04)	−2.01 (−1.15)
E_+^a	2.46 (1.18)	5.36 (2.43)	6.01 (2.59)

^aFor $\tau_{\alpha} = \tau_r = 0$: $E_e = E_+ = \delta = 2.36$ (1.20) eV.

$$N = t_{\alpha} \tau_{\alpha}$$

(9)

$$E_g = (1/2) K_{\alpha} \tau_{\alpha}^2$$

(10)

$$E_e = (1/2) K'_{\alpha} \tau_{\alpha}^2 + \delta$$

(11)

$$\tau_{\alpha} = \sqrt{3R\pi(\theta - 90)}/180$$

(12)

After all, we conclude from the foregoing discussion, that the essential energy gain accompanying the structural transformation stems from vibronic coupling – as induced by the presence of a lone pair. This is supported by DFT calculations on GaF_3 and GaBr_3 , which yield D_{3h} as the stable ground state geometry; Ga^{III} lacks the lone-pair, but is otherwise isoelectronic with As^{III} . As has been discussed extensively elsewhere [9], the PJT coupling constant N increases, when taking the bond length contraction on distortion into account – here by about 15–20% (Table 2). The influence of the radial changes on E_e , E_- and E_+ is also small, comparable to that on N . In the discussed cases of $\text{As}^{\text{III}}\text{F}(\text{Br})_3$ – as well as for other molecules of

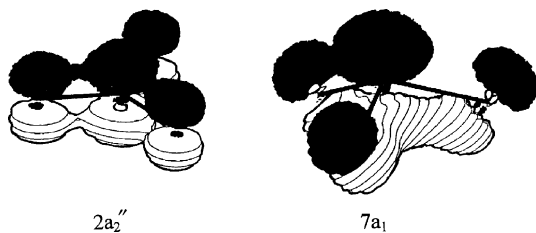


Fig. 4. Contour plots of the π -bonding $2a_2''$ KS-MO in D_{3h} (left) and of the resulting hypothetical ($\pi + \sigma$) bonding MO (right), when distorting the molecule toward C_{3v} and ignoring the PJT coupling ($N = 0$).

this type [9] – it is the angular component of the $D_{3h} \rightarrow C_{3v}$, which largely accounts for the lone pair distortion.

4.2. SeF₄

The PJT effect in a tetrahedral species with one lone pair usually drives the system along the τ_2 nuclear displacement paths (Fig. 2) into a C_{2v} distorted geometry (see Table 3), where the ζ components of the τ_2 modes and the θ component of the ε bending mode become totally symmetric as the stretching α_1 vibration is already in T_d . Thus, for CN = 4 the PJT interaction involves four modes, resulting in a rather complex vibronic interaction scheme. Considering first the dependence on the bending τ_2^b (ζ) mode (displacements τ_b , defined in equation (13)) only, which opens (closes) the θ_1 (θ_2) angles away from their tetrahedral values (109.47°) to the same extent, one calculates the one-dimensional energy plots in Fig. 5. The E_- (τ_b) curve is very flat with a minimum at θ_1 (θ_2) values of 130.9(88.1) and a tiny stabilization energy of only −0.07 eV, which should be compared with −1.04 eV at the absolute C_{2v} minimum, where the coupling with all vibronically active modes (Fig. 2) is allowed for (Table 3). We further notice that the restoring energy $E_g(\tau_b)$ is always positive, with a minimum at the geometry of the undistorted tetrahedron.

$$\tau_b = R(\theta_1 - 109.47^\circ)\pi/180$$

(13)

As for AsF₃ and AsBr₃ a rather good fit of the curves in Fig. 5 to a polynomial series in τ_b as in equation (8) is possible, with parameters listed in Table 4. Again $N(\tau_b)$ is approximated reasonably well by a linear function, while for $E_g(\tau_b)$, $E_e(\tau_b)$ and $E_-(\tau_b)$ at least one additional an harmonic term $a_4\tau_b^4$ is needed in addition to a_2 . τ_b^2 , in contrast to the assumptions in equations (10) and (11).

We now focus on the absolute minimum (m) and consider more closely the influence of an admixture of $\theta(\varepsilon)$ – opening the θ_1 , θ_2 angles in Fig. 2 by the same

Table 3. Energies (eV) and geometrical ($R_{1,2}(\text{\AA})$, $\theta_{1,2}(\text{°})$) parameters for the $T_d \rightarrow C_{2v}$ transition of SeF₄, calculated when taking only variations corresponding to $\tau_{bc} = \tau_b + \tau_\varepsilon$ or $\tau_{sc} = \tau_s + \tau_\alpha$ into account, and when optimizing both, the angular and radial geometry (upper index m); the initial splitting δ is 4.21 eV

Parameter	$\tau_{sc} = 0$; $\tau_{bc} = (\tau_{bc})^m$	$\tau_{sc} = (\tau_{sc})^m$; $\tau_{bc} = 0$	$\tau_{sc} = (\tau_{sc})^m$; $\tau_{bc} = (\tau_{bc})^m$
R_1	1.86	1.83	1.83
R_2	1.86	1.75	1.75
θ_1	187.5	109.5	187.5
θ_2	99.2	109.5	99.2
N	2.28	0.18	2.86
E_g	0.49	0.31	0.70
E_e	3.43	4.66	3.70
E_-	−0.76	0.33	−1.04

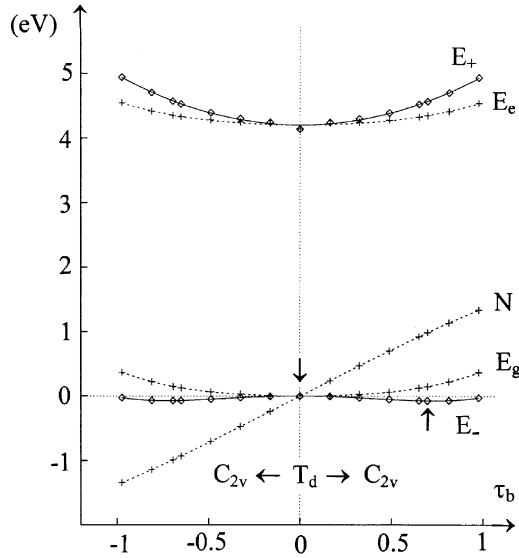


Fig. 5. The dependence of the energies, characterizing the vibronic process, on nuclear displacements according to the τ_2^b bending mode τ_b (Å) for SeF₄, at the Se–F spacing 1.86 Å in T_d . The point-markings and solid lines refer to DFT data and their fitting (equation (8)), respectively.

amount (displacements τ_ε , defined in analogy to equation (13)) – to the bending τ_2^b vibration, and when also accounting for the vibronically active stretching modes, τ_2^s (displacements $\tau_s = 2\delta R_{1,2}$) and α_1 (displacements $\tau_\alpha = 2\delta R_{Td}$). Analyzing the angular polyhedron distortion in the final C_{2v} geometry $\tau_{bc} = \tau_b + \tau_\varepsilon$ (Table 3), one finds that a very significant ε -type component ($\delta\theta \approx +34^\circ$) is present in addition to that induced by τ_2^b ($\delta\theta \approx \pm 44^\circ$); it exceeds the contribution to τ_2^b , which can be expected by normal vibrational coupling. Indeed, as has been outlined elsewhere [10], a further mechanism has to be considered. The excited electronic T_2 state in T_d is subject to a strong first order Jahn–Teller effect induced by the ε mode, leading to

Table 4. Coefficients a_i in the polynomial series expansions of the various energies along the τ_b distortion path $T_d \rightarrow C_{2v}$ for the s^2 -lone pair molecule SeF₄

Parameter	a_0	a_1	a_2	a_3	a_4
E_g	0	0	0.226	0	0.167
E_e	4.206	0	0.263	0	0.095
N	0	1.464	0	−0.092	0
E_-	0	0	−0.276	0	0.260
E_+	4.206	0	0.762	0	0.005

an almost planar structure; the PJT coupling introduces a large part of this distortion component *via* N^m into the ground state. In Table 3 we compare the energy contributions stemming from the bending τ_{bc} ($= \tau_b + \tau_e$) and the stretching τ_{sc} ($= \tau_s + \tau_\alpha$) modes with the total energies for the fully optimized geometry, by decomposing the final distortion into the various components τ_b , τ_e , τ_s and τ_α . The calculated energies N and E_- indicate that – similar to the situation for AsF_3 and AsBr_3 – the bending modes dominate the vibronic effect, supplying about 75% of the total N^m and E_-^m energies (Table 3). It is striking though, that it is apparently not the symmetry breaking τ_2^b mode ($A_1 \otimes \tau_2 \otimes T_2$ PJT coupling), which induces the major energy effect (see Fig. 5), but the ε mode, which is active in the excited state.

We finally analyse the non-diagonal energy N more closely with respect to its components originating from the various nuclear displacements τ_b , τ_e , τ_s and τ_α (equation (14)), where t_b , t_s are the coupling constants for the τ_b , τ_s nuclear motions and t_{be} , $t_{s\alpha}$

$$N = N_b + N_s = (t_b \tau_b + t_{be} \tau_b \tau_e^2) + (t_s \tau_s + t_{s\alpha} \tau_s \tau_\alpha) \quad (14)$$

characterize their mixing with the τ_e and τ_α -type displacements. In addition a N_{bs} term is expected, which takes account of the coupling between the bending τ_{bc} and the stretching τ_{sc} nuclear motions. One deduces from Table 3 that this contribution to N^m ($= 2.86$ eV) amounts to 0.40 eV and is hence of rather significant magnitude with respect to N_b^m ($= 2.28$ eV) and in particular to N_s^m ($= 0.18$ eV). The N_b^s mixing term, which was neglected in an earlier treatment [10] and in equation (14), reflects that the radial motions (reduction of the averaged Se–F spacings and large τ_s -type displacements during the $T_d \rightarrow C_{2v}$ transition) support the energetic effect due to the angular motions considerably.

A striking difference between the $\text{AsF}(\text{Br})_3$ and SeF_4 molecules is the distinctly positive E_g^m energy in the latter case (0.70 eV), with approximately equal contributions from the bending and the stretching modes (Figs 3 and 5). Apparently, the presence of more active modes, particularly of stretching ones, when increasing the CN from 3 to 4, strengthens the resistance of the structure toward lone pair distortions. A similar conclusion is deduced from the *ligand close packing* concept [2,3]; here, repulsive forces are proposed to be responsible for the absence of lone pair activity in some s^2 systems with high CNs (inert pair effect [22]).

5. CONCLUSIONS

(i) Making use of Slaters' TS method [11] in combination with effective Hamiltonian theory [15] and a Löwdin orthogonalisation [14] we have developed a recipe which allows to deduce the diagonal energies of two electronic states – ground state (E_g) and one excited state (E_e) – and their non-diagonal mixing matrix element (N), as induced by nuclear distortion, when leaving the high-symmetry reference geometry [matrix (1)]. Using the s^2 -lone pair $\text{AsF}(\text{Br})_3$ and SeF_4

molecules as model examples, we have studied the dependence of E_g , E_e and N on a single interacting mode (q), which distorts these molecules from D_{3h} and T_d toward C_{3v} and C_{2v} geometries, respectively. The E_g and E_e energy curves can not be approximated by vibronic parameters confined to quadratic terms in the series expansion of q , but need higher order terms as well. In contrast, the non-diagonal N energy is fairly well fitted by one linear term only. Thus, reported E_g^m and E_e^m energies [9,10], calculated assuming a purely quadratic dependence on the respective nuclear displacements (harmonic approximation, equations (10) and (11)), differ considerably from those reported here, while the derived N^m energies (equation (9)) are equal within narrow limits in both approaches. The treatment in this contribution substantiates, that the diagonal energies, as calculated on the basis of Slaters' TS theory, are definitely more reliable than those derived earlier [9,10].

(ii) The E_g energy is positive for SeF_4 , but is found to possess minima at negative values for AsF_3 and AsBr_3 (Figs 3 and 5), with even a negative value for E_g^m (Table 2) in the latter case. Hence, while the ground state $T_d \rightarrow C_{2v}$ energy stabilization in the case of SeF_4 is purely the result of PJT coupling (N), for some AX_3 molecules the $D_{3h} \rightarrow C_{3v}$ distortion may occur already without vibronic mixing ($N = 0$). The respective negative E_g^m energies are rather small [23], but contrast the usual belief that PJT mixing is the only cause of distortion [24].

APPENDIX A

A.1. Many-electron and one-electron (orbital) energies in Slaters' TS theory

Considering two electronic states E_- and E_+ , characterised by electronic configurations with the same occupancies of all orbitals except for ε_- (HOMO) and ε_+ (LUMO), the orbital sequences $\cdots \varepsilon_-^2$ and $\cdots \varepsilon_-^1 \varepsilon_+^1$ describe E_- and E_+ respectively. We expand the total many-electron energies E into a series, which depends on occupation number changes dn_i around a reference configuration $\varepsilon_-^{(2-q)} \varepsilon_+^q$; the energy E_0 with a non-integer but fixed value of q ($0 < q < 1$; equation (A.1)) serves as the reference. Following Janack's [25] theorem, the derivative $(\partial E / \partial n_i)_0$ corresponds to the energy of the KS orbital ε_i .

$$E = E_0(\varepsilon_-^{(2-q)} \varepsilon_+^q) + \sum_{(i)} (\partial E / \partial n_i)_0 dn_i + (1/2) \sum_{(i)} \sum_{(j)} (\partial^2 E / \partial n_i \partial n_j)_0 dn_i dn_j + \cdots \quad (\text{A.1})$$

The theorem holds if the exchange-correlation potential V_{XC} equals the functional derivative of the exchange-correlation energy E_{XC} with respect to the electron density ρ – an operational definition, which is intrinsic to DFT.

The second derivative $(\partial^2 E / \partial n_i \partial n_j)_0$ is the energy of the Coulomb interaction between two electrons occupying orbitals i and j , when taking the screening from all other electrons into account; we designate this quantity as U_{ij} . Choosing

a value of $q = 1/2$ we obtain the energies E_- and E_+ as in equations (A.2) – after having substituted: $dn_- = 1/2$, $dn_+ = -1/2$ and $dn_- = -1/2$, $dn_+ = 1/2$ for E_- and E_+ respectively, into equation (A.1).

$$\begin{aligned} E_-^t &= E_0^t + (1/2)\epsilon_-^t - (1/2)\epsilon_+^t + (1/8)U_{++}^t + (1/8)U_{--}^t - (1/4)U_{+-}^t \\ E_+^t &= E_0^t - (1/2)\epsilon_-^t + (1/2)\epsilon_+^t + (1/8)U_{++}^t + (1/8)U_{--}^t - (1/4)U_{+-}^t \end{aligned} \quad (\text{A.2})$$

It follows for this specific choice (the TS $\dots \epsilon_-^{1.5} \epsilon_+^{0.5}$ with energy E_0), that the Franck–Condon energy $E_{\text{FC}} = E_+ - E_-$ equals the orbital difference $\epsilon_+^t - \epsilon_-^t$, because the two-electron parts cancel – here, the upper index t refers to quantities connected with the TS. This result is violated, if higher order terms in the expansion A.1 are taken into account; however, calculations using a LDA + GGA functional yield, that the error does usually not exceed 2%.

A.2. Evaluation of the coefficients c_1 and c_2

Focussing on the HOMO ϵ_- and the LUMO ϵ_+ , DFT yields the KS eigenvectors u_+ and u_- (equation (A.3)). Effective Hamiltonian theory [15] allows to reduce the size of matrix V to 2×2 . Choosing the latter sub-matrix U , written in the subspace

$$V = \begin{bmatrix} u_{s-} & u_{s+} & \dots \\ u_{pz-} & u_{pz+} & \dots \\ \dots & \dots & \dots \end{bmatrix} \quad (\text{A.3})$$

of the s and p_z orbitals of the central atom, we introduce the overlap matrix S (equation (A.4)) with U^T being the transpose of U . Since ligand functions are neglected, S is not a unit matrix. Following a procedure described by Löwdin [14], ligand functions can be implicitly accounted for by the calculation of the Löwdin matrix $L = S^{-(1/2)}$ following the recipe: find, by diagonalizing S , the diagonal eigenvalue matrix Λ_s and the matrix composed of the corresponding eigenvectors columns U_s , this yielding L (equation (A5)). The multiplication of L and U (equation (A.6)) yields the coefficients in equation (5).

$$S = \begin{bmatrix} u_{-s} & u_{+s} \\ u_{-pz} & u_{+pz} \end{bmatrix} \begin{bmatrix} u_{-s} & u_{-pz} \\ u_{+s} & u_{+pz} \end{bmatrix} = U \cdot U^T \quad (\text{A.4})$$

$$L = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} = U_s \Lambda_s^{-(1/2)} U_s^T \quad (\text{A.5})$$

$$L \cdot U = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{bmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{bmatrix} = C = \begin{bmatrix} c_1 & -c_2 \\ c_2 & c_1 \end{bmatrix} \quad (\text{A.6})$$

REFERENCES

- [1] R. J. Gillespie and R. S. Nyholm, *Q. Rev. (Lond.)*, 1957, **11**, 339.
- [2] R. J. Gillespie and E. A. Robinson, *Angew. Chem.*, 1996, **108**, 539; R. J. Gillespie and E. A. Robinson, *Int. Ed. Engl.*, 1996, **495**.
- [3] R. J. Gillespie, *Coord. Chem. Rev.*, 2000, **197**, 51.
- [4] H. C. Longuet-Higgins, *Proc. R. Soc. Lond., Ser. A*, 1956, **235**, 537.
- [5] U. Öpik and M. H. L. Pryce, *Proc. R. Soc. Lond., Ser. A*, 1957, **238**, 425.
- [6] R. F. W. Bader, *Mol. Phys.*, 1960, **3**, 137.
- [7] I. B. Bersuker, *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry*, Plenum Press, New York, 1984.
- [8] W. J. A. Maaskant and I. B. Bersuker, *J. Phys.: Condens. Matter*, 1991, **3**, 37.
- [9] M. Atanasov and D. Reinen, *J. Phys. Chem. A*, 2001, **105**, 5450.
- [10] M. Atanasov and D. Reinen, *J. Am. Chem. Soc.*, 2002, **124**, 6693.
- [11] J. C. Slater, *Adv. Quantum Chem.*, 1972, **6**, 1, and references therein.
- [12] J. C. Slater, J. B. Mann, T. M. Wilson and J. H. Wood, *Phys. Rev.*, 1969, **184**, 672.
- [13] S. G. Wang and W. H. E. Schwarz, *J. Chem. Phys.*, 1996, **105**, 4641.
- [14] P. O. Löwdin, *Adv. Quantum Chem.*, 1970, **5**, 185, and references therein.
- [15] P. Durand and J.-P. Malrieu, *Advan. Chem. Phys.*, 1987, **67**, 321, Wiley: New York and references therein.
- [16] M. Atanasov, J.-L. Barras, L. Benco and C. Daul, *J. Am. Chem. Soc.*, 2000, **122**, 4718.
- [17] E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.*, 1973, **2**, 41.
- [18] E. J. Baerends and P. Ros, *Int. J. Quantum Chem.*, 1973, **2**, 42.
- [19] E. J. Baerends and P. Ros, *Chem. Phys.*, 1973, **2**, 51.
- [20] P. M. Boerrigter, G. te Velde and E. J. Baerends, *Int. J. Quantum Chem.*, 1988, **33**, 87.
- [21] G. te Velde and E. J. Baerends, *J. Comput. Phys.*, 1992, **99**, 84, and references therein.
- [22] L. S. Bartell, *Coord. Chem. Rev.*, 2000, **197**, 37.
- [23] D. Reinen and M. Atanasov, *Struct. Bonding*, Springer, Berlin, in press.
- [24] I. B. Bersuker, *Chem. Rev.*, 2001, **101**, 1067.
- [25] J. F. Janak, *Phys. Rev. B*, 1978, **18**, 7165.

The *Ab Initio* Analytical Approach of Vibronic Quantities: Application to Inorganic Stereochemistry

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Abstract

This work presents and illustrates the principles and technical strategies necessary to accomplish the *ab initio* vibronic analysis of the pseudo Jahn–Teller effect in molecular systems. For reasons related to the physical meaningfulness of the one-electron picture we confined here to the RHF level, suggesting briefly also the relation to correlated wave functions. Simple molecular systems with prototypical relevance for the inorganic stereochemistry were taken as sample of calculation. We developed and applied here a new heuristic concept, the vibronic orbitals, as the objects able to render the description of the full vibronic curvature into a limited number of effective states. It is worth to note that the concentration of the vibronic effects is made in a manner completely recovering the computed *ab initio* curvature of potential energy surfaces, without imposing any arbitrary reduction in the number of interacting canonical MOs and resulting vibronic orbitals. The vibronic orbitals are the functions most sensitive to the molecular geometry, encoding information about the driving factors of molecular stereochemistry suggesting new applications of the vibronic paradigm.

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1. INTRODUCTION

The vibronic interactions have multiple impacts in various chemical and physical phenomena [1,2]. Especially, the vibronic paradigm is a natural key for the stereochemical problems, to which offers a general methodology and a set of meaningful parameters.

If we try to fit the factors of the stereochemical distortions in the four types of Aristotle's causes, one may assimilate *causa materialis* to the particular molecule that offers the problem, then consider *causa finalis* as tendency of finding the minimum energy, and keeping *causa formalis* for the symmetry reasons of the problem, one arrives to the vibronic interaction as *causa efficiens*, i.e., as a driving force of the stereochemistry.

The strategy of vibronic analysis is to regard the molecular skeleton in the higher possible symmetry, analyzing the forces distorting or keeping this structure. In case of distortion, a Jahn–Teller (JT) or pseudo Jahn–Teller effect (PJT) takes place. Even in the absence of distortion, a vibronic part exists inside of force constants of each normal vibration mode and its analysis could offer particular insight into molecular structure.

Often, the symmetry reasons enable the qualitative assumption of the JT or PJT vibronic effects. The quantitative approach gives rise to particular problems in that concern the accordance between vibronic paradigm and the actual state-of-the-art of quantum chemistry. Here we must point out that the brute force calculation of the optimal structure and the reporting of distortion tendencies is not, however, a vibronic calculation, without the attempt to properly extract the key parameters. A general tacit strategy [3] for obtaining the vibronic parameters is the *ab initio* calculation of potential energy surfaces followed by the fit in the frame of small model Hamiltonians involving few states, constructed according to the traditional cases of JT or PJT effects. Beyond this approach, a nontrivial task is the analytical calculation of vibronic constants, in full accordance with the computed *ab initio* potential surface without any model fit or approximation. We have shown previously [4] that this requires the reconsideration of vibronic formalisms, the literal use of traditional expression of vibronic constants being no longer valid. Implementation to calculus demonstrated the utility of vibronic applications to stereochemical problems [5]. The actual work continues with this idea, choosing prototypical stereochemical problems at small molecules approached with the help of a new concept, the vibronic orbitals.

The vibronic methods represent a way to encompass the Born–Oppenheimer approximation accounting for the forces involved in the molecular dynamics, being, therefore, a natural direction of the modern quantum chemistry. However, one may acknowledge also that the vibronic language looks exotic with respect to common use, in spite of the growing number of applications related to computed potential energy surfaces and molecular dynamics. Searching for strategies and routines of complete *ab initio* computation of vibronic terms, while keeping the concepts of the pure theoretical *organon* of the JT and PJT effects, is a goal helping to close the gap

between the formal and calculus levels, integrating the vibronic paradigm in the actual impetus of the self-consistent vibration fields and molecular dynamics [6].

2. PRINCIPLE AND FORMAL BACKGROUND

We are particularly dealing here with the pseudo Jahn–Teller (PJT) manifestations of the vibronic interactions, which are, in fact, more widespread than the genuine Jahn–Teller effects (JT). Innumerable examples from the inorganic and organo-metallic chemistry of main group elements or compounds of transition metals are subjects of PJT effects, in their molecular or crystal structures. Technically speaking the manifestation of the PJT corresponds to an unstable, symmetry determined, extremum point of the adiabatic potential energy surface, with respect to one or many normal coordinates (i.e., maxima or saddle points). Equivalently, instability corresponds to imaginary vibration frequencies of the higher symmetry structure. The vibronic paradigm follows the goal of revealing the factors determining such effects.

In the master formula for the analysis of the pseudo-Jahn–Teller effect, the total curvature of the adiabatic potential surface, K , is partitioned in a so-called nonvibronic part K_0 and the vibronic one K_v , namely $K = K_0 + K_v$, with

$$K_0 = \left\langle \Psi_0 \left| \frac{\partial^2 \hat{H}}{\partial Q^2} \right| \Psi_0 \right\rangle \quad (1)$$

$$K_v = -2 \sum_{r \neq 0} \frac{\left(\left\langle \Psi_0 \left| \frac{\partial \hat{H}}{\partial Q} \right| \Psi_r \right\rangle \right)^2}{E_r - E_0} \quad (2)$$

In the above formula, Q is the nuclear coordinate, Ψ_0 and Ψ_r are the ground state and excited electronic terms. Here K_v is provided through the traditional Rayleigh–Schrödinger perturbation formula and K_0 have an electrostatic meaning. This expression will be called traditional approach, which has, in principle, quantum correctness, but requires some amendments when different particular approaches of electronic structure calculation are employed (see the Bersuker’s work in this volume). In the traditional formalism the vibronic constants $\langle \Psi_0 | \partial \hat{H} / \partial Q | \Psi_r \rangle$ can be tackled with the electric field integrals at nuclei, while the K_0 is ultimately related with electric field gradients. Computationally, these are easy to evaluate but the literally use of equations (1) and (2) definitions does not recover the total curvature computed by the *ab initio* method at hand.

The reason for such problems is contained in the following quotation from Pulay [7]: “Nuclear coordinates as perturbation parameters are different from other common perturbations, e.g. weak external fields. The reason for this is the deep and singular potential well at the nucleus which leads to large charge density near the nucleus”. The key is suggested by a further quotation from the same source: “...the

basis functions must be coupled to the nuclei". The use of floating basis is, in fact, implicitly practiced when derivatives of molecular integrals are performed. However, this aspect is not explicitly acknowledged in cases when the vibronic constants obtained by fit procedures are reported.

The use of floating basis turns the vibronic curvature to the following form:

$$K_v = -2 \sum_s \frac{(\partial(\langle \Psi_0 | \hat{H} | \Psi_s \rangle - E_0 \langle \Psi_0 | \Psi_s \rangle) / \partial Q)_{Q=0}^2}{E_s - E_0} \quad (3)$$

namely, the role of vibronic constants is played by a derivative from a matrix element of the CI Hamiltonian instead of a matrix element from the derivative of the Hamiltonian operator. Beyond being a simple pedantry, this emphasis is an important hint to advance toward the analytic evaluation of vibronic quantities in a manner made consistent with the *ab initio* electronic structure calculation. For exact wave function (not reachable in usual procedures like HF, MCSCCF, truncated CI, etc.) the relationship (2) becomes equivalent to equation (3), but generally equation (3) is the correct form for practical applications. While in equation (2) the vibronic constant is purely one-electron integral, in equation (3) it includes, as effective part, certain contributions from two-electron terms, this being the price paid for incomplete configuration interaction.

3. THE ORBITAL APPROACH TO PSEUDO JAHN–TELLER EFFECT. A NEW CONCEPT: THE VIBRONIC ORBITALS

Acknowledging the importance of the pioneering idea of Bersuker's orbital vibronic constants [8] we will follow here also an orbital perspective. The orbital language, namely, the effective one-electron picture, relates with the vibronic problems by the fact that the involved electron–nuclear interactions is truly monoelectronic in nature. The Bersuker's traditional formula is

$$\tilde{K}_v = -2 \sum_i^{\text{occ}} \sum_n^{\text{virt}} \frac{(\langle \varphi_n^{(0)} | \partial \hat{H} / \partial Q | \varphi_i^{(0)} \rangle)^2}{\varepsilon_n^{(0)} - \varepsilon_i^{(0)}} \quad (4)$$

where the quantities in the numerator, taken as matrix elements involving MOs are the corresponding orbital vibronic constants. The relation between equations (2) and (4) cannot be completely matched, as equation (2) is formally valid for fully correct polyelectronic ground and excited states, while equation (4) is tacitly confined to the single-determinant frame. A revised formula can be presented as follows [4]:

$$K_v = 2 \sum_i^{\text{occ}} \sum_n^{\text{virt}} \mathbf{u}_{ni}^{(1)} \cdot \mathbf{v}_{in}^{(1)} \quad (5)$$

In this case a full formal correspondence and numerical identity between polyelectronic equation (3) and orbital transcription equation (5) of vibronic

curvature can be established. Here the $u_{ni}^{(1)}$ coefficients correspond to well known **U** matrix from Coupled Perturbed theories [9] while the vibronic constants look as companions of the so-called **B** matrix elements, after operating a sign change at terms factorized by overlap integral derivatives. A short definition of the effective vibronic constant matrix **V** is done by invoking the comparison with well-known pattern of the **B** matrix:

$$\mathbf{V}_{in}^{(1)} = \mathbf{f}_{ni}^{(1)} - \varepsilon_i^{(0)} \mathbf{S}_{ni}^{(1)} - \frac{1}{2} \sum_j^{\text{occ}} \sum_l^{\text{occ}} \mathbf{S}_{ni}^{(1)} \mathbf{A}_{lj}^{ni} \quad (6a)$$

$$\mathbf{B}_{in}^{(1)} = \mathbf{f}_{ni}^{(1)} - \varepsilon_i^{(0)} \mathbf{S}_{ni}^{(1)} + \frac{1}{2} \sum_j^{\text{occ}} \sum_l^{\text{occ}} \mathbf{S}_{ni}^{(1)} \mathbf{A}_{lj}^{ni} \quad (6b)$$

Here we will skip the notation details, as the relation established to the Coupled Perturbed frame allow us the shortcut of passing the references to the comprehensive works devoted to the analytic derivatives of molecular energy [9]. The recent advances in the analytic derivatives and Coupled Perturbed equations into multiconfigurational second order quasi-degenerate perturbation theory is the premise of further development in the *ab initio* approach of vibronic constants of JT effects [10].

In other words, the vibronic analysis made consistent with a given level of electronic structure calculation (say HF or MCSCF) consists of extracting and converting some amount of information from the black box of geometry optimization routines and using it in a manner corresponding to revisited vibronic formalism. Without entering into the details, we note that the above formula have the same pattern in the HF, MCSCF and even DFT solutions of electronic structure. For instance, in the case of multideterminant wave functions, using the natural orbitals and their occupation numbers, n , the corresponding formula becomes $K_v = 2 \sum_i^{\text{all-MO}} \sum_{j \leq i} |n_j - n_i| u_{ji} V_{ij}^{(1)}$. An important note is that the coupled perturbed frame is equivalent to the approach of time dependent (TD) electronic structure theory [11]. The vibronic analysis with respect to electronic structure method is practically based on the concrete form of the **A** matrix which generally have a CI-type appearance. For the HF level, according to demonstration of L. F. Chibotaru, the **A** matrix is those from the Random Phase Approximation (RPA). This is in line with the general acknowledged equivalence between RPA and the TD [11]. A notable aspect is that RPA method can be conveniently approached with newly improved algorithms [12]. For MCSCF the problems relate with quasi-degenerate perturbation theory [13] and multireference RPA [14] while in DFT the vibronic analysis can be approached following the accumulated achievements of TD-DFT.

Here we will focus our attention in developing a new concept related to the orbital paradigm in vibronic analysis, proposing new objects named vibronic orbitals. The general formula (5) and the application in Section 4 shows that in spite of the crude belief that the contributing elements can be limited to the frontier orbitals, the

vibronic terms should be collected from a large number of excitations. The effective functions of ‘vibronic orbitals’ will be designed in order to filter the information, concentrating the terms that are contributing to the vibronic curvature in a minimal number of $\mathbf{u}_{ga}^{(1)} \cdot \mathbf{V}_{ga}^{(1)}$ products whose summation lead to the same K_v as equation (5).

The procedure is based on the invariance of the vibronic curvature with respect to the re-mixing of occupied orbitals among them and of the virtuals in their set:

$$|a\rangle = \sum_i^{\text{oc}} r_{ia} |i\rangle, \quad |g\rangle = \sum_n^{\text{virt}} s_{ng} |n\rangle \quad (7)$$

where i and a refers to occupied functions while n and g to virtuals. Imposing an extremum condition constrained to orthogonality of transformation matrices by means of Lagrange multipliers one arrives to the following equations:

$$\begin{aligned} \frac{d}{dr_{ia}} \left(\sum_a^{\text{oc}} \sum_g^{\text{virt}} \mathbf{u}_{ga}^{(1)} \cdot \mathbf{V}_{ga}^{(1)} - \lambda \left[\sum_i^{\text{oc}} \sum_j^{\text{oc}} r_{ia} \delta_{ij} r_{ja} - 1 \right] \right) &= 0 \\ \frac{d}{ds_{ng}} \left(\sum_a^{\text{oc}} \sum_g^{\text{virt}} \mathbf{u}_{ga}^{(1)} \cdot \mathbf{V}_{ga}^{(1)} - \lambda \left[\sum_n^{\text{virt}} \sum_m^{\text{virt}} s_{ng} \delta_{mn} s_{mg} - 1 \right] \right) &= 0 \end{aligned} \quad (8)$$

These are transformed into

$$\begin{aligned} \sum_a r_{ja} \left[\sum_n^{\text{virt}} (\mathbf{u}_{ni}^{(1)} \cdot \mathbf{V}_{nj}^{(1)} + \mathbf{u}_{nj}^{(1)} \cdot \mathbf{V}_{ni}^{(1)}) - \lambda \delta_{ij} \right] &= 0 \\ \sum_a s_{mg} \left[\sum_i^{\text{oc}} (\mathbf{u}_{ni}^{(1)} \cdot \mathbf{V}_{mi}^{(1)} + \mathbf{u}_{mi}^{(1)} \cdot \mathbf{V}_{ni}^{(1)}) - \lambda \delta_{mn} \right] &= 0 \end{aligned} \quad (9)$$

whose solutions corresponding to the diagonalization of the matrix $\mu_{ij} = \sum_n^{\text{unocc}} (\mathbf{u}_{ni}^{(1)} \cdot \mathbf{V}_{nj}^{(1)} + \mathbf{u}_{nj}^{(1)} \cdot \mathbf{V}_{ni}^{(1)})$ (where, i, j are occupied orbitals) in order to accomplish the maximization of orbital vibronic effects on the occupied orbitals side, while the diagonalization of the matrix $\nu_{mn} = \sum_i^{\text{occ}} (\mathbf{u}_{ni}^{(1)} \cdot \mathbf{V}_{mi}^{(1)} + \mathbf{u}_{mi}^{(1)} \cdot \mathbf{V}_{ni}^{(1)})$ leads to the optimization of the virtual MOs, in the same respect. This technique can be called a localization procedure for the vibronic effects and the resulted eigenvectors give the transformation of canonical orbitals into the here-called vibronic orbitals.

The vibronic orbitals are interesting new objects having properties recommending them for further use and investigation. Namely,

- (i) the vibronic orbitals are the functions proven to be the most sensitive to the molecular geometry;
- (ii) offer a pictorially synthetic account of the excitations triggering a given instability of the PJT type;

- (iii) the occupied-virtual transition densities products of vibronic orbitals offers the best partition of electron density flows of the distortion.

4. RESULTS AND DISCUSSION

The working procedures of the revisited vibronic orbital models will be illustrated taking two classical stereochemical cases: NH_3 and ClF_3 . Both NH_3 and ClF_3 have D_{3h} point group as higher symmetry reference. Then, the pyramidal shape of NH_3 appears as a $(a'_1 + a''_2) \otimes A''_2$ effect [15] and the T-shape of ClF_3 looks like one component of the degenerate coordinate from the $(a'_1 + e') \otimes E'$ effect.

The computation is confined to RHF-6-311++G(2d,2p) level [16]. At one side, the limitation to the RHF is imposed by the actual availability of analytical second derivatives to this level only, but is also justified from other perspectives. A practical reason for the RHF scheme is clearly seen if translate to the same relative position (with D_{3h} reference point as origin) the relaxed potential energy surfaces for the umbrella mode of NH_3 computed at different levels (RHF, MP2, CCSD(T), B3LYP/6-311++G(2d,2p)). Figure 1 shows that the very different methods give

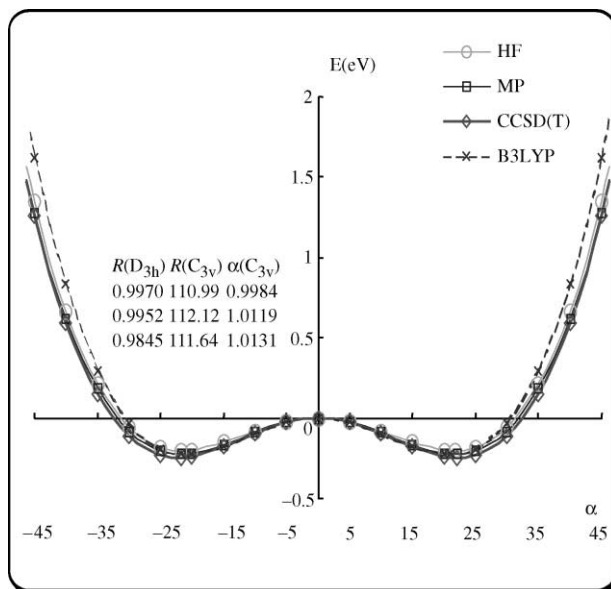


Fig. 1. The relaxed potential surface with respect to pyramidalization (out of planarity) angle of NH_3 with different methods (HF, MP2, CCSD(T), B3LYP) and 6-311++G(2d,2p). Note the close similarity of curves after conventional translation to the same origin of energy at planar reference.

highly similar patterns. This is because the correlation energy is kept almost constant during distortion, as the number and nature of electron pairs are conserved when no breaking of bonds occurs. This means that the essential mechanism of molecular shape is already contained in the HF level, indebting to start the systematic application of *ab initio* revisited PJT analysis from this point.

4.1. NH_3 as $(a'_1 + a''_2) \otimes A''_2$ structural prototype

In the case of ammonia the frontier orbitals are HOMO a''_2 , a p_z -type doubly occupied orbital and LUMO, a'_1 , an antibonding contribution of σ skeleton. Formally, the symmetry of the excited state is related to the HOMO–LUMO monoexcitation, $(a''_2)^2 \rightarrow (a''_2)(a'_1)$. However, the actual quantitative vibronic analysis shows that using split basis sets, the frontier sequence have an extremely low contribution to the vibronic curvature. In Table 1 the different $2u_{ni}V_{ni}$ terms into the vibronic curvature (5) of the A''_2 mode of ammonia are shown, observing that instead of LUMO (orbital no. 6) the excitations to other higher virtuals with a'_1 symmetry (e.g. no. 18 and no. 38) give major contributions. Aside to these major contributing virtual canonical MOs, the full total vibronic curvature is collected from many other small terms (up to 45.4% from its total). This points to the fact that the realistic description of PJT effect drastically differs from the *a priori* HOMO–LUMO picture, noting that, however, the symmetry role of frontier excitation is conserved. Such a conjecture illustrates the need of the full *ab initio* CPHF approach to vibronic terms. Without this stage, a MCSCF calculation would most probably exclude by prejudice the orbital no. 38, while this is presently revealed as important in distortion. One must note that because the terms in equation (5) do not have the strictly perturbational sense claimed in equation (4) and some of them can be positive in sign. However, the number of such terms is small and their absolute values are generally negligible.

In order to recover the conceptual simplicity of the $(a'_1 + a''_2) \otimes A''_2$ effect at planar ammonia we will call now the newly introduced vibronic orbitals. With this tool one may find indeed single pair of occupied (a''_2) -virtual(a'_1) functions that carry a 93.5% from the total of vibronic curvature. The remaining part is coming from vibronic orbitals spanning other symmetry channels, e.g. occupied(a'_1)-virtual(a''_2). The symmetry distribution of different ordered product representation to the total vibronic curvature is given in Table 2a and the total balance of vibronic and nonvibronic terms, in Table 2b.

The LUMO orbital of planar NH_3 molecule was proven to play no role in the tendency toward pyramidal structure. Its shape consists of an s -component on central nitrogen and nonbonding density areas located outside of hydrogen atoms triangle. As the HOMO is practically a pure p_z orbital on nitrogen one may conclude that the simple mixing of s and p functions on this atom, namely, the genuine hybridization picture is not the real force determining the distortion. The picture of

Table 2a. The negative curvature components, in terms of vibronic orbitals

Occ.	Virt.	(mdyne/Å)
a_2''	a_1'	− 0.7745
a_1'	a_2''	− 0.0616
e'	e''	− 0.0724

all the relevant orbital mixings *via* distortion is given with the help of corresponding vibronic orbitals (Fig. 2). To be distinguished from LUMO, this function carries density areas including the full σ skeleton as well as a part suggesting the *d*-like AO on nitrogen. Therefore, the mechanism of pyramidal distortion of molecule seems to be more complicated than the simple textbook hybridization idea, even though from symmetry point of view it retains the same picture. At the same time, the vibronic perspective is also formally in line with the simplistic electron pair repulsion picture, because the $(a_2'')^2 \rightarrow (a_2'')(a_1')$ singlet promotion looks like formation of an off-center lone pair.

4.2. The ClF_3 as $(a_1' + e') \otimes E'$ structural prototype

The distortion of ClF_3 from trigonal reference follows a degenerate E' coordinate. There are two E' sets in the vibration of molecule. When work with the proper normal coordinates that are eigenvectors of the Hessian, the apparently multimode problem, $(a_1' + e') \otimes 2E'$ is practically reduced to single mode $(a_1' + e') \otimes E'$. In this case, the formula (5) can be used separately for each degenerate component of the instability E' normal coordinate, the corresponding data being summarized in Tables 3 and 4.

To be distinguished from previous case, Table 3 shows that the HOMO–LUMO pair exerts visible predominance among the many other small orbital promotions. Correspondingly, the vibronic orbitals are similar to the frontier orbitals (Fig. 3). A nontrivial conclusion drawn from the weight of contributions in terms of vibronic

Table 2b. The total curvature and its non-vibronic (K_0) and vibronic parts (K_v)

	mdyne/Å
K_0	0.25202
K_v	− 0.8279
K	− 0.5759

Table 4a. The negative curvature components, in terms of vibronic orbitals

Occ.	Virt.	mdyne/Å
a'_1	e'	− 1.33394
e'	e'	− 0.5592
A''_2	e''	− 0.00877

case, with respect to different a, b the nuclear coordinates, the vibronic part takes the form:

$$K_v^{(ab)} = \sum_i^{\text{occ}} \sum_n^{\text{virt}} (\mathbf{u}_{ni}^{(a)} \cdot \mathbf{V}_{in}^{(b)} + \mathbf{u}_{ni}^{(b)} \cdot \mathbf{V}_{in}^{(a)}) \tag{10}$$

For ClF₃, using the coordinates denoted in Appendix A, the nonvibronic and vibronic components nondiagonalized Hessian are (in mdyne/Å):

$$K_0^{E'} = \begin{pmatrix} E_{\theta}^{\prime \text{ str}} & E_{\varepsilon}^{\prime \text{ str}} & E_{\theta}^{\prime \text{ sci}} & E_{\varepsilon}^{\prime \text{ sci}} \\ \begin{pmatrix} 10.023 & 0 & 5.542 & 0 \\ 0 & 10.023 & 0 & 5.542 \\ 5.542 & 0 & 3.894 & 0 \\ 0 & 5.542 & 0 & 3.894 \end{pmatrix} \end{pmatrix} \begin{vmatrix} E_{\theta}^{\prime \text{ str}} \\ E_{\varepsilon}^{\prime \text{ str}} \\ E_{\theta}^{\prime \text{ sci}} \\ E_{\varepsilon}^{\prime \text{ sci}} \end{vmatrix},$$
$$K_v^{E'} = \begin{pmatrix} E_{\theta}^{\prime \text{ str}} & E_{\varepsilon}^{\prime \text{ str}} & E_{\theta}^{\prime \text{ sci}} & E_{\varepsilon}^{\prime \text{ sci}} \\ \begin{pmatrix} -5.510 & 0 & -2.302 & 0 \\ 0 & -5.510 & 0 & -2.302 \\ -2.302 & 0 & -2.415 & 0 \\ 0 & -2.302 & 0 & -2.415 \end{pmatrix} \end{pmatrix} \begin{vmatrix} E_{\theta}^{\prime \text{ str}} \\ E_{\varepsilon}^{\prime \text{ str}} \\ E_{\theta}^{\prime \text{ sci}} \\ E_{\varepsilon}^{\prime \text{ sci}} \end{vmatrix}$$

Table 4b. The total curvature and its non-vibronic (K_0) and vibronic parts (K_v)

	mdyne/Å
K_0	0.932321
K_v	− 1.73706
K	− 0.80474

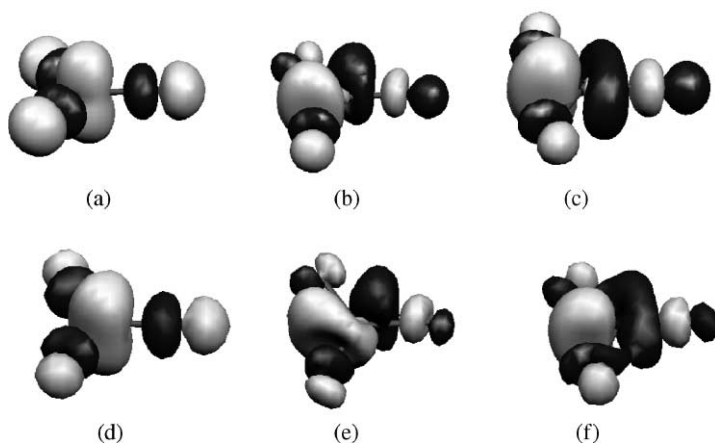


Fig. 3. The canonical frontier MOs and vibronic orbitals of ClF_3 molecule considered as $(a'_1 + e') \otimes E'$ effect in D_{3h} reference. (a) The a'_1 HOMO; (b) and (c) the degenerate e' LUMO; (d) the a'_1 occupied vibronic orbital, (e) and (f) the e' virtual vibronic orbitals. Note the closeness between vibronic orbitals and the frontier ones in this case.

The mass weighted normal coordinates diagonalizing this Hessian are

$$Q(E_a'^{\text{PJT}}) = 0.1921Q(E_\theta'^{\text{str}}) + 0.1432Q(E_\epsilon'^{\text{str}}) \\ + 0.6093Q(E_\theta'^{\text{sci}}) + 0.4542Q(E_\epsilon'^{\text{sci}})$$

$$Q(E_b'^{\text{PJT}}) = 0.1432Q(E_\theta'^{\text{str}}) - 0.1921Q(E_\epsilon'^{\text{str}}) \\ + 0.4542Q(E_\theta'^{\text{sci}}) - 0.6093Q(E_\epsilon'^{\text{sci}})$$

The 'str' and 'sci' superscripts in the E' coordinates correspond to separation into stretch (radial) and scissoring (tangential) movements, respectively. Due to degeneracy, this numerical form is not unique, arbitrary rotations of mixing between θ and ϵ components being admissible.

4.3. A case study for the mixed valence problem

In the following we present a sample of calculation intended as a preliminary illustration about the use of the discussed method in the problems of mixed valence. The chemical literature of mixed valent transition metal complexes is huge and the connection with the vibronic formalism is widely acknowledged [17]. However,

analytical *ab initio* approaches of vibronic parameters are lacking. While in chemical perspective, the delocalization of valence appear as rather sensational issue, leading to fractional oxidation states, the localization phenomena is those which properly correspond to the PJT effect. The delocalized system corresponds to higher symmetry reference.

Because the real systems involving transition metal systems involving few metal ions and big ligand environments are quite difficult as computational effort we will confine here to a very simplified academic case, taking a hypothetical dimer of Al(II). The chemical intuition guarantees that the Al(II) species is not stable, disproportionating into Al(I) and Al(III). The model was designed as the edge-shared tetrahedron corresponding to known pattern of gas-phase neutral Al_2Cl_6 molecules. This case is a simplified model for the heavy metal solid state congeners GaX_2 and InX_2 whose lattice consist of I and III oxidation states instead of the formal II oxidation state. Due to the pure hypothetical nature of this model, having no target in quantitative comparison of structural parameters as function of basis sets and method, we selected here the simple level of 3-21G/RHF. The computed intrinsic reaction coordinate (see Fig. 4) shows that the symmetrical Al(II) dimer evolves toward the Al(I) and Al(III) pair. From population analysis one identifies the Al(III) center as those going toward the isolation of a tetrahedral coordination, while Al(I) goes toward lower coordination number.

With respect to the D_{2h} group of delocalized system, the PJT coordinate has a B_{1u} representation. The vibronic orbital terms are spread over many small

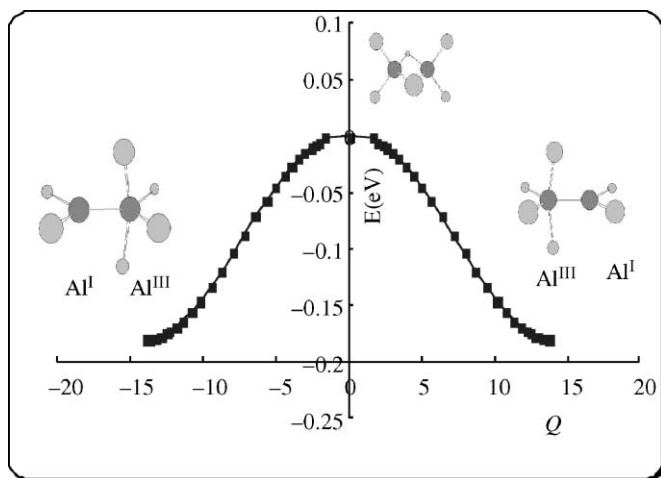


Fig. 4. The intrinsic reaction coordinate (in $[\text{length}][\text{mass}]^{-1/2}$ atomic units) for disproportionation $[\text{Al(II)}_2\text{Cl}_6]^{2-}$ to $[\text{Al(I)Al(III)Cl}_6]^{2-}$.

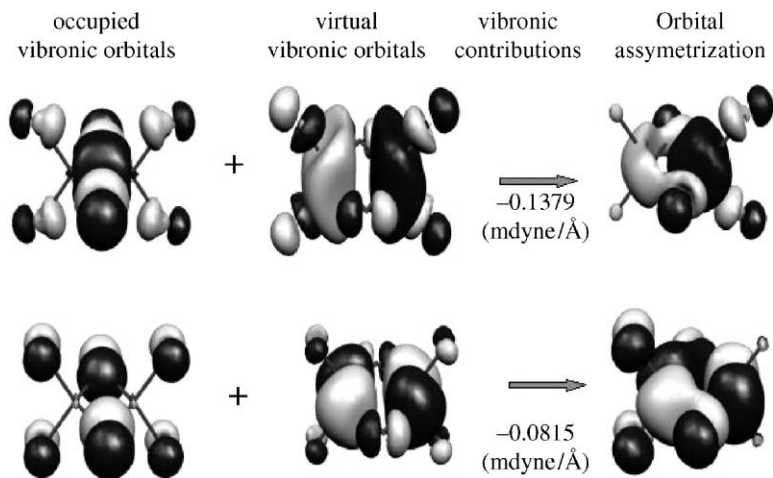


Fig. 5. The vibronic orbitals describing the main part of electron structure change when turning from delocalized to localized mixed valence in hypothetical molecule $[\text{Al}_2\text{Cl}_6]^{2-}$.

percentage of the metal AOs) and appearance of the Al(I) partner with asymmetric electron cloud (lone pair-type). A similar effect is seen in the second important couple of vibronic orbitals in the subsystem of π bonding, with a lower weight in the energy effects.

5. CONCLUSION

Approaching stereochemistry, one may distinguish two aspects: the technical part, concerning salient quantum calculation of the optimal molecular geometries and the heuristic *corpus* enabling qualitative explanation of experimental or computed structures. Even in the computer era the chemists are tempted to use simple language like hybridization, Nyholm–Gillespie rules or Walsh orbital correlation diagrams. These are early achievements of pre-computational quantum chemistry which may deserve re-evaluation from the perspective of modern quantum chemistry, for instance, as we attempted recently in that concern the hybridization paradigm [18].

Heuristically speaking, the vibronic modeling can be regarded as an unified way of Walsh diagram pictures (combining factors which support orbital transcription) and Nyholm–Gillespie factors (explicitly considering the interelectron relaxation effects) by means of mixing of states procedure that somehow resembles hybridization ideas.

We confined here to the RHF level, adaptation to multireference or DFT cases being currently in the progress. The preliminary confining to the RHF level was

a necessary step in the attempt to apply a complete revisiting of vibronic methodology in a formally correct and analytical relation to the practice of *ab initio* calculations.

Moreover, there are further heuristic reasons for devoting a special attention to monodeterminant scheme results from the combination of the following strong theorems:

- (i) a formally correct monoelectronic picture [19] of the electronic structure can be achieved either by Dyson orbitals or following Kohn–Sham theorem;
- (ii) a combination of monoelectronic excitations can be rigorously formulated as a single determinant [20];
- (iii) the Wigner $2n + 1$ theorem [21] states the need of first order perturbed wave function to account for second order of energy, having as a consequence the use of orbital monoexcited states for the sake of analytical Hessian evaluation.

The directions presented and concluded here are the guide to our further investigations and applications in the frame of vibronic paradigm targeting the future approach of multireference methods, including the JT problems beside the PJT ones.

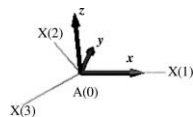
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APPENDIX A

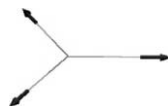
For the sake of completeness we present here technical details about the use of normal modes. The normal modes are directly obtained at frequency calculation in *ab initio* codes, usually in a form that diagonalize the Cartesian form of the Hessian matrix (k_{ij}) , yielding the wave number λ_α of a given vibration, $\alpha : \lambda_\alpha = \sum_{i,j} \tau_{\alpha i} \tau_{\alpha j} k_{ij}$. In this form, the $q_\alpha = \{\tau_{\alpha i}\}_{i=1,3N}$ vectors are not normalized, obeying instead the mass–weight conditions, $\sum_i \tau_{\alpha i} m_i = 0$ and $\sum_i (\tau_{\alpha i})^2 m_i = 1$, the square of normalization factor corresponding to the reciprocal effective mass of the vibration mode: $(\mu_\alpha)^{-1} = \sum_i (\tau_{\alpha i})^2$. The total curvature in vibronic analysis is usually expressed in force/distance units (e.g. mdyne/Å). In order to get the meaning of the total curvature, the diagonalized Hessian components should be multiplied with effective mass of the modes: $K_\alpha = \mu_\alpha \lambda_\alpha$. In this form, corresponding to $Q_\alpha = \sqrt{\mu_\alpha} q_\alpha$ coordinates, are given in the table below the total curvature quantities K and their discussed components.

The symmetry components of normal coordinates of AX_3
in D_{3h} point group



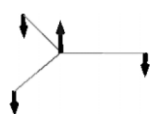
$$q(A'_1) = \frac{1}{6\sqrt{m}}(2\sqrt{3}x_1 - \sqrt{3}x_2 + 3y_2 - \sqrt{3}x_3 - 3y_3)$$

breathing mode



$$q(A''_2) = \frac{1}{\sqrt{3(M+3m)}}\left(3\sqrt{\frac{m}{M}}z_0 - \sqrt{\frac{M}{m}}(z_1 + z_2 + z_3)\right)$$

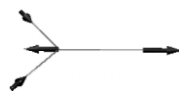
pyramidalization (umbrella mode)



$$q(E'^{\text{str}}_\theta) = \frac{1}{2\sqrt{3(2M+3m)}}$$

$$\times \left(6\sqrt{\frac{m}{M}}x_0 - \sqrt{\frac{M}{m}}(4x_1 + x_2 - \sqrt{3}y_2 + x_3 + \sqrt{3}y_3)\right)$$

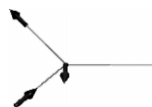
asymmetric stretch



$$q(E'^{\text{str}}_\epsilon) = \frac{1}{2\sqrt{2M+3m}}$$

$$\times \left(2\sqrt{3}\sqrt{\frac{m}{M}}y_0 + \sqrt{\frac{M}{m}}(x_2 - \sqrt{3}y_2 - x_3 - \sqrt{3}y_3)\right)$$

asymmetric stretch



$$q(E'^{\text{sci}}_\theta) = \frac{1}{2\sqrt{2M+3m}}$$

$$\times \left(2\sqrt{3}\sqrt{\frac{m}{M}}x_0 - \sqrt{\frac{M}{m}}(\sqrt{3}x_2 + y_2 + \sqrt{3}x_3 - y_3)\right)$$

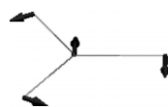
scissoring mode



$$q(E'^{\text{sci}}_\epsilon) = \frac{1}{2\sqrt{3(2M+3m)}}$$

$$\times \left(6\sqrt{\frac{m}{M}}y_0 - \sqrt{\frac{M}{m}}(4y_1 + \sqrt{3}x_2 + y_2 - \sqrt{3}x_3 + y_3)\right)$$

scissoring mode



REFERENCES

- [1] I. B. Bersuker, *Chem. Rev.*, 2001, **101**, 1067.
- [2] (a) I. B. Bersuker, *New. J. Chem.*, 1980, **4**, 139; (b) I. B. Bersuker, N. N. Gorinchoi and V. Z. Polinger, *Theor. Chim. Acta.*, 1984, **66**, 161; (c) I. B. Bersuker, N. N. Gorinchoi and V. Z. Polinger, *J. Mol. Struct. (Theochem)*, 1992, **270**, 369; (d) N. N. Gorinchoi, I. B. Bersuker and V. Z. Polinger, *New. J. Chem.*, 1993, **17**, 125.
- [3] (a) M. Doscher, H. Köppel and P. G. Szalay, *J. Chem. Phys.*, 2002, **117**, 2645; (b) T. A. Barckholtz and T. A. Miller, *J. Phys. Chem. A*, 1999, **103**, 2321; (c) R. Bruyndonckx, C. Daul, P. T. Manoharan and E. Deiss, *Inorg. Chem.*, 1997, **36**, 4251.
- [4] L. F. Chibotaru and F. Cimpoesu, *Int. J. Quantum Chem.*, 1997, **65**, 37.
- [5] (a) N. C. Mösch-Zanetti, H. W. Roesky, W. Zheng, A. Stasch, M. Hewitt, F. Cimpoesu, T. R. Schneider and J. Prust, *Angew. Chem. Int. Ed.*, 2000, **39**, 3099; (b) N. Gorinchoi, F. Cimpoesu and I. B. Bersuker, *J. Mol. Struct. (Theochem)*, 2000, **530**, 281.
- [6] (a) K. Yagi, T. Taketsugu, K. Hirao and M. S. Gordon, *J. Chem. Phys.*, 2000, **113**, 1005; (b) T. Taketsugu, T. Yanai, K. Hirao and M. S. Gordon, *J. Mol. Struct. (Theochem)*, 1998, **451**, 163.
- [7] P. Pulay, Analytical derivative methods in quantum chemistry, in *Ab Initio Methods in Quantum Chemistry*, (ed. K. P. Lawley), Wiley, New York, 1987.
- [8] I. B. Bersuker, *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry*, Plenum Press, New York, 1984.
- [9] Y. Yamaguchi, Y. Osamura, J. D. Goddard and H. Scafeffer, III, *A New Dimension to Quantum Chemistry: Analytic Derivative Methods in Ab Initio Molecular Electronic Structure Theory*, Oxford University Press, Oxford, 1994.
- [10] H. Nakano, K. Hirao and M. S. Gordon, *J. Chem. Phys.*, 1998, **108**, 5660.
- [11] W. Kutzelnigg, *J. Mol. Struct. (Theochem)*, 1989, **61**, 11.
- [12] H. Sekino, T. Yanai and K. Hirao, *Nonlinear Optics*, 2000, **26**, 25.
- [13] K. Hirao, *Recent Advances in Multireference Methods*, (ed. K. Hirao), World Scientific, Singapore, 2001.
- [14] E. Dalggaard and P. Jørgensen, *J. Chem. Phys.*, 1978, **69**, 3833.
- [15] (a) M. Atanasov and D. Reinen, *J. Am. Chem. Soc.*, 2002, **124**, 6693; (b) M. Atanasov and D. Reinen, *J. Phys. Chem. A*, 2001, **105**, 5450.
- [16] The calculations were carried out performing a modification in the GAMESS package: M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su and T. L. Windus, *J. Comput. Chem.*, 1993, **14**, 1347.
- [17] P. Schatz, in *Inorganic Electronic Structure and Spectroscopy*, (eds E. I. Solomon and A. B. P. Lever), Wiley, New York, 1999, Vol. 2.
- [18] M. Ferbinteanu, H. W. Roesky, F. Cimpoesu, M. Atanasov, S. Köpke and R. Herbst-Irmer, *Inorg. Chem.*, 2001, **40**, 4947.
- [19] J. V. Ortiz, *Adv. Quantum Chem.*, 1999, **35**, 33.
- [20] E. S. Kryachko, *Int. J. Quantum Chem.*, 1995, **56**, 3.
- [21] S. T. Epstein, *Chem. Phys. Lett.*, 1980, **70**, 311.

Vibronic Interactions in High Nuclearity Clusters

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Abstract

We discuss here two examples of vibronic effects in polynuclear highly symmetrical transition metal clusters. The existence of degenerate and quasi-degenerate molecular orbitals in their energy spectra results in the Jahn–Teller effect or in the vibronic mixing of different electronic states. We show that both quantum-chemical methods and model approaches can provide valuable information about these vibronic effects. In the case of the hexanuclear rhenium tri-anion, the Jahn–Teller effect is responsible for the experimentally observed tetragonal distortion of the cluster. The vibronic model of mixed-valence compounds allows to explain the nature of a transient in the photo-catalytic reaction of the decatungstate cluster.

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1. INTRODUCTION

During last decades the theory of vibronic interactions became an important tool in rationalizing of numerous physical and chemical properties of multi-atomic systems [1,2]. Initially limited by the particular case of the Jahn–Teller effect inherent to a degenerate electronic state, the description of more complex systems asked for the analysis of vibronic effects within energy spectra containing several degenerate and/or quasi-degenerate electronic states. In application to transition metal complexes, the theory of vibronic interactions during a long period considered mainly mononuclear complexes in which degenerate or quasi-degenerate states were provided by d-orbitals of the transition metal. The octahedral hexaqua copper(II) complex during many years served as the textbook example of a Jahn–Teller effect system. For mononuclear complexes, the crystal field approximation can be used in

many cases to describe the electronic energy spectrum. The introduction by I. B. Bersuker of the notion of orbital vibronic constants [3] became an important step in the MO formulation of the theory of vibronic interactions.

In application to polynuclear transition metal complexes, the theory of vibronic interactions has been mainly focused on systems composed from individual Jahn–Teller centers. The most recent widely discussed in the literature example is given by the highly anisotropic magnetic dodecanuclear manganese clusters [4]. These single molecular magnets contain eight Mn(III) Jahn–Teller centers. However, in some cases vibronic effects can be considered for molecular orbitals covering all or a part of transition metal centers in the cluster. Such description has been widely used for polynuclear mixed-valence systems as well as for some other complexes. Such multi-center vibronic effects become especially important for clusters containing 4d- and 5d-transition metals. A more diffuse character of d-orbitals results in more strong vibronic interactions for cluster molecular orbitals.

In the present review we will discuss the role of vibronic effects for highly symmetric polynuclear clusters. Although the choice of systems considered in the review is rather arbitrary and is due to the activity of our group, we hope that they can illustrate the importance of multi-center vibronic interactions in the analysis of physical and chemical properties of such systems. We will show that carefully used modern DFT methods present an efficient tool for quantum-chemical studies of polynuclear systems. However, due to high symmetry of many clusters some important qualitative conclusions can be drawn up from so called phenomenological models. They use simplified descriptions of cluster energy spectra and nuclear vibrations, but allow performing a more thorough analysis of vibronic problems.

2. HEXANUCLEAR RHENIUM CHALCOHALIDE CLUSTERS

The hexanuclear Re (III) chalcocohalide clusters of general formulae $\{[\text{Re}_6\text{Q}_{4+n}\text{X}_{4-n}]\text{X}_6\}^{n-}$, where Q = S, Se, Te, and X = Cl, Br have attracted much attention during recent years [5]. They constitute a series of anions formed by an octahedron of rhenium included in a cube of eight chalcogen and/or halogen μ_3 -ligands. The coordination of rhenium atoms is completed by six halogen μ_1 -ligands in apical position. Changing the chalcogen/halogen ratio, the total charge of the anions could be varied from -1 to -4 , without noticeable influence on their shape or volume. These clusters provide a rare set of isosteric anions, which allows the modulation of the properties of hybrid inorganic–organic molecular materials. The charge of anions defines the filling of electronic bands whereas their structure is governed by the packing of organic radicals cations. The inorganic anions can contribute to the magnetic or optical properties of solids. The tetra-anionic cluster, $[\text{Re}_6\text{S}_8\text{Cl}_6]^{4-}$, (Fig. 1) occupies a special place in the series. It is distinguished for its solubility, optical properties, chemical reactivity and, especially, for its ability to be easily oxidized. The corresponding paramagnetic cluster $[\text{Re}_6\text{S}_8\text{Cl}_6]^{3-}$ can be isolated and has been found luminescent [6]. The cluster exhibits a distortion from octahedral

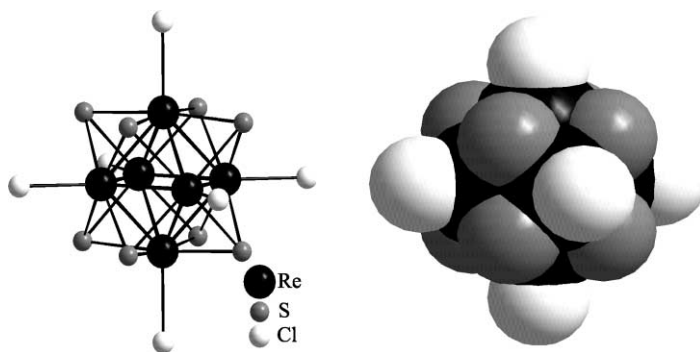


Fig. 1. Ball-and-stick and ball representations of the octahedral rhenium cluster $[\text{Re}_6\text{S}_8\text{Cl}_6]^{4-}$. All sulfur atoms are ‘inner’ ligands and all apical positions are occupied by chlorine atoms.

symmetry, which has not been found in other clusters of such type. EPR and X-Ray diffraction data have shown that, between 100 and 200 K, a distortion of the oxidized species, $[\text{Re}_6\text{S}_8\text{Cl}_6]^{3-}$ occurs in which the cluster is compressed along C_4 axis (Fig. 2). It has been found recently that the similar and isoelectronic cluster $[\text{Re}_6\text{S}_8(\text{CN})_6]^{3-}$ also presents a distortion from octahedral geometry from room temperature, but in this case the cluster is elongated along the C_4 axis [7].

It seems natural to suppose that the tetragonal distortion of the tri-anion results from the Jahn–Teller effect. In order to study the problem more thoroughly we undertook recently the DFT calculations of this cluster as well as of several other hexanuclear rhenium chalcogenide clusters. The technical details of these calculations can be found in the original publication [8]. Here we only want to note that the introduction of relativistic corrections for Re atoms is crucial for the correct reproduction of the geometry of clusters. In our calculations, this was done by the zero order regular approximation (ZORA) Hamiltonian [9] within ADF 2000.02 package [10].

Calculations of the tetra-anionic cluster $[\text{Re}_6\text{S}_8\text{Cl}_6]^{4-}$ have been done in the symmetry group O_h . All attempts to lower the symmetry converged again to the same geometry. The structural parameters obtained as a result of the optimization are in good agreement with the structural data. We found 3.684 Å for the opposite Re–Re distances, 2.436 and 2.486 Å for Re–S and Re–Cl bonds, respectively.

The average experimental values are equal to 3.681, 2.404, and 2.451 Å. The rhenium–rhenium distances are well reproduced and the rhenium–ligand distances are slightly longer than the experimental ones (the difference does not exceed 1.5%). The experimental data show that the structure of the rhenium core remains unchanged for all closed shell clusters. At the same time, it has been reported that the Re–Cl distances strongly depend on the nature of the counter-cation in the salt. This shows that the rhenium–apical ligand bonds are very sensitive to the effects of environment. Our calculations in gas phase do not take into account the crystal

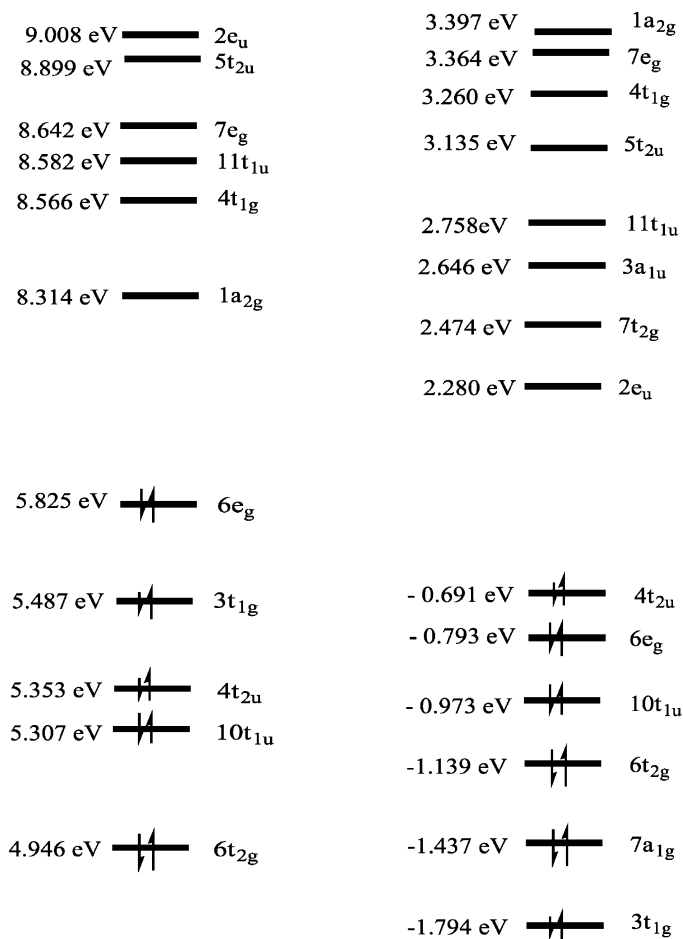


Fig. 2. Molecular orbitals scheme for $[\text{Re}_6\text{S}_8\text{Cl}_6]^{4-}$ (left) and $[\text{W}_6\text{Cl}_{14}]^{2-}$ (right).

effects. The energy levels diagram is shown in Fig. 3. The important feature of the electronic structure is the doubly degenerate HOMO (labeled $6e_g$), well separated (2.4 eV) from the LUMO. In consequence, the Jahn–Teller effect can be expected in oxidized species. The important gap is responsible for the absence of a strong pseudo-Jahn–Teller effect, which could result in a lowering of the symmetry. The frontier orbitals are mostly centered on the metal atoms (in particular HOMO – 1, HOMO, LUMO, LUMO + 1). The electronic structure of $[\text{Re}_6\text{S}_8\text{Cl}_6]^{4-}$ is very similar to the one calculated for the isoelectronic tungsten cluster $[\text{W}_6\text{Cl}_{14}]^{2-}$, from the point of view of the nature and of the symmetry of the orbitals. However, the order of orbitals is slightly changed. The main difference comes from the inversion between HOMO and HOMO – 2, resulting in the degenerate t_{2u} HOMO. This

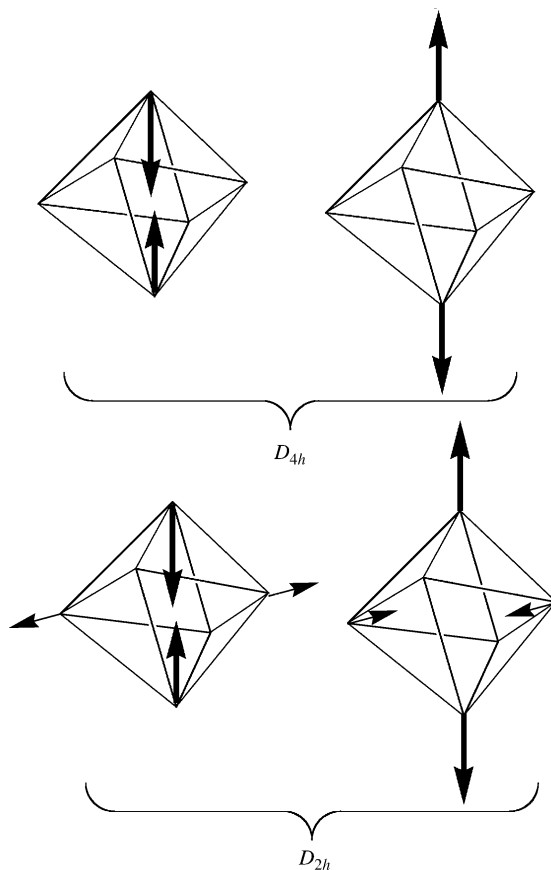


Fig. 3. Schematic representation of the D_{4h} and D_{2h} distortions of the rhenium octahedral cores.

inversion is probably due to the electronegativity difference between tungsten and rhenium from one part, and between sulfur and chlorine μ_3 -ligands from another part.

As expected, the spin-unrestricted calculations of the oxidized $[\text{Re}_6\text{S}_8\text{Cl}_6]^{3-}$ cluster in the O_h point symmetry group led to the partly filled e_g HOMO suggesting the possibility of the Jahn–Teller effect in the oxidized species. We did not want to privilege *a priori* a particular type of Jahn–Teller distortions and studied all possibilities existing for an octahedral system in the space of tetragonal normal coordinates. As it has been shown on the basis of general group-theoretical considerations [1] the adiabatic surface of a cubic system in the space of e-type normal coordinates Q_e and Q_θ can possess either of the following three types of minima: (a) three equivalent minima corresponding to the elongation to D_{4h}

symmetry; (b) three equivalent minima corresponding to the compression to D_{4h} symmetry; (c) six equivalent minima corresponding to the distortion to D_{2h} symmetry. The last possibility is quite rare for vibronic systems. It was predicted theoretically for some hexafluoride complexes with the electronic configuration d^0 [11]. All three types of distorted structures (Fig. 3) were explored by imposing a particular starting distortion in the geometry optimization. In all the cases, a stabilization relatively the high-symmetrical O_h structure was found. Surprisingly, in all the three cases, our calculations converged to a minima of different energy that are ordered as $E(D_{4h}^{com}) < E(D_{4h}^{el}) < E(D_{2h})$. The minima of lowest energy correspond to tetragonally compressed octahedron. We can note that this type distortion was observed experimentally in $(n\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_8\text{Cl}_6]$ at 100 K. [7] The possibility to achieve the convergence of DFT calculations in different contradicting geometries is due to the mono-determinant nature of DFT methods. The stabilization of the distorted structure can be achieved through the stabilization of each orbital (in our case, these are $13a_{1g}$ and $6b_{1g}$) belonging to the degenerate manifold in highly symmetrical geometry. This effect was illustrated in the previous DFT calculations of the VCl_4 complex. The difference between the energy of the cluster in O_h and D_{4h} symmetry allows to estimate the Jahn–Teller stabilization energy [1,2], which is of the order of 0.06 eV. The second order Jahn–Teller coupling, which is responsible for the wrapping of the Mexican hat adiabatic surface, can be estimated from the difference between two D_{4h} configurations. This energy is found to be about 0.005 eV.

A Jahn–Teller distortion could also be expected for the $[\text{W}_6\text{Cl}_{14}]^{1-}$ cluster with the degenerate noncompletely filled t_{2u} HOMO. Indeed, a tetragonal distortion has been proposed for the interpretation of the EPR data in frozen solution [12]. The Jahn–Teller effect in a cubic system characterized by a triply-degenerate T-term can result in distortions either along E_g , or along T_{2g} normal coordinate [1]. Our calculations of the oxidized $[\text{W}_6\text{Cl}_{14}]^{1-}$ cluster resulted in a local minimum corresponding to the symmetry to D_{4h} group. We can conclude that for the tungsten cluster we deal with the $T \otimes e$ -Jahn–Teller effect. However, the energy of the D_{4h} minimum was found to be 0.016 eV higher than the energy of the structure optimized under the constraints of the O_h symmetry group. The reason of this contradiction lies in the very nature of the DFT method. The energy given by the exchange-correlation functionals depends on the distribution of electronic density between states belonging to the degenerate level. The method proposed by Daul *et al.* [13] seems to be a suitable strategy to tackle this problem. Following this procedure, we recalculated the energy of the O_h structure occupying selectively the degenerate t_{2u} orbitals. We supposed that four electrons occupy those orbital states, which are further stabilized in D_{4h} structure, and the destabilized orbital state carries a remaining electron. This new calculation led to the stabilization of the tetragonally distorted structure by 0.001 eV. This value gives a measure of the Jahn–Teller stabilization energy for the tungsten complex. The similar calculation procedure can be performed for the rhenium tri-anion. However, it practically does not modify the value of the Jahn–Teller energy given above. One can conclude that the Jahn–Teller effect is much weaker for the tungsten cluster. This difference results from the

different nature of the HOMOs for the two clusters (e_g and t_{2u}). In fact, as it was indicated by Lin and Williams [14], the t_{2u} orbitals mix significantly with the antibonding combinations derived from the $d(\pi)$ basis sets. The more pronounced bonding nature of the e_g orbital confers upon it more influence over the molecular shape.

Concluding this paragraph we can note that DFT methods can give important qualitative and quantitative results for vibronic effects in polynuclear clusters. However, as for mononuclear complexes the DFT methods can be used with a special care for Jahn–Teller systems.

3. DELOCALIZATION OF EXCITATIONS IN DECATUNGSTATE CLUSTER

Polyoxometalates constitute a large group of polynuclear metal–oxygen anionic clusters [15,16]. Their interesting and potentially valuable physical and chemical properties found impact in several disciplines such as catalysis, material science, and medicine. Polyoxoanions are usually formed by such metals as tungsten, molybdenum, and vanadium in their high-valent states. Their structures present rather symmetric combinations of metal–oxygen octahedra. However, metal ions forming polyoxoanions usually have d^0 electronic configuration. As a result, polyoxoanions have closed-shell electronic configuration and no Jahn–Teller effect can be expected. Even more, the HOMO in polyoxoanions are well separated from LUMOs, so the vibronic pseudo-Jahn–Teller-type mixing is not probable. One possibility of the manifestation of vibronic effects in polyoxoanions appears in hetero- or substituted polyanions, in which hetero- or substituted metal ion can be vibronically active [17]. Another possibility is linked with reduced (often called ‘blue’ due to their color) or electronically excited polyoxoanions, when added or excited electrons occupy a degenerate or quasi-degenerate molecular orbitals. The resulted electronic distribution is then governed by vibronic interactions. Although the electronic structure of the reduced polyoxometalates can be studied by DFT methods [18], the phenomenological (or model Hamiltonian) methods, taking into account vibronic interactions, can also be used for the analysis of electronic distributions [19].

The decatungstate anion $[W_{10}O_{32}]^{4-}$ is an efficient catalyst in the reaction of photooxidation of alkanes [20]. The polyoxoanion is made of two compact W_5O_{14} moieties linked by four corner-sharing oxygen atoms (Fig. 4) [21]. Each W_5O_{14} fragment consists of five edge-sharing tungsten–oxygen octahedra. Therefore, the total symmetry of the POA is D_{4h} . Eight equatorial and two terminal sites can be distinguished for tungsten atoms. The formal oxidation state of tungsten is +6. Singly and doubly reduced forms of the decatungstate anion were also isolated and characterized [22]. Laser flash photolysis studies [23] suggest that the first step of the photocatalytic reaction is the ligand–metal charge-transfer ($O\ 2p \rightarrow W\ 5d$) under laser photoexcitation with $\lambda = 355\text{ nm}$. The excited state relaxes for $t < 30\text{ ps}$

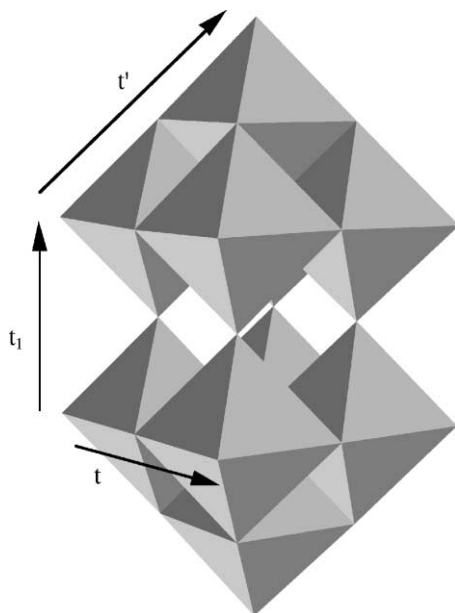


Fig. 4. Polyhedral model of $[W_{10}O_{32}]$. The arrows show possible types of electron transfer with corresponding parameters.

to a long-lived intermediate form where decay time was estimated to 5–15 ns. This intermediate (called X) reacts with all components of the photocatalytic system. It was noted that although the species X are different from singly reduced decatungstate their valence electronic distributions are very similar. In both cases, a valence electron occupies a predominantly tungsten-based molecular orbital. The similarity of electron distributions in excited and singly reduced states is not surprising. In both cases, an electron is added to a LUMO of the initially nonreduced cluster. This analogy was already used in the study of the photoexcited state of $[Ru(bpy)_3]^{2+}$ [24] where the mathematical problem is completely isomorphic to that of the electron distribution in a mixed-valence tri-nuclear cluster. [25] In both cases, we deal with the localization–delocalization problem in a system possessing a 3rd order symmetry axis. The distribution of excess electron within the cluster framework is governed by the competition of two interactions: the transfer interaction, which is responsible for electron's delocalization and the electron-vibrational interaction, which leads to electron's trapping [26]. It was already shown that in high-symmetrical tri-nuclear and four-nuclear mixed-valence clusters these two interactions can lead to coexistence of two electronic distributions, namely localized at on site and delocalized over the whole cluster [25,26]. One can suppose that optically excited state and transient X present two states with different types of electron delocalization.

The method we use [27] is an extension of theoretical models used earlier to describe electronic distribution in bi-, tri-, and four-nuclear mixed-valence clusters [25,26]. Let us consider a system of ten equivalent subunits arranged in a cluster (Fig. 4) described by the symmetry group D_{4h} . In the absence of an excess electron, each subunit has a closed electronic shell, as it is in the case of tungsten ions in the oxidation state +6. We suppose that at the i th center the extra electron can occupy a nondegenerate localized orbital φ_i . We do not specify the origin of the extra electron populating the LUMO. It may be the case either of the reduced cluster, or photoexcited cluster. In the latter case, we neglect the influence of a hole formed in the ligand electronic shell. The energies of all localized orbitals are equal and we assume that these orbitals are orthogonal. The localized orbitals interact through the resonance interaction, which can lead to the delocalization of the excess electron. All previous treatments of high-symmetry mixed-valence clusters of low nuclearity relied on one single parameter for electron transfer. If we focus only on nearest neighbor interactions, our model must take into account three distinct parameters. First t' describes the interaction between a terminal site and four nearest equatorial sites, whereas t is responsible for the electron transfer within each quartet of equatorial sites. The third parameter t_1 links the two W_5O_{14} moieties (Fig. 4). We will discuss the relative values of electron transfer parameters in the following paragraph. Under these assumptions the electronic Hamiltonian in the basis of localized states can be written as

$$H_e = \sum_{ij} t_{ij} a_i^\dagger a_j \quad (1)$$

where $a_i^\dagger$ and a_j are the creation and annihilation operators, respectively. The diagonalization of the Hamiltonian (1) gives the electronic energies

$$\begin{aligned} \varepsilon_{E_g} &= -2t_1, & \varepsilon_{E_u} &= 0, & \varepsilon_{B_{1g}} &= -2t, & \varepsilon_{B_{2u}} &= -2(t - t_1), \\ \varepsilon_{A_{2u}}^{1,2} &= t \pm \sqrt{4(t')^2 + (t)^2}, & \varepsilon_{A_{1g}}^{1,2} &= t + t_1 \pm \sqrt{4(t')^2 + (t + t_1)^2} \end{aligned} \quad (2)$$

Since the ‘excess’ electron is localized on nondegenerate orbital the excess electron vibronic interaction is limited to the totally symmetric distortions of the first coordination sphere. This interaction reflects the difference of metal–ligand distances in different oxidation states. The matrix of the electron-vibrational interaction is diagonal on the basis of localized states with the matrix elements

$$(H_{ev})_{ii} = \lambda q_i \quad (3)$$

where λ is the constant of the electron-vibration interaction with the local totally symmetric vibrations q_i ($i = 1-10$). In order to calculate the adiabatic potential of the model cluster we must diagonalize the full electronic Hamiltonian

$$H = H_e + H_{ev} \quad (4)$$

and to add the potential energy of nuclear distortions

$$H_v = \frac{k}{2} \sum_i q_i^2 \quad (5)$$

where k is the force constant. We suppose in equation (5) that there is no elastic interaction between localized distortions. It is convenient to pass to the normal coordinates of the cluster, which are given by the linear combinations of local coordinates. These symmetric combinations have the same form as the electronic eigenvectors composed from local electronic states and leading to the energies (2). Thus, we have a rather complicated vibronic problem for eight electronic levels interacting with eight normal vibrations. The diagonalization of the electronic Hamiltonian allows us to find the adiabatic potential in the space of normal coordinates of the cluster for different values of model parameters. The analysis of the ground state adiabatic potential gives its extremal points and corresponding equilibrium charge distributions.

The perturbational analysis of the adiabatic surface near the totally symmetric zero point [27] shows that for the realistic values of the electron transfer parameters one of two A_{2u} normal vibrations is much softer than all other vibrations. We can expect that this mode together with two A_{1g} modes play the most important role in the structural distortions and charge redistribution in the cluster.

We performed a numerical search of the ground state potential surface minima in the space of all coordinates for different sets of parameters λ^2/kt , t'/t , t_1/t and examined the nature of the electronic distribution in these minima. For small λ^2/kt value the adiabatic potential exhibits a single minimum with all q_T coordinates equal to zero, except two $q_{A_{1g}}$ vibrations. The electronic density is redistributed between two groups of sites (terminal and equatorial), but within each group it is homogeneously delocalized. When the weakest criterion of the instability of the totally symmetric configuration is fulfilled, we obtain two minima symmetrically displaced in the subspace of coordinates $q_{A_{2u}}$. In each minimum, the excess electron is preferentially distributed over equatorial sites of one W_5O_{14} subunit, upper, or lower (Fig. 4). With further increase in λ^2/kt parameter the structure of the adiabatic potential does not change up to a certain limit value where different type of minima appears. They reflect preferential electron localization at one site and the number of minima is equal to the number of metal sites. The equivalent minima of the adiabatic potential can be transformed one into other by the operations of the total symmetry group D_{4h} . However, the appearance of new minima does not coincide with removal of old ones. In some interval of parameters, the two types of minima coexist, corresponding to the coexistence of localized and partly delocalized electronic distributions. This is a qualitatively new result in the theory of polynuclear mixed-valence compounds, which is due to more complicated topology of decatungstate cluster. Till now only the cases of coexistence of site-localized and homogeneously delocalized electronic distributions have been found. Finally, at very strong vibronic interaction the adiabatic potential has only minima with electron localization at each site. As one may expect, for given values of λ and t , the transition from a completely

delocalized electronic distribution to that delocalized over half of the cluster is mainly governed by the transfer parameter between two W_5O_{14} subunits. By contrast, the transition to the phase with coexisting minima strongly depends on the value of t' parameter which is responsible for redistribution of electronic density between terminal and equatorial sites.

The coexistence of the different types of minima can be a key to understand the nature of the transient X in the photocatalytic reaction. We can suppose that by initial photoexcitation the electron is transferred to a one-site localized electronic state. After some time the electron can relax to another minimum corresponding to more delocalized electronic state which may be considered as the transient X. Although the energy of 'delocalized' minima is slightly higher, this transition can take place at room temperature. A more delocalized electronic distribution can increase the probability for decatungstate to go into reaction with a substrate.

4. CONCLUSIONS

Polynuclear clusters fill the gap between mononuclear and extended solid transition metal vibronic systems. The applications of the theory of vibronic interaction allow to describe physical and chemical properties of these systems, sometimes directly linked to their application. The Jahn–Teller distortion found for the rhenium clusters defines the architecture of hybrid inorganic–organic materials and, as a result, their electric and magnetic properties. The application of the vibronic theory to the decatungstate cluster elucidates the details of its reactivity in the photocatalytic reaction. The modern DFT methods give a key to the calculations of key parameters of the vibronic theory. In future, we will assist at the combination of these methods with phenomenological approaches leading to the description of vibronic effects in physical and chemical properties of polynuclear clusters *from first principles*.

ACKNOWLEDGEMENTS

Although the work presented in this paper was done in France, my knowledge and my vision of vibronic problems was formed in the Laboratory of Quantum Chemistry (Institute of Chemistry, Kishinev) led by Professor I. B. Bersuker. I want to acknowledge the contribution of this laboratory in the development of the vibronic theory and to dedicate this paper to 75th anniversary of Professor I. B. Bersuker. I want to thank my colleagues H. Duclausaud-Jamet and A. Deluzet for their contributions to the work.

REFERENCES

- [1] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, New York, 1983.

- [2] I. B. Bersuker, *Chem. Rev.*, 2001, **101** (4), 1067.
- [3] I. B. Bersuker, *Kinet. Katal.* (in Russian), 1977, **18**, 1268; I. B. Bersuker, *Chem. Phys.*, 1978, **31**, 85.
- [4] Z. Sun, D. Ruiz, N. R. Dilley, M. Soler, J. Ribas, K. Folting, M. B. Maple, G. Christou and D. N. Hendrickson, *Chem. Commun.*, 1999, 1973; S. M. J. Aubin, Z. Sun, H. J. Eppley, E. M. Rumberger, I. A. Guzei, K. Folting, P. K. Gantzel, A. L. Rheingold, G. Christou and D. N. Hendrickson, *Inorg. Chem.*, 2001, **40**, 2127.
- [5] J.-C. P. Gabriel, K. Boubekeur, S. Uriel and P. Batail, *Chem. Rev.*, 2001, **101**, 2307.
- [6] C. G. Guilbaud, A. Deluzet, B. Domercq, P. Molinié, C. Coulon, K. Boubekeur and P. Batail, *Chem. Commun.*, 1999, 1867.
- [7] S. Baudron, A. Deluzet, K. Boubekeur and P. Batail, *Chem. Commun.*, 2002, 2124.
- [8] A. Deluzet, H. Duclusaud, P. Sautet and S. A. Borshch, *Inorg. Chem.*, 2002, **41**, 2537.
- [9] E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1993, **99**, 4597; E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1994, **101**, 9783; E. van Lenthe, J. G. Snijders and E. J. Baerends, *J. Chem. Phys.*, 1996, **105**, 6505; E. van Lenthe, A. E. Ehlers and E. J. Baerends, *J. Chem. Phys.*, 1999, **110**, 8943.
- [10] E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.*, 1973, **2**, 41; L. Versluis and T. J. Ziegler, *J. Chem. Phys.*, 1988, **88**, 322; G. te Velde and E. J. Baerends, *J. Comput. Phys.*, 1992, **84**, 99; C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acta*, 1998, **99**, 391.
- [11] S. A. Borshch, I. Ya. Ogurtsov and I. B. Bersuker, *J. Struct. Chem.* (in Russian), 1982, **23**, 7.
- [12] R. D. Mussel and D. G. Nocera, *Inorg. Chem.*, 1990, **29**, 3711; A. W. Maverick, J. S. Najdzionek, D. MacKenzie, D. G. Nocera and H. B. Gray, *J. Am. Chem. Soc.*, 1983, **105**, 1878.
- [13] R. Bruyndonckx, C. Daul, P. T. Manoharan and E. Deiss, *Inorg. Chem.*, 1997, **36**, 4251.
- [14] Z. Lin and D. I. Williams, *Polyhedron*, 1996, **19**, 3277.
- [15] M. T. Pope and A. Müller (eds), *Polyoxometalates: From Platonic Solids to Retroviral Activity*, Kluwer, Dordrecht, 1994.
- [16] M. T. Pope and A. Müller (eds), *Polyoxometalate Chemistry: From Topology via Self-Assembly to Industrial Applications*, Kluwer, Dordrecht, 2001.
- [17] J. M. Maestre, X. Lopez, C. Bo, J.-M. Poblet and C. Daul, *Inorg. Chem.*, 2002, **41**, 1883; T. M. Anderson, X. Zhang, K. I. Hardcastle and C. L. Hill, *Inorg. Chem.*, 2002, **41**, 2477.
- [18] H. Duclusaud and S. A. Borshch, *J. Am. Chem. Soc.*, 2001, **123**, 2825; J. M. Maestre, J.-M. Poblet, C. Bo, N. Casañ-Pastor and P. Gomez-Romero, *Inorg. Chem.*, 2002, **37**, 3444; A. J. Bridgeman and G. Cavigliasso, *J. Phys. Chem. A*, 2002, **106**, 6114.
- [19] S. A. Borshch, *Inorg. Chem.*, 1998, **37**, 3116; J. J. Borrás-Allmenar, J. M. Clemente, E. Coronado and B. S. Tsukerblat, *Chem. Phys.*, 1995, **195**, 17–29.
- [20] T. Yamase and T. Usami, *J. Chem. Soc., Dalton Trans.*, 1988, 183; M. K. Awad and A. B. Anderson, *J. Am. Chem. Soc.*, 1990, **112**, 1603; R. F. Renneke, M. Kadkhodayan, M. Pasquali and C. L. Hill, *J. Am. Chem. Soc.*, 1991, **113**, 8357; L. A. Combs-Walker and C. L. Hill, *J. Am. Chem. Soc.*, 1992, **114**, 938.
- [21] J. Fuchs, H. Hartl and W. Schiller, *Acta Crystallogr. Sect. B: Struct. Sci.*, 1976, **32**, 740.
- [22] A. Chemseddine, C. Sanchez, J. Livage, J. P. Launay and M. Fournier, *Inorg. Chem.*, 1984, **23**, 2609; T. Yamase, *J. Chem. Soc., Dalton Trans.*, 1987, 1597; D. C. Duncan and C. L. Hill, *Inorg. Chem.*, 1996, **35**, 5828.
- [23] D. C. Duncan, T. L. Netzel and C. L. Hill, *Inorg. Chem.*, 1995, **34**, 4640; L. P. Ermolenko, J. A. Delaire and C. Giannotti, *J. Chem. Soc., Perkin Trans.*, 1997, **2**, 25.
- [24] M. A. Collins and E. Krausz, in *Photochemistry and Photophysics of Coordination Compounds* (eds H. Yersin and A. Vogler), Springer, Berlin, 1987, p. 85.
- [25] S. A. Borshch, I. N. Kotov and I. B. Bersuker, *Chem. Phys. Lett.*, 1982, **89**, 381.
- [26] I. B. Bersuker and S. A. Borshch (eds I. Prigogine and S. A. Rice), *Advances in Chemical Physics*, Wiley, New York, 1992, Vol. 81, p. 703.
- [27] H. Duclusaud and S. A. Borshch, *Chem. Phys. Lett.*, 1998, **290**, 526.

On the Jahn–Teller Origin of the Phosphorus Molecule P_4 Activation by One- and Two-Electron Reduction

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Abstract

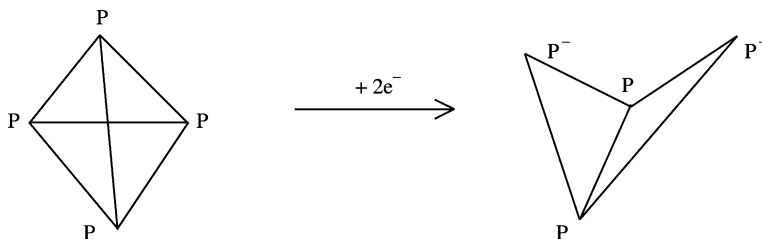
The quantum chemical calculations of the tetra-phosphorus P_4^q were carried out with values of charge $q = 0, -1, -2$. It is shown that the electronic system of the P_4 molecule has equal P–P bond orders. The neutral phosphorus molecule is stable under the reduction of the symmetry from T_d to C_{2v} or C_{3v} . Unlike the neutral molecule, the electronic states of the reduced forms of the P_4 molecule ($^2T_1(P_4^-)$, $^1T_1(P_4^{2-})$ or $^3T_1(P_4^{2-})$) are degenerated in the T_d geometry. Due to the orbital degeneracy of the electronic states, the reduced forms of the phosphorus molecules P_4^- and P_4^{2-} are unstable with the lowering of the symmetry from T_d to C_{2v} or C_{3v} with unsymmetrical changes of the bond order values. On the other hand, the Jahn–Teller effect destabilizes the tetrahedral geometry of the nuclear system, resulting in the bond order's changes too. Thus the phosphorous molecule in the reduced forms is *activated* due to degeneracy of the electronic orbitals and to vibronic instability. The energy of such a type of activation of the *free* phosphorous molecule is estimated as 60–120 kcal/mol.

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1. INTRODUCTION

White phosphorus is the principal source in the manufacture of organophosphorus compounds, pesticides, detergents, etc. Most of the industrial processes in the production of these compounds are based on the oxidation of the phosphorus in the presence of chlorine. Such kinds of processes are accompanied by formation of the hydrochloric acid, which has a negative effect on the surrounding environment. This ecological problem demands the production of the organophosphorus compounds in chlorine-free conditions. Previously it has been established [1–5] that safe chlorine-free processes could be developed utilizing d metals. These compounds activate the P_4 molecule by oxidation or reduction. A qualitative explanation of how the P_4 activation occurs, follows from numerous experimental data. It is generally assumed that in many chemical processes with white phosphorus the tetrahedron P_4 is opened to form the *butterfly* geometry (the P–P bond(s) cleavage) by $2e^-$ -reduction [1] (Scheme 1).



Scheme 1.

To find such effective compounds in activation processes by reduction (or oxidation), it is necessary to study in detail these processes and the *activation* mechanism. This can be done on the basis of the quantum chemical calculations only, which reveal the effects that take place when the phosphorus molecule is changed.

In this article for the simulation of the phosphorus molecule in coordinated states the quantum chemical calculations of P_4^q were carried out with values of charge $q = 0, -1, -2$. Special attention is given to the instabilities of the electronic and nuclear subsystems with the possible reduction of symmetry, resulting in the breaking of the chemical bonds in the tetrahedral phosphorus molecule. Results are analyzed using vibronic theory.

2. COMPUTATIONAL METHODS

Calculations of the electronic structure of the phosphorus molecule were carried out by *ab initio* MO LCAO Hartree–Fock–Roothaan SCF method in the restricted (RHF), restricted-open (ROHF) or unrestricted Hartree–Fock (UHF)

approximations. The STO-6G atomic functions were used. To obtain better (more exact) relative positions of the ground and excited many-electron states, the interaction of the 75 many-electron configurations (CI) was taken into consideration. Numerical calculations were performed using the GAMESS program [6]. For ROHF and RHF in the CI method, the 26 mono-electronic states are considered as frozen. The quantum chemical calculations were carried out with and without the d functions of the P atoms.

3. ELECTRONIC STRUCTURE OF THE P_4^q ($q = 0, -1, -2$) MOLECULAR SYSTEMS

To optimize the geometry of the P_4 molecule with different charges the calculations of the electronic structure were performed using two methods: the optimization algorithm of the GAMESS program and by changing the P–P distances while the total energy did not reach the minimal value. In both cases the results are very close to each other. In this article the results obtained with the second type of optimization are used.

Studies of the electronic structure of the P_4^q molecular system were performed in the T_d symmetry in all charge states (for P_4^{2-} both in the singlet state with total spin value $S = 0$ and in the triplet one with $S = 1$). To study any possible instability of the electronic system to the lowering of symmetry in the fixed T_d configuration of the nuclear subsystem, the calculations were performed using the following three variants:

- when both electronic and nuclear subsystems have the same T_d symmetry;
- when the phosphorus nuclei form the T_d configuration, but the electronic subsystem has symmetry C_{2v} ;
- when the electronic subsystem has symmetry C_{3v} and the phosphorus nuclei are in the T_d configuration.

The values of the total energies in atomic units of energy (a.u.e.), calculated in the above-mentioned conditions, are presented in Table 1. It is seen that the P–P distances (R_{P-P}), obtained after optimization of the neutral molecule of the phosphorus (neglecting the d-orbital), are very close to the experimental value of 2.21 Å [7].

The detailed analysis of the results shows that the main properties of the P_4^q electronic structure are qualitatively independent of the P–P distance. So in the case (a) the order of the energy of the mono-electronics levels and the distribution of the electrons on energetic levels (Table 2) are similar to that presented in Fig. 1 for the experimental distance R_{P-P}^{exp} .

Similar diagrams and tables for the above cases (b) and (c) (when the symmetry of the electronic subsystem is C_{2v} or C_{3v} , but in the high symmetrical T_d nuclear configuration) are given in Figs 2 and 3 and Tables 3 and 4.

Table 1. The total energies of P_4^q ($q = 0, -1, -2$) in the optimized geometry

Systems	Symm.	Without d functions			With d functions		
		R_{P-P} (Å)	$E_{tot} + 1358$ (a.u.e.)	$E_{tot} + 1358$ (a.u.e.) $R_{P-P} = 2.21$ Å	R_{P-P} (Å)	$E_{tot} + 1358$ (a.u.e.)	$E_{tot} + 1358$ (a.u.e.) $R_{P-P} = 2.21$ Å
P_4	T_d	2.26	−0.483	−0.472	2.14	−0.721	−0.712
	C_{2v}	2.30	−0.485	−0.472	2.15	−0.721	−0.711
	C_{3v}	2.31	−0.483	−0.472	2.23	−0.721	−0.711
	T_d, C_{2v}, C_{3v}	2.25	−0.387	−0.384	2.11	−0.663	−0.643
P_4^-	T_d	2.36	−0.353	−0.321	2.29	−0.503	−
	C_{2v}	2.36	−0.354	−	2.18	−0.540	−0.538
	C_{3v}	2.36	−0.357	−0.321	2.29	−0.540	−
	T_d	2.51	−0.145	0.115	2.44	−0.257	−0.102
	C_{2v}	2.27	−0.263	−0.249	2.18	−0.486	−0.483
	C_{3v}	2.32	−0.730	−0.047	2.23	−0.480	0.684
$P_4^{2-}; S = 0$	T_d	2.45	0.011	0.085	2.38	−0.061	−0.033
	C_{2v}	2.41	0.009	0.078	2.27	−0.131	−0.125
	C_{3v}	2.44	0.014	0.096	2.28	−0.124	−0.890
	T_d	2.65	0.233	0.907	2.60	0.176	0.684
	C_{2v}	2.41	0.132	0.185	2.26	−0.027	−0.024
	C_{3v}	2.40	0.132	−	2.25	−0.027	−
$P_4^{2-}; S = 1$	T_d	2.44	0.000	0.069	−	−	−
	C_{2v}	2.43	0.004	−	2.29	−0.137	−0.131
	C_{3v}	2.43	0.004	0.069	2.27	−0.134	−
	T_d	2.61	0.107	0.628	2.57	0.045	0.451
	C_{2v}	2.40	0.082	0.141	2.24	−0.086	−0.080
	C_{3v}	2.32	0.091	0.134	2.29	−0.085	−0.085

The bold (normal) notation of symmetry is used for the calculations performed in the UHF (RHF or ROHF) approximation.

Table 2. The values of the one-electron energies for P_4^q ($q = 0, -1, -2$) in T_d symmetry at $R_{P-P} = 2.21$ Å

Irreduc. repres.	$P_4 (^1A_1)$	$P_4^- (^2T_1)$		$P_4^{2-} (^1T_1)$	$P_4^{2-} (^3T_1)$	
	α, β	α	β	α, β	α	β
t_2	0.276	0.451	0.547	0.722	0.741	0.783
t_1	0.187	0.290	0.463	0.568	0.469	0.711
e	− 0.314	− 0.029	− 0.045	0.237	0.210	0.212
t_2	− 0.349	− 0.161	− 0.102	0.096	0.075	0.157
a_1	− 0.419	− 0.154	− 0.190	0.073	0.056	0.071

Bold numbers correspond to the populated one-electron levels.

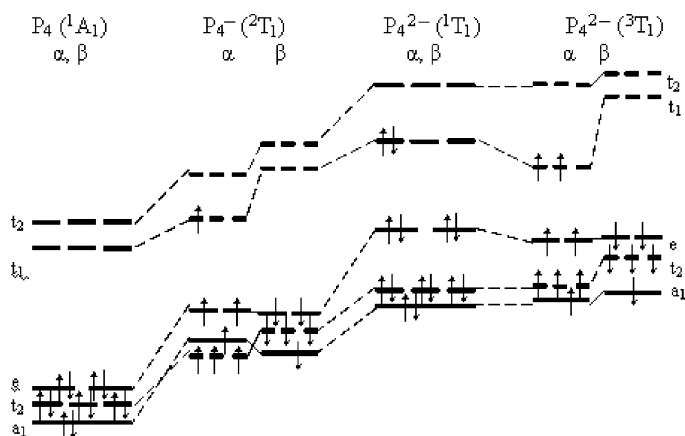


Fig. 1. The correlation diagram of the one-electron levels in active zone for P_4^q ($q = 0, -1, -2$) in T_d symmetry at $R_{P-P} = 2.21$ Å.

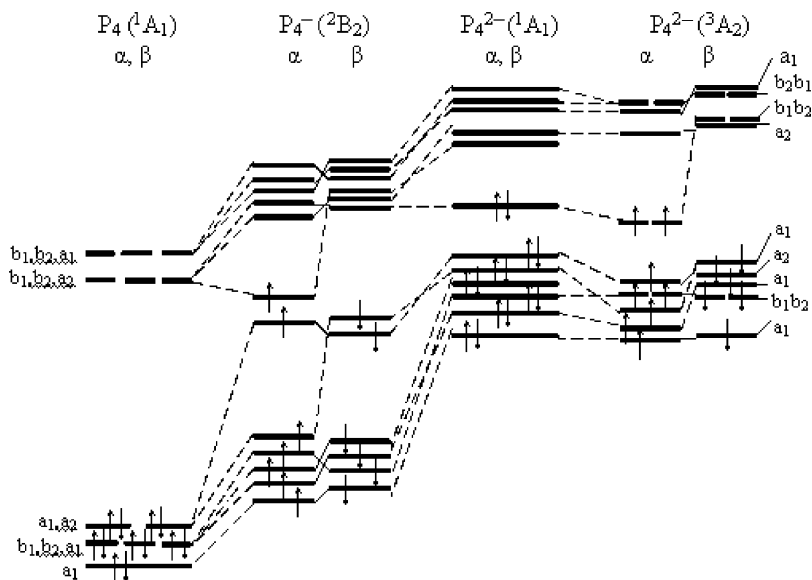


Fig. 2. The correlation diagram of the one-electron levels in the active zone for P_4^q ($q = 0, -1, -2$) in C_{2v} symmetry at $R_{P-P} = 2.21$ Å. Numerical values of the one-electron energies are given in Table 3.

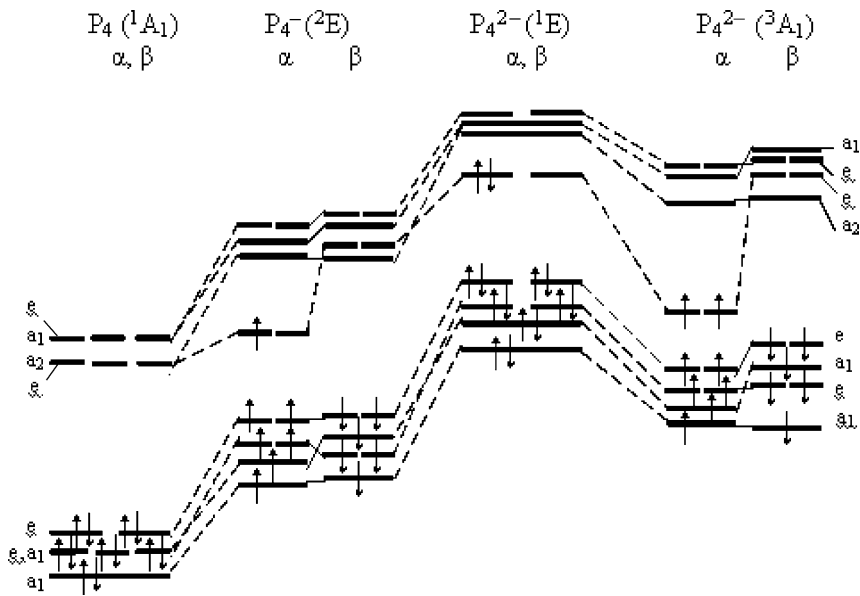


Fig. 3. The correlation diagram of the one-electron levels in the active zone for P_4^q ($q = 0, -1, -2$) in C_{3v} symmetry at $R_{P-P} = 2.21$ Å. Numerical values of the one-electron energies are given in Table 4.

Table 3. The values of the one-electron energies for P_4^q ($q = 0, -1, -2$) in the C_{2v} symmetry at $R_{P-P} = 2.21$ Å (for Fig. 2)

Irreduc. Repres.	P_4 ($1A_1$)	P_4^- ($2B_2$)		P_4^{2-} ($1A_1$)	P_4^{2-} ($3A_2$)	
	α, β	α	β	α, β	α	β
b_1, b_2, a_1	0.276	b_1 0.527 a_1 0.514 b_2 0.512	0.543 b_2 0.541 a_1 0.531 b_1	0.781 b_2 0.774 b_1 0.769 a_1	b_2 0.762 b_1 0.762 a_1 0.760	0.805 a_1 0.796 b_1 0.796 b_2
b_1, b_2, a_2	0.187	b_1 0.430 a_2 0.420 b_2 0.134	0.481 b_2 0.445 a_2 0.431 b_1	0.677 a_2 0.674 b_2 0.433 b_1	a_2 0.653 b_2 0.374 b_1 0.374	0.726 b_2 0.726 b_1 0.702 a_2
a_1, a_2	− 0.314	a_2 − 0.075 a_1 − 0.089	− 0.041 a_1 − 0.058 a_2	0.180 a_2 0.167 a_1	a_2 0.168 b_1 0.119	0.223 a_1 0.198 a_2
b_1, a_1, b_2	− 0.349	b_1 − 0.106 b_2 − 0.126 a_1 − 0.146	− 0.088 b_2 − 0.095 a_1 − 0.107 b_1	0.137 b_2 0.133 b_1 0.130 a_1	b_2 0.119 a_1 0.116 a_1 0.078	0.169 a_1 0.154 b_2 0.154 b_1
a_1	− 0.419	a_1 − 0.183	− 0.175 a_1	0.060 a_1	a_1 0.053	0.072 a_1

The bold numbers correspond to the populated levels.

Table 4. The values of the one-electron energies for P₄^q (*q* = 0, −1, −2) in C_{3v} symmetry at *R*_{P–P} = 2.21 Å (for Fig. 3)

Irreduc. Repres.	P ₄ (¹ A ₁)	P ₄ [−] (² E)		P ₄ ^{2−} (¹ E)	P ₄ ^{2−} (³ A ₁)	
	α, β	α	β	α, β	α	β
<i>e</i>	0.276	0.582	0.606	0.962	0.761	0.797
<i>a</i> ₁	0.276	0.555	0.597	0.870	0.750	0.802
<i>a</i> ₂	0.187	0.529	0.505	0.898	0.661	0.684
<i>e</i>	0.187	0.293	0.531	0.658	0.373	0.735
<i>e</i>	−0.314	−0.010	0.001	0.392	0.147	0.212
<i>e</i>	−0.349	−0.069	−0.046	0.327	0.101	0.148
<i>a</i> ₁	−0.349	−0.093	−0.028	0.313	0.093	0.171
<i>a</i> ₁	−0.419	−0.130	−0.117	0.255	0.055	0.070

The bold numbers correspond to the populated levels.

For further discussion the correlation diagram of the one-electron levels in the active zone for P₄^{1−} in *T_d*, *C_{2v}* and *C_{3v}* symmetry at *R*_{P–P} = 2.21 Å are given in Fig. 4. In addition, the dependencies of the total energies of P₄^q in function of the P–P distance are represented in Fig. 5.

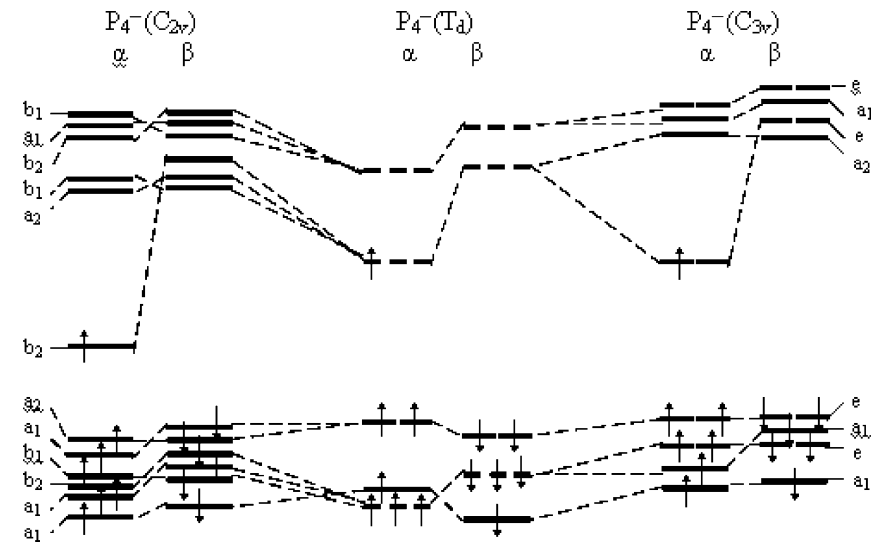


Fig. 4. The correlation diagram of the one-electron levels for P₄[−] in *T_d*, *C_{2v}*, *C_{3v}* symmetry at *R*_{P–P} = 2.21 Å.

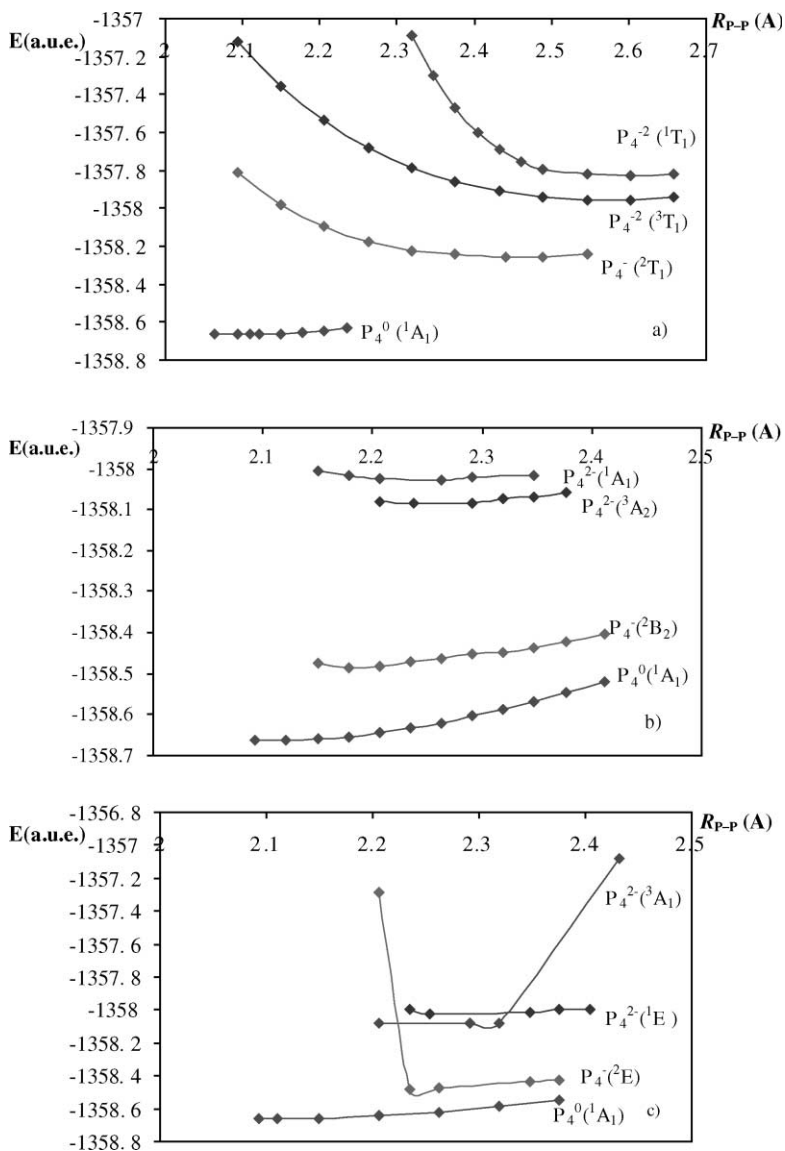


Fig. 5. Dependencies of total energies on the P-P distance in symmetry: (a) T_d , (b) C_{2v} , (c) C_{3v} .

4. DISCUSSION OF THE RESULTS

The results of the quantum chemical calculations, which were carried out for the phosphorus neutral molecule in T_d symmetry, are in good agreement with the

experimental data and earlier quantum chemical calculations [7]. A comparison of the results for the P₄ molecule is presented in Table 5. It can be seen that the optimal values of the P–P distances obtained in this work are close to experimental data and, in general, all the results score better when neglecting the phosphorus d orbitals.

One of the most important qualitative results is probably the effect of orbital degeneracy on the multielectronic states of the P₄ molecule in the reduced forms (see Figs 1, 4, and 5). In the ROHF approximation the degenerated many-electronic wave functions of the P₄[−] ground states can be presented as follows:

$$\begin{aligned}\Psi_{xz}(T_1) &= (N!)^{-1/2} \det|(1a_1)^2 \cdots (6t_2)^6 (5a_1)^2 (2e)^4 (2t_{1xz})^1| \\ \Psi_{yz}(T_1) &= (N!)^{-1/2} \det|(1a_1)^2 \cdots (6t_2)^6 (5a_1)^2 (2e)^4 (2t_{1yz})^1| \\ \Psi_{xy}(T_1) &= (N!)^{-1/2} \det|(1a_1)^2 \cdots (6t_2)^6 (5a_1)^2 (2e)^4 (2t_{1xy})^1|\end{aligned}\tag{1}$$

where *N* is the number of electrons in the system and the one-electron MOs (see Fig. 6).

$$\begin{aligned}2t_{1xz} &= 0.437(P_{1x} + P_{1z} + P_{2x} - P_{2z} - P_{3x} - P_{3z} - P_{4x} + P_{4z}) \\ 2t_{1yz} &= 0.437(P_{1y} - P_{1z} + P_{2y} + P_{2z} - P_{3y} - P_{3z} - P_{4y} + P_{4z}) \\ 2t_{1xy} &= 0.437(P_{1x} + P_{1y} - P_{2x} - P_{2y} - P_{3x} - P_{3y} - P_{4x} + P_{4y})\end{aligned}\tag{2}$$

are the HOMOs in the many-electron degenerated wave functions; the *P*_{γ_x}, *P*_{γ_y} and *P*_{γ_z} are the 3p-functions of the γth phosphorus atom.

To study the possible lowering of the symmetry of the electronic system, which can improve the results in accordance with the Löwdin dilemma [8], the P₄^q systems were considered in the above (b) and (c) cases. From the data of Table 1 it can be

Table 5. Orbital one-electron energies (in a.u.e.) for the P₄ molecule

	Exper. data	NOCOR without d-funct. ^a	NOCOR with d-funct. ^a	RHF without d-funct.	RHF with d-funct.	UHF without d-funct.	UHF with d-funct.
<i>R</i> _{P–P} (Å)	2.21	2.38	–	2.26	2.14	2.25	2.11
2 <i>e</i>	−0.357	−0.357	−0.333	−0.333 − 0.343	−0.326 − 0.314	−0.334 − 0.343	−0.330 − 0.314
6 <i>t</i> ₂	−0.384	−0.359	−0.361	−0.361 − 0.367	−0.356 − 0.349	−0.362 − 0.367	−0.359 − 0.349
5 <i>a</i> ₁	−0.421	−0.396	−0.419	−0.413 − 0.422	−0.434 − 0.419	−0.414 − 0.422	−0.439 − 0.419

The orbital energies for the experimental P–P distance of 2.21 Å are presented as bold characters.

^aNeglect of the core orbital (NOCOR) calculations [7].

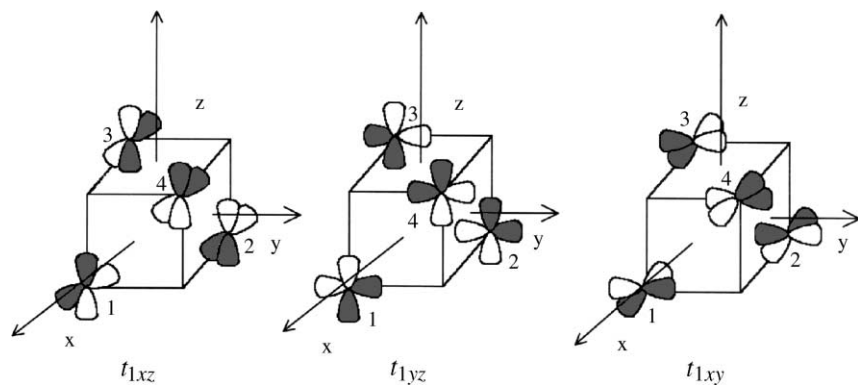


Fig. 6. The triples degenerate MOs ($2t_{1xz}$, $2t_{1yz}$, $2t_{1xy}$) of the P_4^- anion.

seen that an artificial lowering of the electronic subsystem symmetry of the neutral P_4 molecule from T_d to C_{2v} or C_{3v} does not change essentially the values of the total energy contrary to the Löwdin dilemma prediction [8]. It is not the case, when the reduced forms of the P_4 molecule (P_4^{1-} and P_4^{2-}) are considered. In case (a), the symmetry of every degenerate state (see equation (1) and Fig. 6) for the P_4^- anion is lower than the supposed symmetry T_d of the P_4^- and P_4 systems. This can be seen by the calculations of the bond orders $P_{\mu\nu}^\kappa$

$$P_{\mu\nu}^\kappa = \sum_{i(\text{populated})} C_{i\mu}^\kappa C_{i\nu}^\kappa \quad \kappa = \alpha, \beta \quad (3)$$

where $C_{i\mu}^\kappa$ are the coefficients in the i th MO LCAO populated by the electron with the projection $\kappa = \alpha, \beta$ of the spin. In the MO LCAO approximation, all of the physical mean values can be expressed using $P_{\mu\nu}^\kappa$.

It can be easily seen that the contributions of closed shells $((1a_1)^2 \cdots (6t_2)^6 \times (5a_1)^2 (2e)^4)$ are equal in all degenerated states (1). The differences in bond orders in the states (1) are due to the differences in the coefficients in the HOMO LCAO: ($2t_{1xz}$, $2t_{1yz}$, $2t_{1xy}$) (equation (2)). The results of the bond orders $P_{\mu\nu} = P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta$ calculations for the P_4 , P_4^- (in the state $\Psi_{xz}(T_1)$), P_4^{2-} (in the singlet state) and P_4^{2-} (in the triplet state) are given in Table 6. It follows from these data that the tetrahedral P_4^q molecule in the reduced form with $q = -1$ or -2 , being in one of the orbitally triple degenerated states (${}^2T_1(P_4^-)$, ${}^1T_1(P_4^{2-})$ or ${}^3T_1(P_4^{2-})$), has non-equal bond orders. The lowering of the electronic subsystem symmetry in these cases is accompanied by the stronger polarization of the electronic system, the lowering of the HOMO levels and total energies (see the correlation of the mono electronic levels in Fig. 4 for P_4^- and by changing of the bond orders (Table 6). It should be noted that in case (b) (energetically more preferable lowering of symmetry to C_{2v}) one of the bonds is weakened exactly as in Scheme 1.

Table 6. The values of bond orders $P_{\mu\nu}$ for $P_4^q(q = 0, -1, -2)$ in the nuclear configuration with T_d symmetry at $R_{\text{P-P}} = 2.21 \text{ \AA}$

Symmetry	Bond order	P ₄	P ₄ [−]	P ₄ ^{2−}	P ₄ ^{2−}
<i>T_d</i>	<i>P</i> ₁₂ , <i>P</i> ₃₄	1.011	0.867	0.750	0.865
	<i>P</i> ₁₃ , <i>P</i> ₂₄		0.995	1.037	0.895
	<i>P</i> ₁₄ , <i>P</i> ₂₃		0.867	0.750	0.895
<i>C_{2v}</i>	<i>P</i> ₁₂	1.011	1.027	1.046	0.709
	<i>P</i> _{μν} (μ = 1, 2; ν = 3, 4)		0.969	0.910	0.954
	<i>P</i> ₃₄		0.704	0.536	0.709
<i>C_{3v}</i>	<i>P</i> ₁₂ , <i>P</i> ₁₃	1.011	0.929	0.898	0.745
	<i>P</i> ₁₄		0.907	0.642	0.745
	<i>P</i> ₂₃		1.024	1.046	0.961
	<i>P</i> ₃₄ , <i>P</i> ₂₄		0.899	0.965	0.961

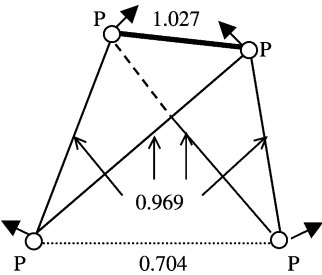


Fig. 7. The bond orders for P_4^- in the C_{2v} symmetry and one of the Jahn–Teller active distortions.

At the same time, as it is known, the molecular systems in the degenerated states are dynamically unstable with respect to symmetry distortions due to the Jahn–Teller effect [9]. Such kinds of distortions are expected both in the electronic and nuclear subsystems (vibronic instability). The Jahn–Teller effect destabilizes the tetrahedral geometry of the nuclear system, which results in the bond order’s changes too. In particular, according to the theory of the Jahn–Teller effect [9] the tetrahedral molecular systems in the $^2T_1(P_4^-)$, $^1T_2(P_4^{2-})$ or $^3T_1(P_4^{2-})$ states are dynamically unstable to the e - and t_2 -type nuclear distortions, one of which is presented in Fig. 7.¹ Evidently such a kind of distortion to the *butterfly* geometry

¹ General considerations of the butterfly geometry (opening (C_{2v})) of the 62-electron tetra nuclear metal clusters are given in Ref. [10] by solving the $(T_1 + T_2) \times (e + t_2)$ Jahn–Teller problem.

contributes to the further weakening of one of the P–P bonds (*activation* of the reduced phosphorus molecule).

5. CONCLUSIONS

Results discussed above show that the theoretical value of the total energy and the geometric parameters for the P_4 molecule in the ground $^1A_1$ state does not depend essentially on the approximations used in the calculations. The P–P distances (R_{P-P}) are very close to the experimental value of 2.21 Å, possessed by the free molecule P_4 . The P_4 molecule has equal P–P bond orders and it is stable under the reduction of the symmetry from T_d to C_{2v} or C_{3v} .

Unlike the neutral molecule, the electronic states of the reduced forms of the P_4 (P_4^- and P_4^{2-}) in the T_d geometry are degenerated ($^2T_1(P_4^-)$, $^1T_1(P_4^{2-})$ or $^3T_1(P_4^{2-})$). Due to the orbital degeneracy, the equivalence of the P–P bonds in all of the degenerated states is broken, the values of the bond order become different, their electronic and nuclear subsystems are vibronically unstable, and the molecule is *activated*. Thus the *activation* (breaking of the equivalence and cleavage of the bonds) of the phosphorous molecule in the reduced anionic forms is due to the electronic orbital degeneracy and to the vibronic instability. The energies of such a type of phosphorus activation can be estimated as the differences of the phosphorus molecule energies in the reduced and neutral forms. In accordance with data from Table 1 the energies of the one- and two-electron *activation* of the phosphorus molecule are equal to ~ 60 –120 kcal/mol.

ACKNOWLEDGEMENTS

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REFERENCES

- [1] O. J. Scherer, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 1104.
- [2] M. Peruzzini, L. Marvelli, A. Romerosa, R. Rossi, F. Vizza and F. Zanobini, *Eur. J. Inorg. Chem.*, 1999, 931.
- [3] M. Peruzzini, S. Manas, A. Romerosa and A. Vacca, *Mendeleev Commun.*, 2000, 134.
- [4] W. W. Schoeller and C. Lerch, *Inorg. Chem.*, 1983, **22**, 2992.
- [5] M. Baudler, *Angew. Chem. Int. Ed. Engl.*, 1982, **21**, 492.
- [6] M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
- [7] R. Osman, P. Coffey and J. R. Van Wazer, *Inorg. Chem.*, 1976, **15**, 287.
- [8] P. O. Löwdin, *Rev. Mod. Phys.*, 1963, **35**, 496; (b) P. O. Löwdin, *Adv. Chem. Phys.*, 1969, **14**, 283.
- [9] I. B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds. Introduction to the Theory*, Wiley, New York, 1996.
- [10] A. Ceulemans, *J. Chem. Phys.*, 1986, **84**, 6442.

Magnetic Properties of a Low Symmetry d^5 Complex: An Adiabatic Pseudo-Jahn–Teller Problem

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This chapter is dedicated to Professor Isaak Bersuker on the occasion of his 75th birthday – as a sign of our appreciation of his outstanding contribution to the theory of the Jahn–Teller effect

Abstract

A vibronic model for the magnetic properties of a low-spin d^5 metal complex is reported. The splitting of the ground $^2T_2$ -term by the strong spin–orbital interaction and the trigonal component of the crystal field as well as the covalency effects are taken into account. The pseudo-Jahn–Teller mixing of the low-lying states is also considered in the framework of the semiclassical adiabatic approximation. The influence of the named interactions on the g -tensor and on the tensor of the temperature-independent paramagnetism is elucidated.

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1. INTRODUCTION

Complexes of heavy metal ions attract considerable interest due to the strong spin–orbital interaction giving rise to a significant magnetic anisotropy. This study was initiated by the unusual magnetic data obtained at Texas A&M University for two compounds of Re(II): $[\text{Et}_4\text{N}][\text{Re}(\text{triphos})(\text{CN}_3)]$ and $[\text{Re}(\text{triphos})(\text{MeCN}_3)] [\text{BF}_4]_2$ in which Re(II) ions occupy the sites with a strong cubic crystal field and a significant trigonal component. These complexes exhibit anomalously large temperature-independent paramagnetism (TIP) that can be related to the low-lying levels that arise from the interplay between the low-symmetry crystal field, spin–orbital and vibronic interactions. Since the cubic crystal field for the heavy metal ions is usually strong the d^5 electronic configuration is expected to be the low-spin ground term $^2T_2(t_2^5)$ that is split by spin–orbital interaction and trigonal crystal field. The studies of the orbital triplets in the crystal field were focused mainly on the calculation of the EPR parameters [1–4]. In the present study we will use the T–P isomorphism [2] and pay attention to the magnetic properties of the d^5 complexes. The vibronic Jahn–Teller (JT) interaction is of crucial importance for the interpretation of the magnetic and spectroscopic properties of transition metal complexes [5–7]. A special role of the JT interaction in the magnetic problem has been demonstrated in [8], where the giant second-order Zeeman effect has been discovered. This effect was shown to arise from the set of closely spaced hybrid electron-vibrational levels. The JT interaction for the extended 5d electronic shells is expected to be strong and should be taken into account along with the spin–orbital interaction. For the case under study (d^5 -ion) this leads to a pseudo-JT (PJT) vibronic problem. Using semiclassical adiabatic approach [9] we elucidate the main manifestations of the PJT interaction and the combined action of PJT and trigonal crystal field in the magnetic properties of complex d^5 ions.

2. THE MODEL

We consider d^5 -ions in the cubic and axially distorted complexes. Axial distortions are assumed to arise from the heteronuclear ligand surrounding or from deviation of the local surrounding of the metal ion from the octahedral one. This gives rise to a trigonal or a tetragonal component of the crystal field. The model takes into account the following relevant interactions defining the magnetic properties of the complexes: (1) Strong cubic crystal field. In a strong cubic crystal field the d^5 -ion proves to be the low-spin one and has a triplet ground state $^2T_2(t_2^5)$; (2) spin–orbital coupling that splits the $^2T_2$ -term into the doublet Γ_7 and the quadruplet Γ_8 ; (3) trigonal component of the crystal field which is compatible with the structure of the titled Re(II) complexes; (4) vibronic coupling in the orbital triplet with the tetragonal (e) modes that leads to a PJT vibronic problem $T_2 \otimes (e + \text{SO})$ in d^5 complexes. Here we will consider the combined effect of the low-symmetry fields and PJT interaction with the tetragonal vibrations that usually is the most important.

We shall employ the adiabatic approximation that was shown to provide a rather good accuracy in the calculation of the magnetic susceptibility for the vibronic mixed valence systems exhibiting PJT in a wide range of parameters [9]. At the same time this approximation allows us to gain a descriptive comprehension of the physical role of the JT interaction. The full Hamiltonian of the system in the adiabatic approximation can be written as follows:

$$\mathbf{H} = \mathbf{H}_{\text{SO}} + \mathbf{V}_{\text{trig}} + \mathbf{H}_Z + \frac{1}{2} \omega_E (q_u^2 + q_v^2) \mathbf{I} + v_E (q_u \mathbf{O}_u + q_v \mathbf{O}_v) \quad (1)$$

The Hamiltonian of the electronic subsystem includes the spin–orbital coupling ($\mathbf{H}_{\text{SO}}$), trigonal crystal field ($\mathbf{V}_{\text{trig}}$) and Zeeman interaction ($\mathbf{H}_Z$). The vibronic part of the Hamiltonian contains the energy of free vibrations associated with the tetragonal (e) JT modes and the vibronic coupling with these modes, v_E is the vibronic constant. The dimensionless normal coordinates of the tetragonal vibrations are denoted as q_u, q_v (basis $u \propto 3z^2 - r^2$, $v \propto x^2 - y^2$) and ω_E is the frequency of these vibrations. In equation (1), $\mathbf{I}$ is the unit matrix and the matrices $\mathbf{O}_{E\gamma} \equiv \mathbf{O}_\gamma$ ($\gamma = u, v$) are defined in the cubic T_2 -basis (ξ, η, ζ) as follows:

$$\mathbf{O}_{Eu} = \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathbf{O}_{Ev} = \begin{pmatrix} \sqrt{3}/2 & 0 & 0 \\ 0 & -\sqrt{3}/2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (2)$$

In the framework of the adopted semiclassical adiabatic approximation the nuclear kinetic energy is omitted.

3. MATRIX REPRESENTATION OF THE MAIN INTERACTIONS

We shall use the T – P -isomorphism that allows us to consider the orbital triplet T_2 as a state possessing the fictitious orbital angular momentum $\mathbf{L} = 1$, keeping in mind that the matrix elements of the angular momentum operator $\mathbf{L}$ within T_2 and P bases are of the opposite signs, $\mathbf{L}(T_2) = -\mathbf{L}(P)$ [2]. As it was shown in our recent paper [10] this approach provides both an efficient computational tool and a clear insight on the magnetic anisotropy of the system that appears due to the orbital contributions. Within T – P formalism the spin–orbital and Zeeman terms can be represented as:

$$\mathbf{H}_{\text{SO}} = -\kappa \lambda \mathbf{L} \mathbf{S}, \quad \mathbf{H}_Z = \beta (g_e \mathbf{S} - \kappa \mathbf{L}) \mathbf{H} \quad (3)$$

The operators in equation (3) act within the ground manifold possessing $S = \frac{1}{2}$ and $\mathbf{L} = 1$ (κ is the orbital reduction factor, g_e is the electronic g -factor). The axial (trigonal) component of the crystal field directed along the C_3 -axis is defined as a linear combination of the irreducible tensors of O_h that becomes scalar in the

trigonal point groups let say, (D_{3d}):

$$\mathbf{V}_{\text{trig}} = -\frac{1}{2}\Delta(\mathbf{O}_\xi + \mathbf{O}_\eta + \mathbf{O}_\zeta) \quad (4)$$

where the matrices $\mathbf{O}_{T_2\gamma} \equiv \mathbf{O}_\gamma$ ($\gamma = \xi, \eta, \zeta$) are given by:

$$\mathbf{O}_{T_2\xi} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \mathbf{O}_{T_2\eta} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \mathbf{O}_{T_2\zeta} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (5)$$

In equation (4) Δ is the parameter of the trigonal crystal field. This crystal field splits the T_2 -state into an orbital singlet and a doublet, the parameter Δ is defined in such a way that for positive Δ the ground state is the orbital singlet.

To take advantage from the pseudo-angular momentum representation we shall employ the technique of the irreducible tensor operators as suggested in Ref. [10]. One can easily establish the following interrelations between the matrices $\mathbf{O}_{\Gamma\gamma}$ and the orbital angular momentum operators:

$$\begin{aligned} \mathbf{O}_{Eu} &= 1 - \frac{3}{2}\mathbf{L}_Z^2, & \mathbf{O}_{Ev} &= -\frac{\sqrt{3}}{2}(\mathbf{L}_X^2 - \mathbf{L}_Y^2) \\ \mathbf{O}_{T_2\xi} &= -\frac{1}{\sqrt{2}}(\mathbf{L}_Y\mathbf{L}_Z + \mathbf{L}_Z\mathbf{L}_Y), & \mathbf{O}_{T_2\eta} &= -\frac{1}{\sqrt{2}}(\mathbf{L}_X\mathbf{L}_Z + \mathbf{L}_Z\mathbf{L}_X) \\ \mathbf{O}_{T_2\zeta} &= -\frac{1}{\sqrt{2}}(\mathbf{L}_X\mathbf{L}_Y + \mathbf{L}_Y\mathbf{L}_X) \end{aligned} \quad (6)$$

Let us express the operators $\mathbf{L}_X$, $\mathbf{L}_Y$ and $\mathbf{L}_Z$ in terms of the components of the first rank spherical irreducible tensor $\mathbf{L}_{1q}$ ($q = 0, \pm 1$):

$$\mathbf{L}_X = \frac{1}{\sqrt{2}}(\mathbf{L}_{1-1} - \mathbf{L}_{11}), \quad \mathbf{L}_Y = \frac{i}{\sqrt{2}}(\mathbf{L}_{1-1} + \mathbf{L}_{11}), \quad \mathbf{L}_Z = \mathbf{L}_{10} \quad (7)$$

The same relations can be applied to the spin operators. Then, using the Clebsch–Gordan decomposition [11] one can express the bilinear forms of the orbital angular momentum operators in equation (6) in terms of the irreducible tensorial products:

$$\mathbf{L}_{1q_1}\mathbf{L}_{1q_2} = \sum_{kq} \{\mathbf{L}_1 \otimes \mathbf{L}_1\}_{kq} C_{1q_1 1q_2}^{kq} \quad (8)$$

Here $\{\mathbf{L}_1 \otimes \mathbf{L}_1\}_{kq}$ is the complex irreducible tensor of the rank k composed from the angular momentum operators, $q = -k, -k+1, \dots, k$ and $C_{1q_1 1q_2}^{kq}$ are the Clebsch–Gordan (Wigner) coefficients. Now one can express all matrices $\mathbf{O}_{\Gamma\gamma}$ in terms of the complex irreducible tensors $\mathbf{T}_{kq}(\mathbf{L}) = \{\mathbf{L}_1 \otimes \mathbf{L}_1\}_{kq}$ acting in the orbital subspace:

$$\begin{aligned}
\mathbf{O}_{Eu} &= -\sqrt{\frac{3}{2}}\mathbf{T}_{20}(\mathbf{L}), & \mathbf{O}_{Ev} &= -\sqrt{\frac{3}{2}}[\mathbf{T}_{22}(\mathbf{L}) + \mathbf{T}_{2-2}(\mathbf{L})] \\
\mathbf{O}_{T_2\xi} &= -\frac{i}{\sqrt{2}}[\mathbf{T}_{21}(\mathbf{L}) + \mathbf{T}_{2-1}(\mathbf{L})], & \mathbf{O}_{T_2\eta} &= \frac{1}{\sqrt{2}}[\mathbf{T}_{21}(\mathbf{L}) - \mathbf{T}_{2-1}(\mathbf{L})] \\
\mathbf{O}_{T_2\zeta} &= \frac{i}{\sqrt{2}}[\mathbf{T}_{22}(\mathbf{L}) - \mathbf{T}_{2-2}(\mathbf{L})]
\end{aligned} \quad (9)$$

These relations allow us to evaluate the matrix elements of all involved interactions using the irreducible tensor operator technique and to exploit the results derived from the theory of magnetically coupled systems. The matrix of the Hamiltonian can be built either in uncoupled or in coupled bases. It is convenient to choose such a basis in which spin–orbital coupling proves to be diagonal. This means that in this basis the orbital angular momentum and spin are coupled $|LSJM_J\rangle \equiv |1\frac{1}{2}JM_J\rangle$ in order to get the total angular momentum $J = \frac{1}{2}$ (Kramers doublet Γ_7) and $J = \frac{3}{2}$ (quadruplet Γ_8). The quantization axis for the total angular momentum in the trigonally distorted system is C_3 . In the coupled basis the spin–orbital operator is represented by the diagonal matrix:

$$\langle 1SJ'M_J | \mathbf{H}_{SO} | 1SJ M_J \rangle = -\frac{1}{2}\kappa\lambda[J(J+1) - S(S+1) - 2]\delta_{JJ'}\delta_{M_J M_J'} \quad (10)$$

Then, using the matrix elements for the complex irreducible tensor operators (see Ref. [11]) we arrive at the following expression for the matrix elements of the vibronic interaction:

$$\begin{aligned}
&\langle 1SJ'M_J | \mathbf{H}_{vib} | 1SJ M_J \rangle \\
&= (-1)^{S+J}\sqrt{5(2J+1)}\left\{ \begin{matrix} 1 & 2 & 1 \\ J' & S & J \end{matrix} \right\} v_E \frac{\sqrt{3}}{2} [q_u \sqrt{2} C_{JM_J 20}^{J' M_J'} \\
&\quad + q_v (C_{JM_J 22}^{J' M_J'} + C_{JM_J 2-2}^{J' M_J'})]
\end{aligned} \quad (11)$$

where $\left\{ \begin{smallmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{smallmatrix} \right\}$ are the $6j$ -symbols [11]. For the matrix elements of Zeeman interaction one gets:

$$\begin{aligned}
&\langle 1SJ'M_J | \mathbf{H}_Z | 1SJ M_J \rangle \\
&= \sqrt{(2J+1)}(-1)^{J+S} \left\{ \begin{matrix} 1 & 1 & 1 \\ J' & S & J \end{matrix} \right\} \beta [g_e \sqrt{S(S+1)(2S+1)} + \kappa \sqrt{6}] (C_{JM_J 10}^{J' M_J'} H_{10} \\
&\quad - C_{JM_J 11}^{J' M_J'} H_{1-1} - C_{JM_J 1-1}^{J' M_J'} H_{11})
\end{aligned} \quad (12)$$

where $H_{10} = H_Z$, $H_{1\pm 1} = \mp(1/\sqrt{2})(H_X \pm iH_Y)$ are the cyclic components of the magnetic field. Particular direction of the magnetic field can be selected by means of an appropriate choice of the corresponding terms in equation (12).

Finally, for the matrix elements of the trigonal crystal field operators we find:

$$\begin{aligned} & \langle 1 S J' M_J' | V_{\text{trig}} | 1 S J M_J \rangle \\ &= (-1)^{1+S+J} \sqrt{5(2J+1)} \begin{Bmatrix} 1 & 2 & 1 \\ J' & S & J \end{Bmatrix} \frac{1}{2\sqrt{2}} \Delta [(i-1)C_{J M_J 2 1}^{J' M_J'} \\ &+ (i+1)C_{J M_J 2 -1}^{J' M_J'} - i(C_{J M_J 2 2}^{J' M_J'} - C_{J M_J 2 -2}^{J' M_J'})] \end{aligned} \quad (13)$$

In the following sections we will consider the interplay of the vibronic interaction, spin–orbital coupling and static trigonal field with regard to the problem of the magnetic properties of the low-symmetry d^5 -complexes.

4. ENERGY PATTERN FOR A d^5 COMPLEX IN A STATIC MODEL

Before studying the magnetic properties in the vibronic model we will inspect the arrangement of the energy levels taking into account only electronic interactions: spin–orbital coupling and trigonal crystal field. The spin–orbital coupling parameter is negative for the low-spin d^5 -ions, so that in the cubic crystal field the Kramers doublet Γ_7 is the ground state and the quadruplet Γ_8 is the excited one. The corresponding energies are the following:

$$E\left(\frac{1}{2}\right) = -\kappa|\lambda|, \quad E\left(\frac{3}{2}\right) = \frac{\kappa|\lambda|}{2} \quad (14)$$

The energy separation between the doublet and quadruplet is $3\kappa|\lambda|/2$. When the system is distorted along the C_3 axis the O_h symmetry is lowered to D_{3d} . Then the irreducible representation Γ_7 passes to Γ_4 while Γ_8 splits into $\Gamma_4 + \Gamma_5 + \Gamma_6$ [12]. The representations Γ_5 and Γ_6 form the complex conjugated double-valued representation with the basis $M_J = \pm 3/2$, while the basis for Γ_4 is $M_J = \pm 1/2$. Two Γ_4 states (from $J = 1/2$ and $3/2$) with the same quantum number M_J are mixed by the trigonal crystal field. In the absence of external magnetic field the energy levels are solely determined by $|M_J|$ due to the axial symmetry of the system. The expressions for the energy levels $E(|M_J|)$ are found to be the following:

$$E_{\pm}\left(\frac{1}{2}\right) = \frac{1}{4} \left[-\Delta - |\lambda|\kappa \pm \sqrt{(\Delta - 3|\lambda|\kappa)^2 + 8\Delta^2} \right], \quad E\left(\frac{3}{2}\right) = \frac{\Delta}{2} + \frac{|\lambda|\kappa}{2} \quad (15)$$

Hereunder we use the notations $E_{\pm}(\frac{1}{2})$ for the energies of the Γ_4 -states and $E(\frac{3}{2})$ for the energy of the $\Gamma_5 + \Gamma_6$ -state. The corresponding wave-functions depend on the sign of the trigonal crystal field. So, provided $\Delta \leq 0$, the wave-functions of the ground Γ_4 -state are the following:

$$\Psi_{-}\left(\pm\frac{1}{2}\right) = \sqrt{\frac{1+R}{2}} \Phi\left(\frac{1}{2}, \pm\frac{1}{2}\right) \pm \sqrt{\frac{1-R}{2}} \Phi\left(\frac{3}{2}, \pm\frac{1}{2}\right) \quad (16)$$

where:

$$R = \left[1 + 8 \left(1 - 3 \frac{|\lambda|\kappa}{\Delta} \right)^{-2} \right]^{-1/2} \quad (17)$$

Figure 1 shows the energy levels of the d^5 system as a function of Δ providing $\lambda = -2100 \text{ cm}^{-1}$ and $\kappa = 0.7$. Independently of the sign and magnitude of the trigonal crystal field the doublet Γ_4 with the energy $E_{-}(\frac{1}{2})$ is the ground state. In the limit of strong positive trigonal field the spin–orbit coupling is completely suppressed within the ground state, so this state becomes ${}^2A_1$. The symmetry of the first excited state depends on the sign of the trigonal field. Providing $\Delta < 0$ the first excited level is $E(\frac{3}{2})$. In the limit of strong negative field two low-lying levels $E_{-}(\frac{1}{2})$, $E(\frac{3}{2})$ vs. trigonal field are parallel, these levels can be attributed to the first order spin–orbital splitting of the trigonal ${}^2E$ term in D_{3d} symmetry. Only the $\mathbf{L}_Z$ component is operative within the orbital trigonal E -basis, so that spin–orbital coupling becomes axial ($-\kappa\lambda\mathbf{L}_Z\mathbf{S}_Z$) and one easily finds that the spin–orbital splitting in ${}^2E$ is $\kappa\lambda$. This value is reduced by the trigonal crystal field with respect to its initial value ($3\kappa\lambda/2$) in a cubic ${}^2T_2$ term. Using equations (16) and (17) one can find the following formulas for the g -factors that are valid in the case of a negative trigonal field:

$$g_{\parallel} = 1 + R + 2\sqrt{2(1 - R^2)}, \quad g_{\perp} = 1 + R - \sqrt{2(1 - R^2)} \quad (18)$$

In the limit of strong negative trigonal field the parameter R takes on the value $\frac{1}{3}$, we approach the following principal values of g -factor: $g_{\parallel} = 4$ and $g_{\perp} = 0$. This case can be referred to as the fully anisotropic limit.

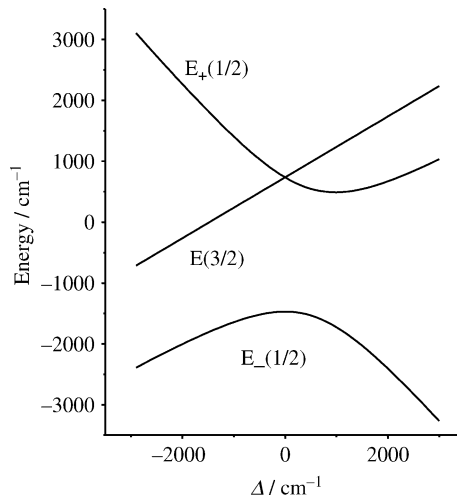


Fig. 1. Splitting of the ${}^2T_2(t_2^5)$ term by the spin–orbital interaction and trigonal crystal field.

When $\Delta > 0$ the first excited level is $E_+(\frac{1}{2})$. Now the above discussed first-order spin–orbital splitting of ${}^2E$ -term occurs for the excited levels $E(\frac{3}{2})$, $E_+(\frac{1}{2})$ that are parallel in the strong crystal field limit.

5. g -FACTORS AND TIP IN THE ${}^2T_2 \otimes (e + \text{SO} + \mathbf{V}_{\text{trig}})$ PSEUDO-JT VIBRONIC PROBLEM

The tetragonal vibrational modes couple the states $E_-(\frac{1}{2})$ and $E_+(\frac{1}{2})$ (Fig. 1) that results in the PJT problem. In order to make clear the behavior of the g -factors and TIP contributions to the magnetic susceptibility we start with the inspection of the adiabatic surfaces. Figure 2(a) illustrates the ground adiabatic potential sheet of a perfect octahedral system ($\Delta = 0$) in the case of weak vibronic coupling when this interaction is not strong enough to produce the tetragonal minima. Then the only minimum corresponds to a non-distorted octahedron ($q_u = q_v = 0$). With the increase of the vibronic coupling the adiabatic well in the vicinity of the minimum is getting more flat and for some critical value of the vibronic constant this single-minimum is split into three equivalent minima located at the positions $(q_u, q_v) = (-q_0, 0)$, $(q_0/2, -q_0\sqrt{3}/2)$, $(q_0/2, q_0\sqrt{3}/2)$ lying on the ring with the radius q_0 , q_0 being a function of all relevant parameters of the system. In each minimum the system is distorted along one of three tetragonal axes. With further increase of the vibronic coupling these minima become deeper (Fig. 2(b)).

The trigonal field and vibronic coupling with the tetragonal modes are in competition and the field modulates the energy separation between the $E_-(\frac{1}{2})$ and $E_+(\frac{1}{2})$ states governing thus the strength of the PJT effect. With the increase of the trigonal field, the minima of the lower adiabatic surface become shallower, the barrier separating the minima decreases (Fig. 2(c)) and at some critical value of the field (Fig. 2(d)) they are transformed into one minimum. This tendency remains irrespectively of the sign of the static distortion. Note, however, that for $\Delta > 0$ the shape of the adiabatic surface changes non-monotonically. In fact, with the increase of Δ , firstly, the two low-lying doublets become closer and then diverge (Fig. 1).

Positions of the minima in (q_u, q_v) space are related to the tetragonal distortions of the system. At the same time this space does not contain points corresponding to the additional trigonal distortions related to the trigonal field. The real distortions of the system in each minimum of the adiabatic potential can be presented as a superposition of the tetragonal distortion produced by the JT interaction and the trigonal distortion arising from the static crystal field; the last can be described in the extended vibrational space involving also trigonal (t_2) vibrations as a shift of the trigonal coordinate $Q = (q_\xi + q_\eta + q_\zeta)/\sqrt{3}$. In order to find the real symmetry of the system (that should be implied in the description of g -tensors and tensors of the TIP) one can construct the effective crystal field potential arising from the combined tetragonal (JT type) and trigonal (static) distortions, i.e., shift of Q . Crystal field potentials corresponding to the tetragonal distortions along C_4 axes X , Y and Z can be

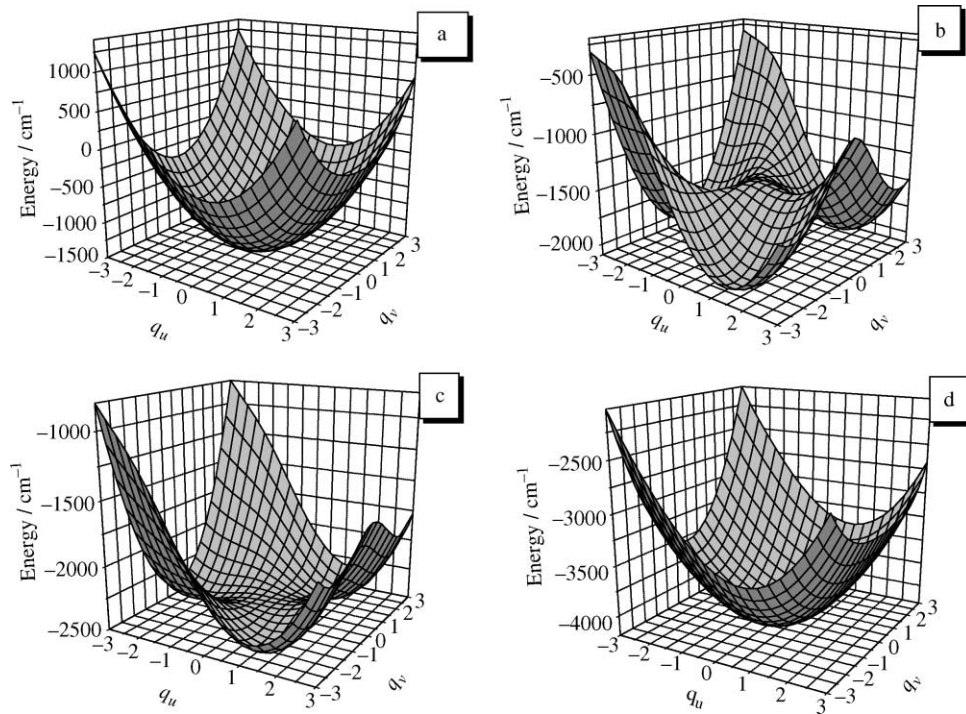


Fig. 2. The lower sheet of the adiabatic potential: $\lambda = -2100 \text{ cm}^{-1}$, $\kappa = 0.7$, $\hbar\omega = 400 \text{ cm}^{-1}$ and (a) $v = 1.5 \hbar\omega$, $\Delta = 0$, (b) $v = 3 \hbar\omega$, $\Delta = 0$, (c) $v = 3 \hbar\omega$, $\Delta = 2000 \text{ cm}^{-1}$, (d) $v = 3 \hbar\omega$, $\Delta = 4000 \text{ cm}^{-1}$.

associated with three non-orthogonal combinations of the E_g -type:

$$V_Z = V_{Eu}, \quad V_Y = -\frac{1}{2}V_{Eu} - \frac{\sqrt{3}}{2}V_{Ev}, \quad V_X = -\frac{1}{2}V_{Eu} + \frac{\sqrt{3}}{2}V_{Ev} \quad (19)$$

The trigonal distortion with C_3 axis [111] is related to the operator of T_2 -type:

$$(V_{T_2\xi} + V_{T_2\eta} + V_{T_2\zeta}/\sqrt{3}) \quad (20)$$

By substituting the coordinate representation for the operators involved in equations (19) and (20) one can find three crystal field operators corresponding to three tetragonal minima in the trigonally distorted system:

$$\begin{aligned} W_Z &= A(3z^2 - r^2) + B(yz + xz + xy) \\ W_Y &= A(3y^2 - r^2) + B(yz + xz + xy) \\ W_X &= A(3x^2 - r^2) + B(yz + xz + xy) \end{aligned} \quad (21)$$

Inspecting these potentials one can easily see that in each tetragonal minimum the system really belongs to the C_s point group (that is, in fact, the intersection of D_{4h} and D_{3d}) with the symmetry planes σ_{XY} , σ_{ZY} and σ_{XZ} , respectively. The parameters A and B are defined by competition of the PJT interaction and trigonal field, in particular, when the trigonal field suppresses tetragonal distortions and the potential becomes single-minimum, the parameter A vanishes. In this case the system proves to be trigonal.

The g and TIP tensors under the actual symmetry prove to be tri-axial. The main axes of g and TIP in each minimum are located in the corresponding planes σ and the directions of these axes cannot be determined by symmetry arguments solely, they move from C_4 (limit of strong PJT) to C_3 (strong trigonal field). When the tunneling processes are fast enough the observable g -factors are to be averaged over tetragonal minima that correspond to an average potential in equation (21). Summation over C_4 directions (over three minima) leaves only trigonal component, so that we arrive to the axial g -factors with the main axis C_3 . For the static susceptibility experiment the time scale is practically infinite, so the TIP tensor can be always regarded to C_3 axis.

To illustrate the behavior of g -factors in a simple way we assume that the tunneling is fast so that we are dealing with the averaged, i.e., trigonal symmetry. In this case for a three-well surface one can obtain the approximate expressions for the main components of g -factors and TIP:

$$\begin{aligned} g_{\parallel} &= \left(\frac{1}{3} \sum_{i=1}^3 g_{\bar{Z}\bar{Z}}^2(q_u^i, q_v^i) \right)^{1/2}, & g_{\perp} &= \left(\frac{1}{3} \sum_{i=1}^3 g_{\bar{X}\bar{X}}^2(q_u^i, q_v^i) \right)^{1/2} \\ \text{TIP}_{\parallel} &= \frac{1}{3} \sum_{i=1}^3 \text{TIP}_{\bar{Z}\bar{Z}}(q_u^i, q_v^i), & \text{TIP}_{\perp} &= \frac{1}{3} \sum_{i=1}^3 \text{TIP}_{\bar{X}\bar{X}}(q_u^i, q_v^i) \end{aligned} \quad (22)$$

where $\bar{X}$, $\bar{Y}$ and $\bar{Z}$ are the trigonal axes, $\bar{Z}$ coincides with the C_3 axis, q_u^i and q_v^i are the

coordinates of the i th minimum ($i = 1, 2, 3$). In the case of one minimum the g -factors and TIP are simply defined in the point $q_u = q_v = 0$, in this case the electronic wave-function can be associated with the function of a trigonal singlet, $(\xi + \eta + \zeta)/\sqrt{3}$.

In order to simplify the understanding of the magnetic behavior of the PJT system first we give some results for the limiting cases of strong crystal field ($|\Delta| \gg \nu$) when the PJT effect is completely quenched. Depending on the sign of Δ we face two cases. For $\Delta > 0$ the ground orbital singlet is well separated from excited ones so the spin–orbital coupling is suppressed. The system becomes isotropic and the g -factor takes on the spin-only value. Provided that $\Delta < 0$ the spin–orbital interaction is partially reduced. In this case we arrive at the fully anisotropic limit with $g_{\parallel} = 4$ and $g_{\perp} = 0$. Finally, when $\Delta = 0$ we obtain the isotropic g -factor that is different from the spin-only value due to the effect of covalence. In our case ($\kappa = 0.7$) g is equal to 1.6.

Figure 3 shows the averaged $g_{\parallel}$ and $g_{\perp}$ values as functions of the vibronic coupling parameter for $\Delta < 0$. When the vibronic coupling is weak, the g vs. $\nu/\hbar\omega$ curves exhibit plateaus. These plateaus appear due to the fact that for small vibronic coupling the lower sheet of the adiabatic surface has the only minimum. In this case $g_{\parallel}$ and $g_{\perp}$ values are just the same as those calculated within the static model. The increase of the absolute value of Δ tends to increase the anisotropy ($g_{\parallel}$ goes up and $g_{\perp}$ goes down). In the limiting case of very strong field the anisotropy reaches its

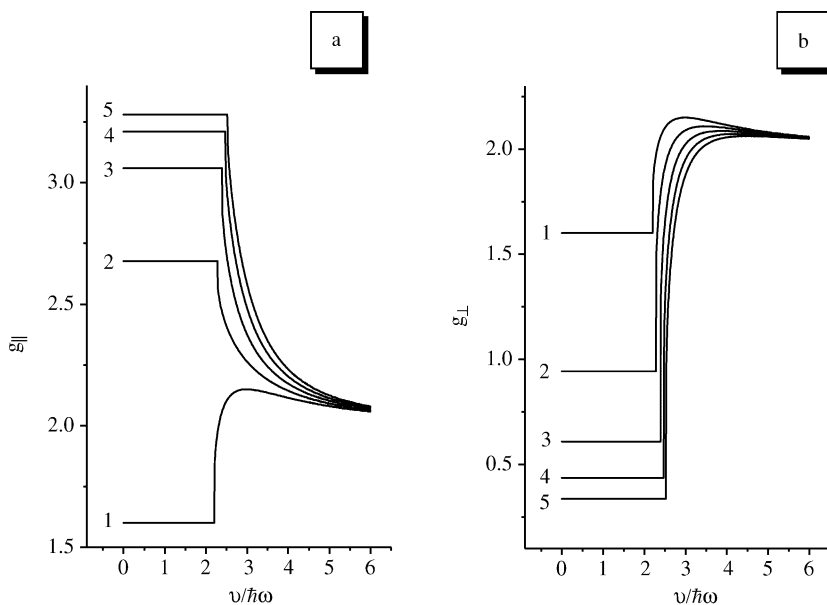


Fig. 3. Calculated principal values of the g -factors as functions of the vibronic coupling parameter for (1) $\Delta = 0$, (2) $\Delta = -1000 \text{ cm}^{-1}$, (3) $\Delta = -2000 \text{ cm}^{-1}$, (4) $\Delta = -3000 \text{ cm}^{-1}$, (5) $\Delta = -4000 \text{ cm}^{-1}$.

maximum ($g_{\parallel} = 4$ and $g_{\perp} = 0$). Each plateau ends at some critical value $\nu = \nu_C$ corresponding to the condition of instability for which a single-minimum surface is transformed into the surface possessing three quasi-tetragonal minima (Fig. 2). In this case both components of g -factor start to change in such a way that the anisotropy decreases. In the limit of strong vibronic coupling the anisotropy of g -factor disappears and g -factor reaches its pure spin value.

The case $\Delta > 0$ is presented in Fig. 4. The behavior of the g -factors is similar to that in the previous case but two differences should be noted. With the increase of trigonal field the difference between $g_{\parallel}$ and $g_{\perp}$ (i.e., the anisotropy of the g -factor) increases, passes through the maximum and then decreases. In the strong crystal field limit the g -factor becomes isotropic with $g_{\parallel} = g_{\perp} = g_e$. For relatively small positive Δ the non-monotonic dependence of the g -factors vs. $\nu/\hbar\omega$ is connected with the behavior of the energy levels in this range (see discussion in Section 4). Irrespective of the sign of the crystal field the strong vibronic coupling stabilizes the ground singlet state and consequently suppresses the spin–orbital interaction.

The TIP contributions as functions of $\nu/\hbar\omega$ are shown in Figs 5 and 6. The main common feature of $\text{TIP}_{\parallel}$ and $\text{TIP}_{\perp}$ is the presence of the plateau for relatively small values of vibronic parameter. However, for $\Delta < 0$ contrary to the g -factors the $\text{TIP}_{\parallel}$ values decrease with the growth of $|\Delta|$. In the limit of strong fields $\text{TIP}_{\parallel}$ vanishes. At the same time in the range of small ν -values $\text{TIP}_{\perp}$ remains practically constant. Thus TIP demonstrates a strong anisotropy just like the g -factors. This anisotropy comes

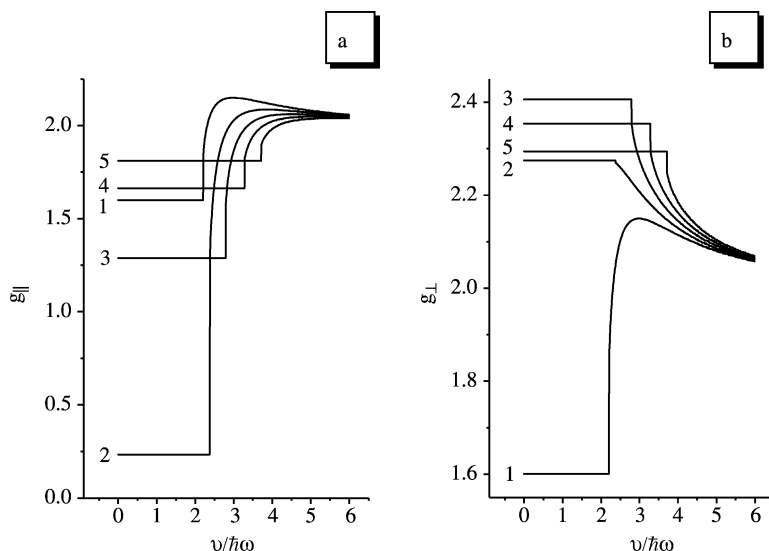


Fig. 4. Calculated principal values of the g -factors as functions of the vibronic coupling parameter for (1) $\Delta = 0$, (2) $\Delta = 1000 \text{ cm}^{-1}$, (3) $\Delta = 2000 \text{ cm}^{-1}$, (4) $\Delta = 3000 \text{ cm}^{-1}$, (5) $\Delta = 4000 \text{ cm}^{-1}$.

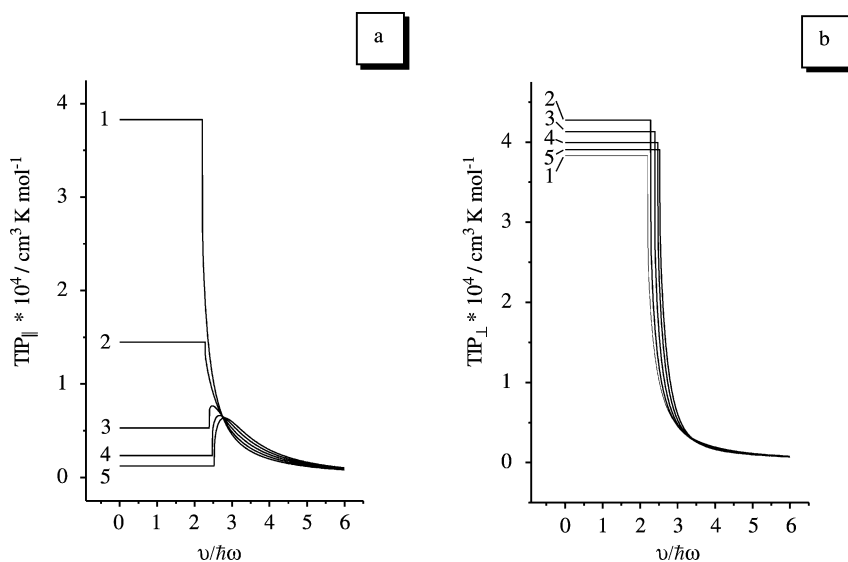


Fig. 5. Calculated principal values of TIP as functions of the vibronic coupling parameter for (1) $\Delta = 0$, (2) $\Delta = -1000 \text{ cm}^{-1}$, (3) $\Delta = -2000 \text{ cm}^{-1}$, (4) $\Delta = -3000 \text{ cm}^{-1}$, (5) $\Delta = -4000 \text{ cm}^{-1}$.

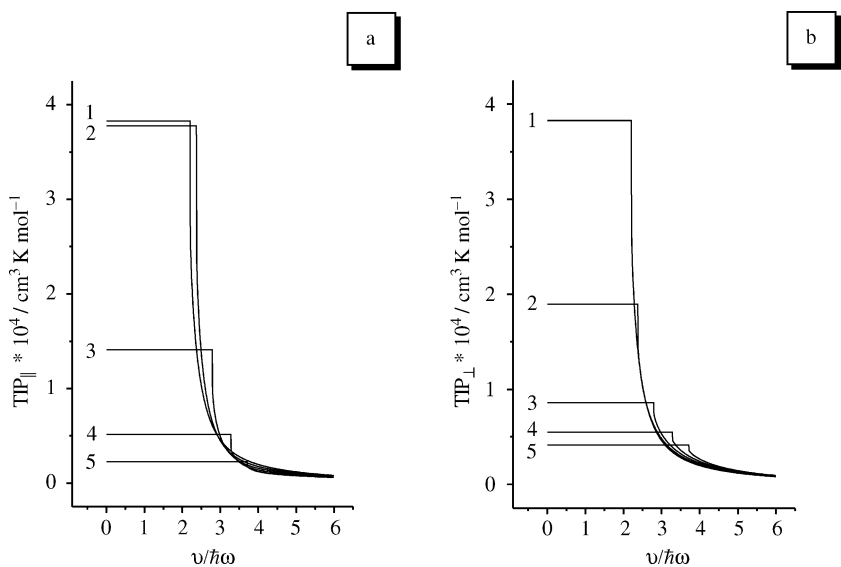


Fig. 6. Calculated principal values of TIP as functions of the vibronic coupling parameter for (1) $\Delta = 0$, (2) $\Delta = 1000 \text{ cm}^{-1}$, (3) $\Delta = 2000 \text{ cm}^{-1}$, (4) $\Delta = 3000 \text{ cm}^{-1}$, (5) $\Delta = 4000 \text{ cm}^{-1}$.

from the unquenched axial part of the spin–orbital interaction. For higher values of the vibronic constants when the ground adiabatic surface has three minima both components of TIP turn to zero. For positive values of the crystal field $TIP_{\parallel}$ and $TIP_{\perp}$ behave in a similar manner, namely, they demonstrate a strong decrease with the increase of Δ .

The behavior of the $TIP_{\parallel}$ and $TIP_{\perp}$ contributions in all cases is closely interrelated with that of the g -factors. The same physical reasons, i.e., the strength of the PJT effect (efficiency of the mixing of the ground and excited states) form the basis of such a behavior.

6. CONCLUDING REMARKS

In this chapter we have discussed the magnetic properties of the low-spin d^5 -ion in octahedral and quasi-octahedral ligand coordination. The developed model involves all relevant electronic interactions (the strong cubic crystal field, the spin–orbital splitting of the ground $^2T_2$ -state and the trigonal crystal field) as well as the vibronic coupling with the tetragonal vibrations that leads to the PJT effect. These interactions were shown to determine the magnetic characteristics, namely, the parallel and perpendicular components of the g -factor and TIP. The efficiency of mixing of two Kramers doublets (ground and excited) by the tetragonal modes active in PJT plays a crucial role in the magnetic anisotropy of the system. At the same time the trigonal crystal field facilitates or suppresses this mixing resulting thus either in the appreciable anisotropy or in the fully isotropic behavior.

This chapter is the first step in the study of the magnetic behavior of the complexes of 5d-ions. The model is based on the Born–Oppenheimer version of the adiabatic approximation, i.e., only the minima of the lower adiabatic surfaces are taken into account while calculating g -factors and TIP.

The validity conditions for the semiclassical adiabatic approach in the description of the systems with orbitally non-degenerate levels are elucidated in the basic works of Born and Oppenheimer (comprehensive discussion can be found in Refs. [6,7]). In these systems, the slow nuclear motion can be separated from the fast electronic one. The situation is quite different in the JT systems where, in general, this separation is impossible due to hybridization of the electronic and vibrational states. Nevertheless, in many important cases the adiabatic approach can serve as a relatively simple and at the same time powerful tool for the theoretical study of the JT systems giving accurate quantitative results and clear insight on the physical nature of the physical phenomena.

The question of the applicability of the semiclassical adiabatic approach to the vibronic problems in the JT systems is rather complicated in general and the thorough answer can be done with regard to a particular problem. In our brief discussion of this question we will refer to two areas – thermodynamic properties and resonance (optical) problems. In Ref. [9] the magnetic properties of mixed-valence dimeric and trimeric clusters are considered in the framework of

the PJT model with due account of Heisenberg exchange and double exchange. The results of the semiclassical calculations of the magnetic moments vs. temperature were carefully tested by comparison with quantum-mechanical results. The results exhibit surprisingly high accuracy of the semiclassical theory in a wide range of the temperature and coupling parameters (the worst error is less than 0.03%). The qualitative difference in the estimation of magnetic behavior between the semiclassical and dynamic approaches was intentionally found for a specific choice of the parameters when the ground vibronic levels belonging to different spin values are close. One can believe that this conclusion is common for the thermodynamic (non-resonance) characteristics of the JT systems that are defined exceptionally by the partition function.

On the contrary, the semiclassical approach in the problem of the optical absorption is restricted to a great extent and the adequate description of the phonon-assisted optical bands with a complicated structure caused by the dynamic JTE cannot be done in the framework of this approach [13]. An expressive example is represented by the two-humped absorption band of $A \rightarrow E \otimes e$ transition. The dip of absorption curve for $A \rightarrow E \otimes e$ transition to zero has no physical meaning because of the invalidity of the semiclassical approximation for this spectral range due to essentially quantum nature of the density of the vibronic states in the conical intersection of the adiabatic surface. This result is peculiar for the resonance (optical) phenomena in JT systems; full discussion of the condition of the applicability of the adiabatic approximation is given in Ref. [13].

Keeping in mind these results, in the present study we shall take advantage of the semiclassical adiabatic approach that seems to be rather good in the case of strong vibronic coupling. When the vibronic coupling is moderate the model provides less accuracy. However, even in this case it leads to a qualitatively adequate description of the magnetic properties and reasonable accuracy of the quantitative results. More exact treatment demands the solution of the dynamic PJT vibronic problem. The plateau discovered in the curves of TIP and g vs. vibronic coupling parameter is expected to exist also in the dynamic model but the stepwise behavior will change into stepless due to more smoothed distribution of nuclear configurations in the quantum-mechanical approach.

Using the developed model we are going to study two low-spin Re(II) compounds of the formulas $[\text{Re}(\text{triphos})(\text{CH}_3\text{CN})_3][\text{BF}_4]_2$ (compound **1**) and $[\text{Et}_4\text{N}][\text{Re}(\text{triphos})(\text{CN})_3]$ (compound **2**) containing the tripodal phosphine ligand $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ 1,1,1-tris(diphenylphosphinomethyl)ethane; abbreviated triphos). In both compounds the nearest quasi-octahedral ligand environment of the Re(II)-ion can be regarded approximately as the trigonal system belonging to the C_{3v} -symmetry group. The C_3 axis passes through the triangular face composed from the phosphorous ions and another face containing three nitrogen ions in compound **1** and three carbon atoms in compound **2**. Experimentally found effective magnetic moments 1.53 and 1.28 BM are lower than the pure spin $-\frac{1}{2}$ value 1.73 BM. At the same time TIP contributions to χ are 1.796×10^{-3} and 1.363×10^{-3} for compounds

1 and **2**, respectively. These values are one order of magnitude larger than the typical TIP values in the 3d-ions.

Interpretation of this unusual magnetic behavior requires consideration also of the terms arising from the excited electronic configurations (t_2^4e , $t_2^3e^2$, etc.). Along with the interactions so far considered the magnetic contribution coming from these states is expected to be of primary importance when the TIP is significant. This work is in progress.

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REFERENCES

- [1] B. Bleaney and M. C. M. O'Brien, *Proc. Phys. Soc.*, 1956, **B69**, 1216.
- [2] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 1970.
- [3] A. C. Chakravarty, *Introduction to the Magnetic Properties of Solids*, Wiley, New York, 1980.
- [4] S. A. Al'tshuler, B. M. Kozirev, *Electron Paramagnetic Resonance*, Nauka, Moskva, 1972.
- [5] R. Englman, *The Jahn–Teller Effect in Molecules and Crystals*, Wiley, London, 1972.
- [6] I. B. Bersuker, *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry*, Plenum Press, New York, 1984; I. B. Bersuker, *Chem. Rev.*, 2001, **101**, 1067.
- [7] I. B. Bersuker and V. Z. Polinger, *Vibronic Interaction in Molecules and Crystals*, Springer, New York, 1989.
- [8] P. L. W. Tregenna-Piggot, M. C. M. O'Brien, H. Weiche and H. U. Güdel, *J. Chem. Phys.*, 1998, **109**, 2967.
- [9] J. J. Borrás-Almenar, E. Coronado, H. M. Kishinevsky and B. S. Tsukerblat, *Chem. Phys. Lett.*, 1994, **217**, 525.
- [10] J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, A. V. Palii and B. S. Tsukerblat, *Chem. Phys.*, 2001, **274**, 131; J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, A. V. Palii and B. S. Tsukerblat, *Chem. Phys.*, 2001, **274**, 145.
- [11] D. A. Varshalovich, A. N. Moskalev and V. K. Khersonskii, *Quantum Theory of Angular Momentum*, World Scientific, Singapore, 1988.
- [12] G. F. Koster, J. O. Dimmock, R. G. Wheeler and H. Statz, *Properties of the Thirty-Two Point Groups*, M.I.T. Press, Cambridge, MA, 1963.
- [13] Yu. E. Perlin and B. S. Tsukerblat, Optical bands and polarization dichroism of Jahn–Teller Centers, *Dynamical Jahn–Teller Effect in Localized Systems*, Elsevier, Amsterdam, 1984, pp. 251–346.

Pseudo-Jahn–Teller Origin of the Metastable States in Sodium Nitroprusside

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This chapter is dedicated to Professor Isaak Bersuker on the occasion of his 75th birthday – to highlight his exceptional achievements and kudos

Abstract

A new model for the photochromic effect in sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]\cdot 2\text{H}_2\text{O}$ based on the concept of the pseudo-Jahn–Teller effect is proposed. The model takes into account the electron transfer from the Fe^{2+} ion to the π^* orbitals of the NO-ligand as well as the vibronic mixing of three electronic states of the Fe–NO fragment through the non-symmetric and full symmetric modes. The problem is solved within the adiabatic approximation. Under certain conditions, the lower sheet of the adiabatic potential is shown to possess three minima with the increasing energies that correspond to the N-bound, sideways bound, and O-bound NO group. The barriers between the minima are estimated and the excited minima are attributed to the MS2 and MS1 metastable states observed experimentally.

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1. INTRODUCTION

During the last decade, the fascinating phenomena of the photochromic effect became a hot problem of molecular structure and spectroscopy due to its promising application in the design of new memory storage systems at the molecular level. This phenomenon has been discovered and studied in several nitrosyl complexes of transition metal ions [1–6]. At low temperatures, the most extensively studied sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]\cdot 2\text{H}_2\text{O}$ (SNP) demonstrates two excited

metastable states (MS1 and MS2) induced by the visible light in the region 350–600 nm. At temperatures below 150 K the metastable states are long-living and do not show any indications of spontaneous and thermal decay. Both the metastable states can be depopulated by temperature rise or reversibly converted back to the ground state (GS) by red light irradiation. During the thermal decay of the metastable states no emission of radiation could be observed in the energy range 0.3–5 eV. Calorimetry experiments [7] show that the MS1 state is higher in energy than the MS2 state. Above 160 K, the decay of the metastable states in SNP obey the Arrhenius law with the activation energies 0.7 and 0.5 eV for MS1 and MS2, respectively [8]. The change in color exhibited with the generation of the excited MS1 and MS2 states has been proposed as the basis for the information storage system, since information can be written and erased reversibly using the light of two different wavelengths [8]. An essential advance in the study of the photochromic effect came from X-ray diffraction experiments [9,10] with the aid of which the geometries of the ground and the two excited metastable states have been determined. The atomic rearrangements were proved to be far from those that usually accompany optical excitation in molecules. The Fe–(NO) group was found to be linear in the GS. The diffraction evidences a bent geometry of the system in the MS2 state in which NO is sideways bound, while in the MS1 state an interchange of N and O takes place so that the NO group is connected with Fe through oxygen. Mössbauer [11] and electron-spin resonance (ESR) measurements [12] proved that the GS and both the metastable states are diamagnetic. The downshift of NO stretch and Fe–(NO) stretch frequencies suggest weaker bonds for MS1 and MS2 [13]. The phenomenon is quite general, in fact, metastable states with similar properties have been found in several nitrosyl–ruthenium and nitrosyl–osmium complexes [3–6].

Previous theoretical studies were focused on the DFT calculations of the energy of the SNP [14–16] as a function of the angle $\angle \text{FeNO}$. In Refs. [14–16], it was revealed that three minima of the ground term correspond to three possible configurations of the Fe–NO fragment: linear, bent, and inverted. At the same time DFT calculations [14–16] give a correct order of the energies of the GS, MS1, and MS2 states. In the detailed *ab initio* calculations carried out in the paper [17], the number of the variable structural parameters is extended and along with the consideration of the ground potential surface of the SNP the consideration in Ref. [17] takes into account the transition states connecting the states GS with MS2 and MS2 with MS1 that makes clear the effect of the transition states on the photo-isomerization. The Jahn–Teller coupling mechanism is discussed as an origin of the structural rearrangement.

Here we suggest a new model of the phenomenon based on the concept of the pseudo-Jahn–Teller (PJT) effect [18–20]. As distinguished from the previous work, our vibronic model allows us to examine the physical origin of the nuclear rearrangement and the underlying mechanism of the photochromic effect at the electronic level. At the same time, the proposed approach can be considered as a background for the dynamical (quantum–mechanical solution) of the problem of light absorption and emission including the crucial question of interpretation of the anomalous lifetimes for the excited states and shape-functions of the optical bands.

2. THE MODEL

At the first step, we consider the FeNO fragment of the whole SNP that is really involved in the photochromic reorganization. This approximation enables us to simplify the problem and to give clear insight on the mechanism of the phenomenon. Following the idea of the PJT effect we start with the ‘reference’ configuration of the FeNO fragment that is chosen to be triangular. For the sake of simplicity we will neglect the differences in the masses of N and O in the determination of normal vibrations, so the symmetry is supposed to be C_{2v} (Fig. 1). Although the atomic displacements in the photochromic reorganization cannot be considered as being small we will exploit an approximate way of consideration based on the presentation of the energy in terms of the normal coordinates. This difficult problem is common for JT systems with strong coupling and some efficient approaches have been formulated in the theory of so-called non-rigid molecules. We leave this important question out of the scope of the present consideration that is aimed to draw qualitative picture of the phenomenon.

The triangular molecule has [21,22] two normal vibrational coordinates that span two irreducible representations A_1 . In order to diagonalize the nuclear kinetic and potential energy we solve the classical problem of normal vibrations. In this way one obtains two A_1 coordinates

$$Q_{A_1}^{(1)} = \frac{\sqrt{M}(y_1 + y_3) - 2\sqrt{m}y_2}{\sqrt{4m + 2M}}, \quad Q_{A_1}^{(2)} = \frac{x_1 - x_3}{\sqrt{2}} \quad (1)$$

and one normal B_1 -mode

$$Q_{B_1} = \frac{(2\sqrt{m}x_2 - \sqrt{M}(x_1 + x_3))\sin(\varphi) + (y_3 - y_1)\sqrt{M}\cos(\varphi)}{\sqrt{4m\sin^2(\varphi) + 2M}} \quad (2)$$

where m is the mass of the Fe-atom, M is the mean mass of the N and O atoms, x_i, y_i, z_i are the Cartesian displacements of the Fe, N, and O atoms, and 2φ is the $\angle\text{NFeO}$ -angle in the ‘reference’ configuration (Fig. 1). For the two A_1 normal vibrational

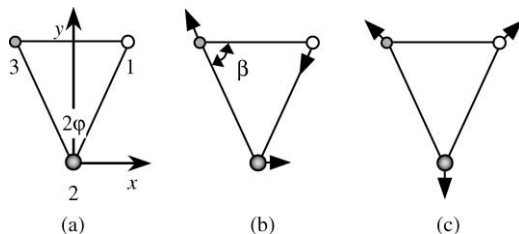


Fig. 1. Vibrations of the Fe–(NO) fragment: 1 – O; 2 – Fe; 3 – N; (a) ‘reference’ configuration; (b) non-symmetric B_1 -vibration; (c) full-symmetric A_1 -vibration.

modes we obtain:

$$q_{A_1}^{(1)} = 0.68Q_{A_1}^{(1)} + 0.26Q_{A_1}^{(2)}, \quad q_{A_1}^{(2)} = 0.32Q_{A_1}^{(1)} - 0.26Q_{A_1}^{(2)} \quad (3)$$

here the coefficients of transformation from $Q_{A_1}^{(i)}$ to $q_{A_1}^{(i)}$ ($i = 1, 2$) coordinates have been calculated with $m = 93 \times 10^{-24}$ g, $M = 25 \times 10^{-24}$ g, $\varphi = 16.5^\circ$ [10] and the typical value of $k = 10^5$ dyn cm $^{-1}$ for the force constant. The normal vibrational modes Q_{B_1} and $q_{A_1}^{(1)} \equiv q_{A_1}$ of the FeNO fragment are shown in Fig. 1. Further, on the second full symmetric vibration $q_{A_1}^{(2)}$ of the triangular moiety will not be taken into account insofar as its effect is similar to that of q_{A_1} . The frequencies corresponding to the Q_{B_1} and q -mode are found to be the following:

$$\begin{aligned} \omega_{B_1} &= \left(\frac{k}{m} \left(1 + \frac{2m}{M} \sin^2(\varphi) \right) \right)^{1/2} \\ \omega_{A_1} &= \left(\frac{k}{2mM} (3(m+M) - M \cos(2\varphi) - [(M \cos(2\varphi) - 3(m+M))^2 \right. \\ &\quad \left. - 8m(m+2M)]^{1/2}) \right)^{1/2} \end{aligned} \quad (4)$$

Starting from the accepted idealized C_{2v} symmetry of the FeNO fragment of the nitroprusside ion it is assumed that the metastable states are formed upon the light-induced charge transfer from the highest occupied molecular orbital (Fe, mainly a_2) to the lowest unoccupied orbitals a_1 and b_1 of mostly π^* NO character [17], here a_2 , a_1 , and b_1 are the irreducible representations of the C_{2v} group. Hereunder, small letters are used for labeling the symmetry of single orbitals, while capital letters denote the states of the whole FeNO moiety. The electronic basis includes the states of the system with the following fixed oxidation degrees of the fragments: ${}^1A_1(\text{Fe}^{2+}(a_1^2b_1^2a_2^2))$, ${}^1B_2(\text{Fe}^{3+}(a_1^2b_1^2a_2)b_1(\pi_x^*\text{NO}))$, ${}^1A_2(\text{Fe}^{3+}(a_1^2b_1^2a_2)a_1(\pi_y\text{NO}))$ (Fig. 2). These states are coupled by the electron transfer from the Fe^{2+} -ion to the π^* level of the NO-ligand. The PJT problem arises from the mixing of the ${}^1A_2$ and ${}^1B_2$ states by the B_1 -vibration of the triangle. The coupling of the states ${}^1A_1$, ${}^1A_2$, ${}^1B_2$ with the full symmetric vibration of the FeNO fragment is taken into account as well. In such a way, we face a two-mode-three level PJT problem $(A_1 + A_2 + B_2) \otimes (A_1 + B_1)$.

The full Hamiltonian of the fragment is presented in the form

$$H = H_e + H_{eL} + H_L \quad (5)$$

Here H_e is the electronic Hamiltonian determining the wave functions and the eigenvalues of the Fe–(NO) fragment in the fixed nuclear configuration. Reading off the coordinate q_{A_1} of the full symmetric vibration from its equilibrium position in the state ${}^1A_1(\text{Fe}^{2+}(d^6))$, one can write down the operator of the linear electron-vibrational interaction in the following form:

$$H_{eL} = (v_{A_1}(\mathbf{r}) - v)(q_{A_1} - q_{A_1}^o) + V_{B_1}(\mathbf{r})Q \equiv V_{A_1}(\mathbf{r})q + V_{B_1}(\mathbf{r})Q \quad (6)$$

here $\mathbf{r}$ represents the set of electronic coordinates of the Fe–(NO) fragment, $v = \langle {}^1A_1 | v_{A_1}(\mathbf{r}) | {}^1A_1 \rangle$, $q_{A_1}^o = -v/\hbar\omega_{A_1}$, $q = q_{A_1} - q_{A_1}^o$, the second term in equation (6) describes the operator of interaction with the B_1 -mode. Finally, H_L is the

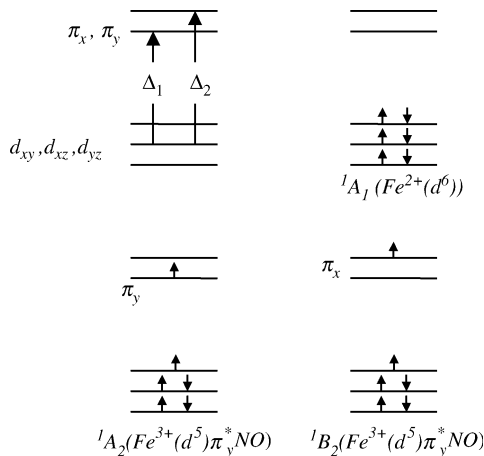


Fig. 2. Scheme of the electronic states of the Fe–(NO) fragment.

Hamiltonian of free lattice vibrations

$$H_L = \frac{\hbar\omega_{A_1}}{2} \left(q^2 - \frac{\partial^2}{\partial q^2} \right) + \frac{\hbar\omega_{B_1}}{2} \left(Q^2 - \frac{\partial^2}{\partial Q^2} \right) \quad (7)$$

The non-diagonal matrix elements $\langle {}^1A_2 | H_e | {}^1A_1 \rangle$ and $\langle {}^1B_2 | H_e | {}^1A_1 \rangle$ of the electronic Hamiltonian H_e represent parameters describing the electron transfer from the Fe^{2+} -ion to the π^* level of the NO ligand. At the first step these parameters were put equal to $\langle {}^1A_2 | H_e | {}^1A_1 \rangle = \langle {}^1B_2 | H_e | {}^1A_1 \rangle = t$. In the model under consideration, three vibronic parameters are involved. The parameter $V = \langle {}^1A_2 | V_{B_1} | {}^1B_2 \rangle$ characterizes the coupling of the states ${}^1B_2(\text{Fe}^{3+}(\text{d}^5)\pi_x^*\text{NO})$ and ${}^1A_2(\text{Fe}^{3+}(\text{d}^5)\pi_y^*\text{NO})$ by the B_1 -mode. The parameters $v_1 = \langle {}^1A_2 | v_{A_1} | {}^1A_2 \rangle - v$ and $v_2 = \langle {}^1B_2 | v_{A_1} | {}^1B_2 \rangle - v$ describe the interaction of the states ${}^1A_2$ and ${}^1B_2$ with the full-symmetric A_1 -mode. The matrix of the Hamiltonian H on the basis of the states ${}^1A_2$, ${}^1B_2$, ${}^1A_1$ can be represented in the following form:

$$H = \begin{pmatrix} \Delta_2 + v_2 q & VQ & t \\ VQ & \Delta_1 + v_1 q & t \\ t & t & 0 \end{pmatrix} + H_L \hat{I} \quad (8)$$

where $\hat{I}$ is the unit 3×3 -matrix. Then we employ the adiabatic approximation, neglecting thus the nuclear kinetic energy in the Hamiltonian H_L (equation (7)). In this approximation, the energies of the Fe–(NO) fragment represent the adiabatic potentials. In the general case, the analytical expression for the adiabatic potential is cumbersome and for this reason this expression is not given here. For negligible transfer $t = 0$ simple analytical expressions for the adiabatic surfaces can be found

from equation (8):

$$u_1(q, Q) = \frac{\hbar\omega_{A_1}q^2}{2} + \frac{\hbar\omega_{B_1}Q^2}{2} \quad (9)$$

$$u_{2,3}(q, Q) = \frac{\hbar\omega_{A_1}q^2}{2} + \frac{\hbar\omega_{B_1}Q^2}{2} + \frac{1}{2} \left[\Delta_1 + \Delta_2 + q(v_1 + v_2) \right. \\ \left. \mp \sqrt{4V^2Q^2 + (\Delta_1 - \Delta_2 + q(v_1 - v_2))^2} \right]$$

The adiabatic potential sheet $u_2(q, Q)$ has two equivalent minima at the points:

$$q_0 = \frac{\hbar\omega_{B_1}(\Delta_1 - \Delta_2)(v_1 - v_2) - 2v^2(v_1 + v_2)}{4V^2\hbar\omega_{A_1} - \hbar\omega_{B_1}(v_1 - v_2)^2} \quad (10)$$

$$Q'_{1,3} = \pm \frac{1}{2V} \left(\left(\frac{2V^2}{\hbar\omega_{B_1}} \right)^2 - (\Delta_1 - \Delta_2 + (v_1 - v_2)q_0)^2 \right)^{1/2}$$

One can see that the branches $u_2(q, Q)$ and $u_3(q, Q)$ do not have an oscillator form.

3. GROUND ADIABATIC POTENTIAL SHEET

The shapes of the adiabatic potential sheets are governed by eight parameters – V , v_1 , v_2 , Δ_1 , Δ_2 , t , ω_{B_1} , ω_{A_1} . In order to elucidate the conditions that favor the photochromic effect, first we shall try to discuss the values of the above-mentioned parameters. For the usually accepted value of $k \approx 10^5$ dyn cm⁻¹ the frequencies ω_{B_1} and ω_{A_1} are estimated as 340 and 400 cm⁻¹, respectively. The energy gaps Δ_2 and Δ_1 can be approximately identified with those between the HOMO and the split components of LUMO in the MS2 state. These values are calculated in paper [17] by the DFT method and prove to be equal to $\Delta_2 = 21185$ cm⁻¹ and $\Delta_1 = 15850$ cm⁻¹.

The vibronic coupling parameter V was roughly evaluated under the assumption that $v_1 = v_2 = 0$, $t = 0$. If the energy

$$E_a = \frac{\hbar\omega_{B_1}}{8V^2}(\Delta_2 + \Delta_1)^2 + \frac{V^2}{2\hbar\omega_{B_1}} - \frac{\Delta_1 + \Delta_2}{2} \quad (11)$$

of the thermally activated transition from the sheet $u_2(q=0, Q)$ to the sheet $u_1(q=0, Q)$ is set to be equal to the value 0.5 eV estimated by the calorimetry methods [7] for the MS2 state, one can estimate the parameter V as $V = 9.65\omega_{B_1}$. The validity of this estimation will be discussed below. The parameter t was taken in the range $0 \leq t \leq 10\omega_{B_1}$. Insofar as the energy gap Δ_2 exceeds significantly the gap Δ_1 the parameter v_2 was taken bigger than the parameter v_1 . Such a relation is predicted by the crystal field theory [21]. In Fig. 3, two different side views of the ground adiabatic potential sheet are shown for the set of parameters $V = 9.8\hbar\omega_{B_1}$, $t = 5.5\hbar\omega_{B_1}$, $v_2 = 6.2\hbar\omega_{B_1}$, $v_1 = 1.5\hbar\omega_{B_1}$, $\Delta_1 = 15850$ cm⁻¹, $\Delta_2 = 21185$ cm⁻¹, $\omega_{B_1} = 340$ cm⁻¹, $\omega_{A_1} = 400$ cm⁻¹. From Fig. 3a it is seen that the lower adiabatic

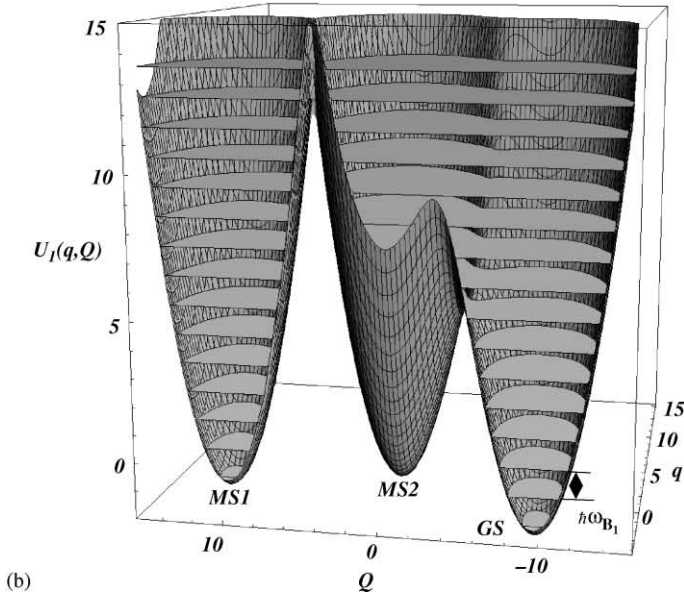
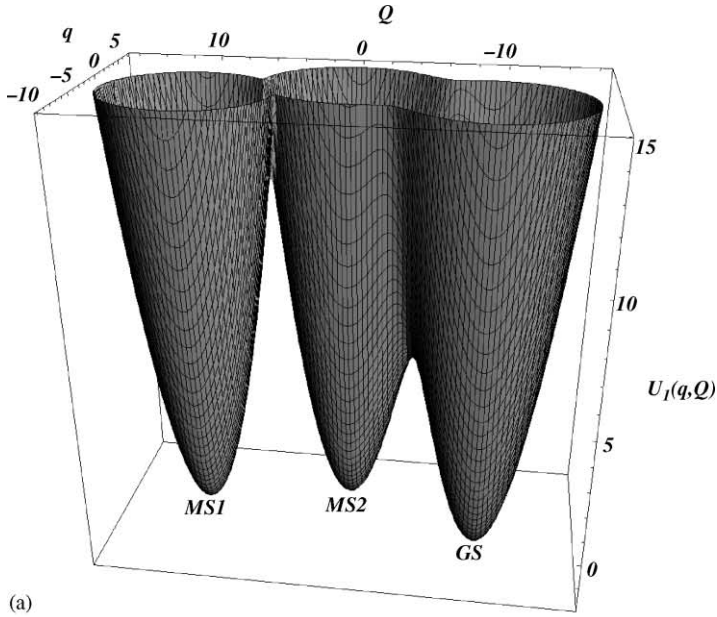


Fig. 3. Different views of the lower adiabatic potential sheet $U_I(q, Q)$ in the case of $V = 9.8\hbar\omega_{B_1}$, $t = 5.5\hbar\omega_{B_1}$, $v_2 = 6.2\hbar\omega_{B_1}$, $v_1 = 1.5\hbar\omega_{B_1}$, $\Delta_1 = 15850 \text{ cm}^{-1}$, $\Delta_2 = 21185 \text{ cm}^{-1}$, $\omega_{B_1} = 340 \text{ cm}^{-1}$, $\omega_{A_1} = 400 \text{ cm}^{-1}$.

potential branch has three minima, the energies of these minima are successively increased, so that the energy of the ground minimum is $-1.93\hbar\omega_{B_1}$, whereas the energies of the excited minima equal to $-1.15\hbar\omega_{B_1}$ and $-0.84\hbar\omega_{B_1}$. Thus, at temperatures below 180 K the thermal population of both excited minima is negligible. The order of minima alternation are also depicted in Fig. 4 illustrating the contour plot. At the same time Fig. 3a clearly demonstrates that the potential barrier separating the ground and first excited minima is lower than that separating the excited minima. A quantitative estimation of the barrier heights can be made with the aid of Fig. 3b wherein the adiabatic potential wells are cut by horizontal planes separated by the gaps $\hbar\omega_{B_1}$. The height of the barrier between the ground and the first excited minima is about $7.3\hbar\omega_{B_1} \approx 0.3$ eV. The barrier between the first and the second excited minima attains the value $13.7\hbar\omega_{B_1} \approx 0.6$ eV. At the next stage we determine the geometrical structure of the Fe-(NO) cluster corresponding to the minima of the ground adiabatic potential surface. With allowance for the relations between the Cartesian displacements of the Fe, N, and O atoms and the normal vibrational coordinates q and Q [equations (1)–(3)] of the FeNO fragment the angle $\beta \equiv \angle FeNO$ (Fig. 1) can be expressed as a function of the coordinates $\tilde{Q}_i$ and $\tilde{q}_i$ of the minima of the ground adiabatic potential sheet:

$$\begin{aligned} \beta_i = \frac{\pi}{2} - \arcsin \left[\tilde{Q}_i \sqrt{m} \sqrt{M + m - m \cos(2\varphi)} \cot(\varphi) / \left(l \sqrt{2M} (\sqrt{M} + \sqrt{m} \right. \right. \\ \left. \left. - \sqrt{M} \cos(2\varphi)) \right) \right] - \arcsin \left[\sin(\varphi) + \tilde{Q}_i \sqrt{M} \sqrt{2M + 4m \sin^2(\varphi)} \right. \\ \left. \times \sin(\varphi) \cos^2(\varphi) / \left(l (m + 2\sqrt{Mm} \sin^2(\varphi)) \right) + \left(\tilde{q}_i \sin(2\varphi) (2M + m) \right. \right. \\ \left. \left. \times \left(\sqrt{2M + 4m} (3M - \sqrt{(M \cos(2\varphi) - 3(M + m))^2 - 8m(2M + m)}) \right. \right. \right. \\ \left. \left. + \sqrt{2} \sqrt{M + 2m} (m - M \cos(2\varphi)) \right) \right) / \left(4l \sqrt{Mm} (\sqrt{2M} + \sqrt{m}) ((M + m) \right. \right. \\ \left. \left. \times \cos(2\varphi) - 3M + \sqrt{(M \cos(2\varphi) - 3(M + m))^2 - 8m(2M + m)}) \right) \right] \end{aligned} \quad (12)$$

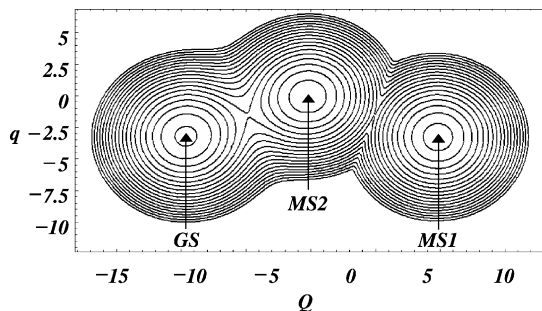


Fig. 4. Contour plot of the lower sheet $U_1(q, Q)$. The parameters are the same as in Fig. 3.

here l is the mean distance between Fe and N or between Fe and O atoms in the ‘reference’ configuration (Fig. 1), the indices $i = 1-3$ label the dimensional coordinates $\tilde{q}_i$, $\tilde{Q}_i$ and the angle β_i corresponding to the ground, first and second excited minima of the lower adiabatic potential branch. The values $\tilde{Q}_i$ and $\tilde{q}_i$ are connected with the dimensionless coordinates Q_i and q_i of the minima by the relations:

$$\tilde{Q}_i = Q_i \sqrt{\hbar/M_{B_1} \omega_{B_1}}, \quad \tilde{q}_i = q_i \sqrt{\hbar/M_{A_1} \omega_{A_1}} \quad (13)$$

where M_{B_1} and M_{A_1} are the effective masses for the B_1 and A_1 -vibrations [22,23]. The numerical values of M_{B_1} and M_{A_1} are equal to 3.545×10^{-23} g and 1.15×10^{-22} g, correspondingly. In Table 1 the calculated values of the angle β_i corresponding to the lowest (β_1) and the excited minima (β_2 , β_3) of the ground adiabatic potential sheet are given together with the experimental values of these angles determined by X-ray diffraction studies [10]. The angles β_i were evaluated with the value $l = 1.95 \times 10^{-8}$ cm⁻¹ taken from Ref. [10]. In Table 1, the dimensionless coordinates Q_i and q_i of the adiabatic potential minima are also listed. For the chosen set of parameters, the obtained values of the angles β_i are in quite a good agreement with experimental data [10]. So, the lowest minimum corresponds to the usual bonding of the Fe-ion with the NO-group and can be identified with the GS. The first excited minimum describes the bent geometry and can be assigned to the MS2 state. The highest minimum relates to a linear configuration, in which the NO-ligand has rotated by $\sim 180^\circ$ compared to the GS. Such an arrangement of the NO-group is characteristic of the MS1-state.

It should be mentioned that the coordinates Q_1 and Q_3 (see Table 1) of the ground and second excited minima nearly coincide with those estimated for $V = 9.83\hbar\omega_{B_1}$ with the aid of equation (10) in the case of $v_1 = v_2 = 0$. At the same time, the coordinate Q_2 of the first excited minimum is close to zero. From this it follows that the minima of the sheet $u_2(q = 0, Q)$ [equations (9) and (10)] convert into the minima GS and MS1 at the points Q_1 and Q_3 given in the table, whereas the minimum of the sheet $u_1(q = 0, Q)$ turns into the first excited minimum MS2 at the point Q_2 , when the values v_1 , v_2 , and t are non-vanishing. Such a minima conversion justifies to an extent the evaluation of the starting value of the parameter

Table 1. Angles (degrees) for the ground, first and second excited minima of the lower adiabatic potential sheet in the case of $V = 9.8\hbar\omega_{B_1}$, $t = 5.5\hbar\omega_{B_1}$, $v_2 = 6.2\hbar\omega_{B_1}$, $v_1 = 1.5\hbar\omega_{B_1}$, $\Delta_1 = 15850$ cm⁻¹, $\Delta_2 = 21185$ cm⁻¹, $\omega_{B_1} = 340$ cm⁻¹, $\omega_{A_1} = 400$ cm⁻¹

Minimum	Q_i	q_i	Angle β (theory)	Angle β (experiment[10])
Ground	-9.63	-3.21	146	176
First excited	-0.21	-0.06	74.8	82
Second excited	9.83	-3.28	0.1	3

V with the aid of equation (10) and the experimental value of the activation energy for the MS2-state. However, the inclusion in the model of the interaction with the full-symmetric vibration A_1 (Fig. 1) and of the electron transfer processes brings to a lower value of the barrier height between the ground (GS) and first excited minima (MS2) as compared with experimental data (see Fig. 3). The changes in Fe–N and Fe–O bonds have been also estimated. The calculated and experimental values of the lengthening are comparable. For instance, the difference between the Fe–O bond length in the GS and MS2 states was obtained to be equal to 0.4 Å, while the experimental value [10] is 0.7 Å.

In Fig. 5a, the energy gaps between the ground and excited minima as functions of the vibronic parameter V are reported. In Fig. 5b for the same values of the parameters the angles β_i describing the geometrical configurations of the Fe–(NO) moiety in these minima are given. When the vibronic parameter V falls inside the range $7 < V/\hbar\omega_{B_1} < 8.3$ the ground adiabatic potential sheet possesses only two minima. The ground minimum conforms with the bent configuration. In this case, the angle $\beta_2 = \beta_1 = 75^\circ$ remains practically unchanged in the above mentioned range of the parameter V . The first excited minimum lies much higher than the ground one. Meanwhile, with the increase of the parameter V the energy gap between the two minima diminishes. The angle β_3 that relates to the excited minimum decreases slowly for $V < 8.3\hbar\omega_{B_1}$ and corresponds to a slightly kinked configuration in which the NO-ligand is O-bound to the iron ion. In the range $8.3 < V/\hbar\omega_{B_1} < 9.72$ the lower adiabatic potential sheet has three minima. However, in the ground minimum the geometrical structure of the Fe–NO moiety remains bent ($\beta_1 = 75^\circ$). The first excited minimum conforms to a kinked configuration with the N-bound NO fragment. The corresponding angle β_2 increases with the growth of the parameter V , and the moiety Fe–N–O begins to straighten. At the same time the angle β_3 characterizing the geometrical structure of the FeNO molecule in the highest adiabatic potential minimum tends to zero. Only in a small range of the vibronic parameter V values $9.72 < V/\hbar\omega_{B_1} < 9.85$ the configurations of the Fe–NO cluster in the minima of the ground adiabatic potential sheet conform to those observed for SNP [10]. If the parameter ν_1 characterizing the coupling of the $^1A_2$ state with the full-symmetric vibration varies and all other parameters are fixed (Figs 6a and b) again only in a narrow range $0.95 < \nu_1/\hbar\omega_{B_1} < 1.63$ the situation resembles that in SNP. It is worth to note that changing the parameter ν_2 we also have found a single narrow range of its values allowing to interpret qualitatively the experimental data. As to the transfer integral (Figs 7a and b) in comparison with other characteristic parameters a much wider range of its change ($t/\hbar\omega_{B_1} > 4.4$) provides the observed order of the increase of the energy from the GS to MS2 and MS1 states. For ($t/\hbar\omega_{B_1} > 4.4$) the angles β_1 , β_2 , β_3 (Fig. 7b) corresponding to the states GS, MS1, and MS2 as well as the energy gap between the states GS and MS2 remain practically unchanged (Fig. 7a). Simultaneously the energy gap between GS and MS1 states increases with the growth of the parameter t (Fig. 7a). At the same time the increase of the parameter t in the range ($t/\hbar\omega_{B_1} > 4.4$) leads to the decrease of the heights of the barriers between GS and MS2 and

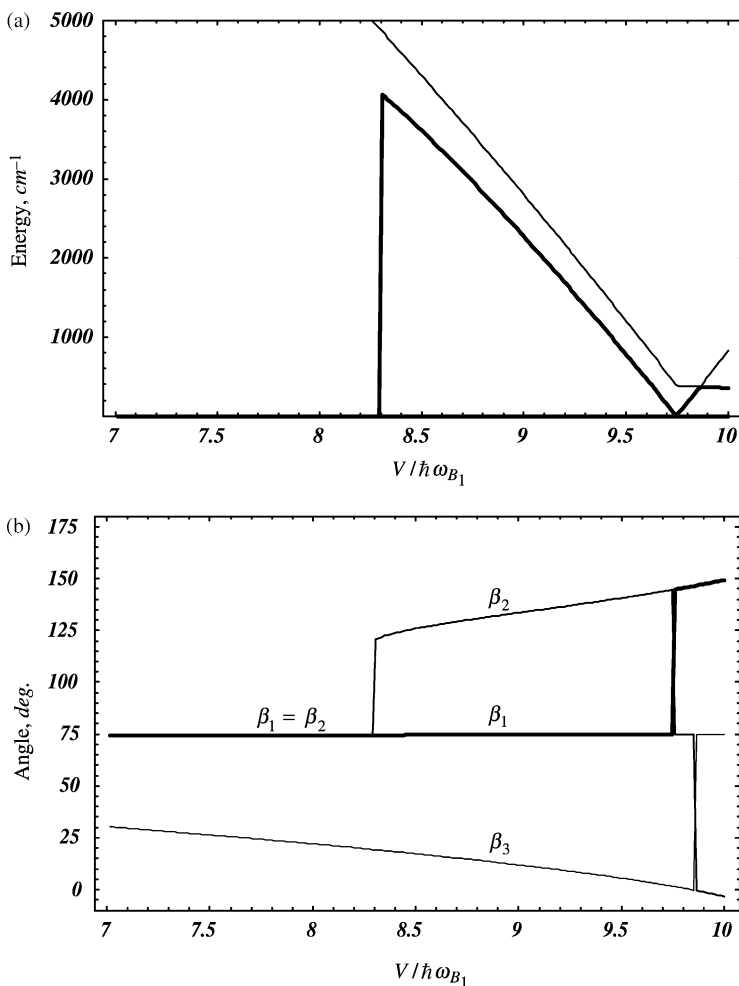


Fig. 5. Energy gaps (a) between the ground and excited minima of the lower adiabatic potential sheet $U_1(q, Q)$ and angles β_i (b) characterizing the configuration of the Fe–(NO) fragment in these minima as functions of the vibronic parameter V with $t = 5.5\hbar\omega_{B_1}$, $v_2 = 6.2\hbar\omega_{B_1}$, $v_1 = 1.5\hbar\omega_{B_1}$, $\Delta_{1;1} = 15850 \text{ cm}^{-1}$, $\Delta_2 = 21185 \text{ cm}^{-1}$, $\omega_{B_1} = 340 \text{ cm}^{-1}$, $\omega_{A_1} = 400 \text{ cm}^{-1}$.

—ground minimum, β_1 ;
 —energy gap between the first excited and ground minima, β_2 ;
 —energy gap between the second excited and ground minima, β_3 .

between MS2 and MS1. For instance, for $t = 5.5\hbar\omega_{B_1}$ the barrier height between GS and MS2 amounts to 0.3 eV, while for $t = 8\hbar\omega_{B_1}$ this height is equal to 0.2 eV. Survey of Figs 5b, 6b and 7b illustrating the influence of the parameters V , v_1 , and t on the angle $\angle \text{FeNO}$ (Fig. 2) leads to a conclusion that a range of these parameters

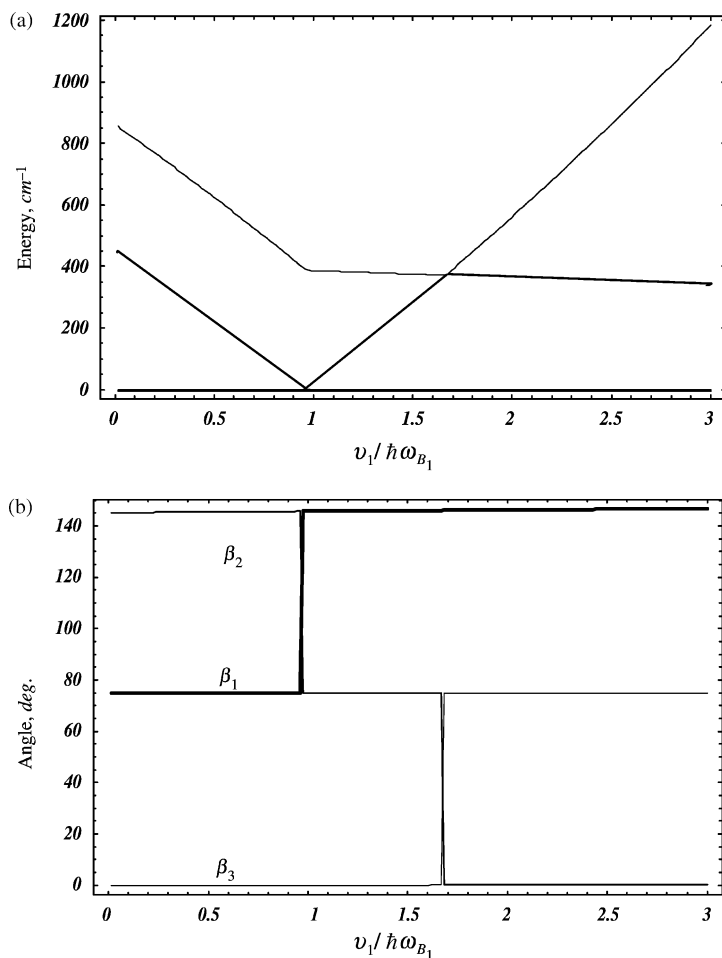


Fig. 6. Dependence of the energy gaps (a) between the ground and excited minima of the lower adiabatic potential sheet $U_1(q, Q)$ and of the angles β_i (b) determining the configuration of the Fe–(NO) moiety in these minima on the vibronic parameter v_1 with $V = 9.8\hbar\omega_{B_1}$, $t = 5.5\hbar\omega_{B_1}$, $v_2 = 6.2\hbar\omega_{B_1}$, $\Delta_1 = 15850 \text{ cm}^{-1}$, $\Delta_2 = 21185 \text{ cm}^{-1}$, $\omega_{B_1} = 340 \text{ cm}^{-1}$; $\omega_{A_1} = 400 \text{ cm}^{-1}$.

—ground minimum, β_1 ;

—energy gap between the first excited and ground minima, β_2 ;

—energy gap between the second excited and ground minima, β_3 .

can be indicated wherein the model reproduces the main experimental features of the photoexcited long-living metastable states in SNP and other transition-metal nitrosyl complexes [1–6]. In accordance with the experiment, we have obtained that in the MS1-state the nitrosyl group is linked with the iron ion on the oxygen atom

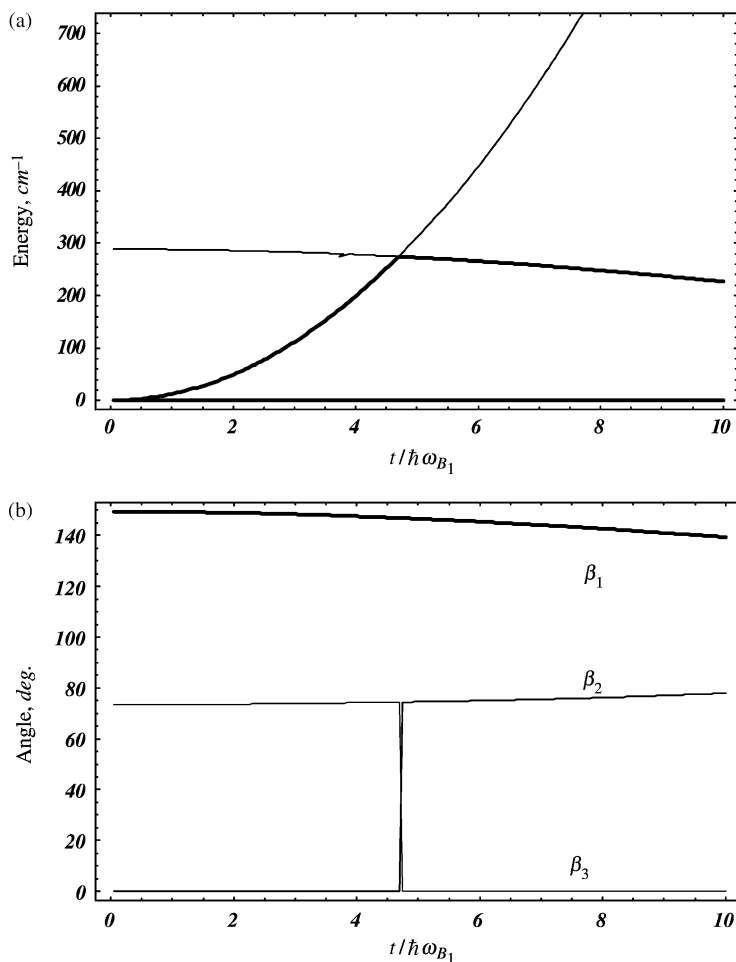


Fig. 7. Energy gaps (a) between the ground and excited minima of the lower adiabatic potential sheet $U_1(q, Q)$ and angles β_i (b) characterizing the configuration of the Fe–(NO) fragment in these minima as functions of the transfer parameter t with $V = 9.8\hbar\omega_{B_1}$, $v_2 = 6.2\hbar\omega_{B_1}$, $v_1 = 1.5\hbar\omega_{B_1}$, $\Delta_1 = 15850 \text{ cm}^{-1}$, $\Delta_2 = 21185 \text{ cm}^{-1}$, $\omega_{B_1} = 340 \text{ cm}^{-1}$, $\omega_{A_1} = 400 \text{ cm}^{-1}$.

—ground minimum, β_1 ;
—energy gap between the first excited and ground minima, β_2 ;
---energy gap between the second excited and ground minima, β_3 .

side, while in the MS2-state the coordination of nitrosyl is side-on. It should be noted that the study reported in this paper demonstrates the possibility of the existence of two metastable states that differ in energy and the corresponding configurations of the Fe–(NO) fragment. At the same time quantitative estimation

of the characteristic parameters for the Fe–(NO) cluster remains outside of our consideration. This problem needs special analysis in future.

4. QUALITATIVE DISCUSSION: CONCLUDING REMARKS

Below we briefly discuss the question of the heights of the barriers separating GS, MS1, and MS2 states and the mechanism of population of the metastable states by photoexcitation. In Fig. 8, the three adiabatic potential surfaces obtained by diagonalization of the Hamiltonian (8) are reported. The first excited adiabatic potential sheet $U_2(q, Q)$ has two minima, the highest sheet $U_3(q, Q)$ is cone-shaped and possesses one minimum. The light induced Franck–Condon transition from the lowest minimum (GS) of the ground adiabatic potential sheet $U_1(q, Q)$ to the sheet $U_3(q, Q)$ leads to the population of the single minimum of this sheet, then the relaxation can be followed by a radiative (or non-radiative) de-excitation onto the ground adiabatic potential surface populating thus with a significant probability the local minimum MS2. Another way of depopulation of the minimum of the branch $U_3(q, Q)$ passes through two minima of the middle adiabatic potential sheet $U_2(q, Q)$. In this case, GS, MS2, and MS1 may be populated. The light-induced transition of the system from GS to the $U_2(q, Q)$ surface results in the population of the highest minimum of this surface. The decay of this excitation may lead to the population of GS and MS2. The optical transitions from MS1 and

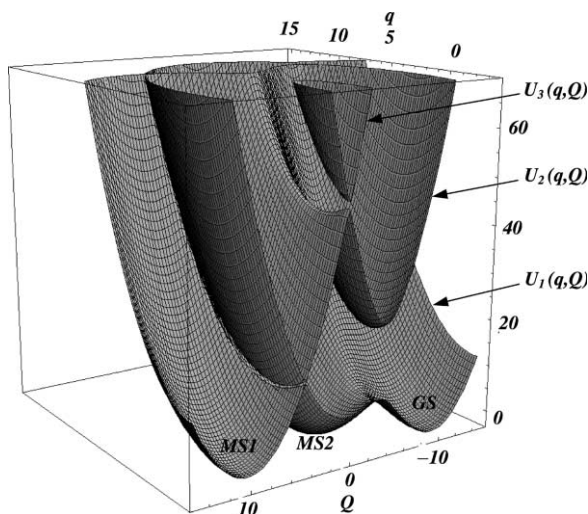


Fig. 8. The adiabatic potential sheets $U_1(q, Q)$, $U_2(q, Q)$, and $U_3(q, Q)$ in the case of $V = 9.8\hbar\omega_{B_1}$, $t = 5.5\hbar\omega_{B_1}$, $v_2 = 6.2\hbar\omega_{B_1}$, $v_1 = 1.5\hbar\omega_{B_1}$, $\Delta_1 = 15850\text{ cm}^{-1}$, $\Delta_2 = 21185\text{ cm}^{-1}$, $\omega_{B_1} = 340\text{ cm}^{-1}$, $\omega_{A_1} = 400\text{ cm}^{-1}$.

MS2 to $U_2(q, Q)$ have lower energies than that from GS to $U_3(q, Q)$. However, the transition $MS1 \rightarrow U_2(q, Q)$ populates MS2, whereas the transition $MS2 \rightarrow U_2(q, Q)$, in its turn, transfers the system to MS1. In such a way, the consideration carried out shows that in the framework of the adiabatic potential scheme presented in Fig. 8 it is possible to go from GS into MS1 and MS2, from MS1 into MS2 and *vice versa*. The indicated ways of population of the metastable states on the basis of the obtained adiabatic potential scheme are in qualitative agreement with experimental data [8]. However, at this stage, the estimation of the wavelengths of the corresponding transitions seems to be premature.

As to the obtained values of the barrier heights they have the same order of magnitude as the experimental values of the activation energies for the metastable states MS1 and MS2 [8]. The obtained relation between the barrier heights (Fig. 3b) separating the GS-state and the metastable states seems to be also correct. At the same time the order of the minima of the ground potential sheet, the higher barrier between the MS1 and MS2 states along with the absence of a direct contact between the potential wells corresponding to GS and MS1 (Figs 3b and 4) allows us to make a conclusion that our model gives a decay temperature for the MS2-state lower than that of the MS1-state, and this is in agreement with experimental data [7,8]. In spite of the fact that the calculated barriers are smaller than the experimental values of the activation energies these barriers are sufficiently large to explain the long lifetimes of the MS1 and MS2 states.

Qualitative comparison of the theory with experiment shows that the employed model takes into account the main physical interactions responsible for the existence of long-living metastable states which differ in energy and geometrical configuration. These interactions are: vibronic coupling with the non-symmetric B_1 -mode which bends the triangular fragment Fe–NO, vibronic coupling with the full-symmetric A_1 -mode mode and tunnel interaction which provoke different barrier heights and different energies of the lower adiabatic potential sheet minima. However, for a more complete description of the photochromic effect and metastable states it is necessary to solve the dynamic vibronic problem. The solution of this problem will give detailed information about the localization of the excitation in the minima of the lower adiabatic potential sheet. Not less important is the problem of quantum–mechanical calculation of the vibronic coupling constants and of the transfer parameter. Both these problems we are going to address to in future.

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REFERENCES

- [1] U. Hauser, V. Oestreich and H. D. Rohrweck, *Z. Phys.*, 1977, **A280**, 17, see also p. 125.
- [2] U. Hauser, V. Oestreich and H. D. Rohrweck, *Z. Phys.*, 1978, **A284**, 9.
- [3] Th. Woike, H. Zöllner, W. Krasser and S. Haussühl, *Solid State Commun.*, 1990, **73**, 149.
- [4] Th. Woike and S. Haussühl, *Solid State Commun.*, 1993, **86**, 333.
- [5] J. A. Güida, O. E. Piro and P. J. Aymonino, *Inorg. Chem.*, 1995, **34**, 4113.
- [6] K. Ookubo, Y. Morioka, H. Tomizawa and E. Miki, *J. Mol. Struct.*, 1996, **379**, 241.
- [7] H. Zöllner, Th. Woike, W. Krasser and S. Haussühl, *Z. Kristallogr.*, 1989, **188**, 139.
- [8] T. Woike, W. Kirchner, G. Schetter, T. Barthel, K. Hyung-Sang and S. S. Haussühl, *Opt. Commun.*, 1994, **106**, 6.
- [9] M. R. Pressprich, M. A. White, Y. Vekhter and P. Coppens, *J. Am. Chem. Soc.*, 1994, **116**, 5233.
- [10] M. D. Carducci, M. R. Pressprich and P. Coppens, *J. Am. Chem. Soc.*, 1997, **119**, 2669.
- [11] H. Zöllner, W. Krasser, T. Woike and S. Haussühl, *Hyperfine Interact.*, 1993, **7**, 265.
- [12] C. Terrile, O. R. Nascimento, I. J. Moraes, E. E. Castellano, O. E. Piro, J. A. Guida and P. J. Aymonino, *Solid State Commun.*, 1990, **73**, 481.
- [13] J. A. Guida, O. E. Piro and P. J. Aymonino, *Solid State Commun.*, 1986, **57**, 175.
- [14] B. Delley, J. Scheffer and Th. Woike, *J. Chem. Phys.*, 1997, **107**, 10067.
- [15] P. Boulet, M. Buchs, H. Chermette, C. Daul, F. Gilardoni, F. Rougemond, C. W. Schläpfer and J. Weber, *J. Phys. Chem.*, 2001, **A105**, 8991.
- [16] P. Boulet, M. Buchs, H. Chermette, C. Daul, F. Gilardoni, F. Rougemond, C. W. Schläpfer and J. Weber, *J. Phys. Chem.*, 2001, **A105**, 8999.
- [17] M. Atanasov and T. Schönherr, *J. Mol. Struct. (Theochem)*, 2002, **592**, 79.
- [18] R. Englman, *The Jahn–Teller Effect in Molecules and Crystals*, Wiley, London, 1972.
- [19] I. B. Bersuker, *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry*, Plenum Press, New York, 1984; I. B. Bersuker, *Chem. Rev.*, 2001, **101**, 1067.
- [20] I. B. Bersuker and V. Z. Polinger, *Vibronic Interaction in Molecules and Crystals*, Springer, New York, 1989.
- [21] L. D. Landau and E. M. Lifshits, *Mechanics*, Nauka, Moscow, 1965, p. 203.
- [22] J. P. Elliot, P. G. Dawler, *Symmetry in Physics*, Principles and Simple Applications, The Macmillan Press Ltd, London, 1979, Vol. 1, p. 364.
- [23] Yu. E. Perlin and B. S. Tsukerblat, *Effects of Electron-Vibrational Interaction in the Optical Spectra of Paramagnetic Impurity Ions*, Kishinev, Shtiintsa, 1974.

Jahn–Teller Ions in Cubic Crystals Explored Through DFT Calculations

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Abstract

The behaviour of Jahn–Teller ions in cubic insulating lattices has been explored by means of cluster calculations within the density functional theory (DFT) framework. In systems with octahedral coordination parameters like the Jahn–Teller energy, E_{JT} , or the angular frequency, ω_E , have been derived from the Q_θ ($\approx 3z^2 - r^2$) dependence of total energy. Results for NaCl:Rh²⁺ have been obtained for $(3z^2 - r^2)^1$, $(x^2 - y^2)^1$, and also $(3z^2 - r^2)^{0.5} \times (x^2 - y^2)^{0.5}$ electronic configurations. In agreement with experimental data for NaCl:Rh²⁺ the present calculations lead to a strong Jahn–Teller effect ($E_{JT}/\hbar\omega_E \approx 6$) and to an elongated octahedron as equilibrium geometry characterised by $Q_\theta^0 = 0.30 \text{ \AA}$. For a compressed geometry the corresponding energy minimum is found to be about 0.03 eV above and characterised by $Q_\theta^0 = -0.22 \text{ \AA}$. As salient feature these facts are shown to come essentially from the anharmonicity involved in the E_g vibrational mode and not from the quadratic coupling between this mode and the ground electronic state. The value $E_{JT}/\hbar\omega_E = 0.65$ obtained for MgO:Cu²⁺ is consistent with the observation of electron paramagnetic resonance (EPR) spectra displaying a cubic angular pattern. The $E_{JT}/\hbar\omega_E$ ratio is shown to increase by a factor of three on passing from MgO:Cu²⁺ to SrO:Cu²⁺. The origin of this important variation, consistent with the observation of static EPR spectra for SrO:Cu²⁺, are briefly discussed. Finally the present results on SrCl₂:Cu²⁺ support the existence of a big off-centre motion of Cu²⁺ along $\langle 001 \rangle$ directions. This conclusion stresses the importance of theoretical calculations for cases where model Hamiltonians based in truncated series expansion can hardly be meaningful.

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1. INTRODUCTION

Impurities like d^7 (Rh^{2+}) or d^9 (Cu^{2+} , Ag^{2+}) ions placed substitutionally in cubic insulating lattices with octahedral coordination would exhibit an orbitally degenerate E_g ($\sim x^2 - y^2$; $3z^2 - r^2$) ground state if ligand ions are kept frozen. Nevertheless the angular pattern of associated electron paramagnetic resonance (EPR) spectra at low temperature often displays a tetragonal symmetry and, less frequently, a cubic one [1–6]. The first situation reflects what is called a static Jahn–Teller effect, whereas in the second one the ground state wavefunction has a vibronic character and thus it cannot properly be described within the adiabatic approximation [1–3,6]. Moreover, when temperature is raised the EPR spectrum can become isotropic. This variety of behaviours has been accounted for [1,3,6] through a parameterised model-Hamiltonian involving basically a *linear* coupling between the orbitally degenerate E_g state and the vibrational E_g mode of the MX_6 complex formed with ligands and characterised by an angular frequency ω_E . To this end it is also crucial to take into account the effects of random strains which are unavoidably present in any real crystal [2,3,5]. Such strains are the ultimate responsible for the observation of EPR spectra displaying a tetragonal symmetry [3].

The vibrational E_g mode is described by the Q_θ ($\sim 3z^2 - r^2$) and Q_e ($\sim x^2 - y^2$) coordinates. Under a $Q_\theta > 0$ distortion a MX_6 complex becomes tetragonally *elongated* (Fig. 1) with four short equatorial ligands at a distance $R_{\text{eq}} = R_0 - a$ and

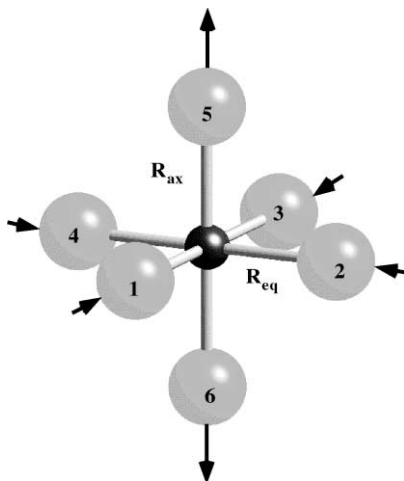


Fig. 1. Picture of a tetragonally elongated MX_6 complex.

two further axial ligands lying at $R_{\text{ax}} = R_0 + 2a$. Here R_0 denotes the equilibrium metal–ligand distance expected for an octahedral coordination while $Q_\theta = \sqrt{12}a$.

The ground state behaviour observed for Jahn–Teller impurities in cubic lattices has often been explained *a posteriori* by fitting experimental data to quantities like the average random strains, the Jahn–Teller energy, E_{JT} , or the ω_{E} frequency [5]. In particular when $E_{\text{JT}}/\hbar\omega_{\text{E}} \leq 1$ the observation at low temperatures of a cubic angular pattern is favoured, while if $E_{\text{JT}}/\hbar\omega_{\text{E}} > 1$ a static EPR spectrum is expected [1–3].

Theoretical calculations can help to improve this situation as reasonable values of the $E_{\text{JT}}/\hbar\omega_{\text{E}}$ quantity can, in principle, be obtained from them. Furthermore theoretical calculations can be useful for *checking the validity* of the model-Hamiltonian as well as for providing values of involved parameters. Therefore, from this approach the relative weight of different terms involved in the model-Hamiltonian can be assessed. In this sense it is worth remarking that the anharmonic term and the so-called quadratic Jahn–Teller coupling term can *both* explain the existence of adiabatic minima displaying tetragonal symmetry [1,3,7,8]. Density functional theory (DFT) is particularly suitable for achieving the present goals mainly because it allows one to deal with fractional electronic occupancy [9]. Therefore it can easily be used for exploring the influence of the electronic degeneracy upon total energy for *any value* of the distortion coordinate.

The present work is firstly focused on the D_{4h} Rh^{2+} centre in NaCl where active electrons are lying just in the RhCl_6^{4-} complex formed with six closest anions [10]. By means of adiabatic DFT calculations performed for the perfect O_h geometry and also for different values of the Q_θ coordinate the meaning and weight of parameters involved in the model-Hamiltonian are analysed. To this aim particular attention is paid to the Q_θ dependence of one electron energies, ε_a and ε_b , associated with the antibonding a_{1g} ($\sim 3z^2 - r^2$) and b_{1g} ($\sim x^2 - y^2$) orbitals.

In a second step, first results obtained for the $E_{\text{JT}}/\hbar\omega_{\text{E}}$ quantity for Cu^{2+} in cubic oxides [1–6] (MgO and SrO) are shown. This study sheds some light on the occurrence of dynamic vibronic effects in Cu^{2+} -doped MgO [2–4,6]. The present methodology can also be applied to systems where the distortion coordinate at equilibrium becomes *comparable* to interatomic distances. Along this line some results reached for d^9 ions in crystal with fluorite structure [2,11] will also briefly discussed.

2. ANALYSIS OF THE MODEL-HAMILTONIAN

For the sake of clarity let us take as a guide the case of a substitutional Rh^{2+} impurity in NaCl with a remote charge compensation [10]. If the local symmetry displayed by ligands of RhCl_6^{4-} is kept octahedral the ground state configuration for this $4d^7$ system is $t_{2g}^6 e_g^1$ and the electronic ground state ${}^2E_g$ involves orbital degeneracy. In DFT it is however possible to deal also with the *artificial* $(3z^2 - r^2)^{0.5}(x^2 - y^2)^{0.5}$ configuration (implying a ${}^1A_{2g}$ ground state) where orbital degeneracy is excluded [12]. Looking at the dependence of the total energy, E , on the metal–ligand distance, R , for such a configuration the equilibrium R_0 value

corresponding to RhCl_6^{4-} embedded in the host lattice can be derived. In this situation the corresponding orbitals $|a_{1g}^0\rangle$ and $|b_{1g}^0\rangle$ would have the *same* one-electron energy.

Let us now consider the adiabatic variation of the total energy, $E(Q_\theta, Q_\varepsilon)$, induced by a E_g distortion of the RhCl_6^{4-} complex keeping the $(3z^2 - r^2)^{0.5}(x^2 - y^2)^{0.5}$ electronic configuration. In the absence of orbital degeneracy it is expected that for such a configuration $E(Q_\theta, Q_\varepsilon)$ has the form [1–3,7]:

$$E = E_0 + (1/2)K(Q_\theta^2 + Q_\varepsilon^2) - A_3(Q_\theta^3 - 3Q_\varepsilon^2 Q_\theta) \quad (1)$$

The force constant, K , determines ω_E in the harmonic approximation by the relation

$$M_L \omega_E^2 = K \quad (2)$$

where M_L is the ligand mass. The last term in equation (1) reflects the anharmonicity *inevitably* present in any potential energy of a *real* molecule [7]. Considering a distortion involving only Q_θ it can reasonably be expected that

$$|A_3| \sqrt{12} R_0 \approx K \quad (3)$$

Of course the truncated expansion in equation (1) is meaningful provided

$$Q_\theta < \sqrt{12} R_0 \quad (4)$$

For comparison purposes between the $(3z^2 - r^2)^{0.5}(x^2 - y^2)^{0.5}$ and $(3z^2 - r^2)^1$ or $(x^2 - y^2)^1$ configurations the small exchange interaction between the two half electrons in $(3z^2 - r^2)^0(x^2 - y^2)^{0.5}$ should be removed from E_0 in equation (1). When in a subsequent step the $(3z^2 - r^2)^{0.5}(x^2 - y^2)^{0.5}$ configuration is replaced by $(3z^2 - r^2)^1$ or $(x^2 - y^2)^1$ in D_{4h} symmetry then an *additional* contribution to the total energy comes out. Such a contribution basically arises from the different occupancy of antibonding a_{1g} ($\sim 3z^2 - r^2$) and b_{1g} ($\sim x^2 - y^2$) orbitals which are not degenerated in D_{4h} symmetry. In the DFT framework [9] the Q_θ dependence of ε_a and ε_b reflects the changes, $\Delta v_e(\mathbf{r})$, experienced by the so-called *external potential* $v_e(\mathbf{r})$. If the distortion is *small* the effect of $\Delta v_e(\mathbf{r})$ is considered in the basis set formed *only* by the $|a_{1g}^0\rangle$ and $|b_{1g}^0\rangle$ kets. In this situation the Q_θ dependence of ε_a and ε_b is described by the following effective Hamiltonian:

$$H_{\text{eff}} \approx H^1 + H^2 \quad (5)$$

The first term, H^1 , reflects the *linear* coupling between the electronic state (displayed by $|a_{1g}^0\rangle$ and $|b_{1g}^0\rangle$) and the E_g distortion mode [1–3]

$$H^1 = V(\mathbf{U}_\theta Q_\theta + \mathbf{U}_\varepsilon Q_\varepsilon), \quad \mathbf{U}_\theta = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \mathbf{U}_\varepsilon = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (6)$$

The two 2×2 matrices have zero trace following the centre of the gravity theorem [13]. The second term in equation (5), H^2 , corresponds to quadratic coupling and, according to symmetry requirements, depends on *two* independent constants,

V_q and V_s , and has the form:

$$H^2 = -V_q\{\mathbf{U}_\theta(Q_\varepsilon^2 - Q_\theta^2) + 2\mathbf{U}_\varepsilon Q_\varepsilon Q_\theta\} + V_s(Q_\varepsilon^2 + Q_\theta^2)\mathbf{I} \quad (7)$$

where $\mathbf{I}$ is the 2×2 identity matrix.

If *only* H^1 is considered in H_{eff} the Q_θ dependence of ε_a and ε_b (for $Q_\varepsilon = 0$) is simply linear

$$\varepsilon_a = \varepsilon_0 - VQ_\theta, \quad \varepsilon_b = \varepsilon_0 + VQ_\theta \quad (8)$$

When the role of H^2 cannot be neglected the Q_θ dependence of ε_a and ε_b has departures from the linearity described by equation (7), with

$$\varepsilon_a = \varepsilon_0 - VQ_\theta + (V_s - V_q)Q_\theta^2, \quad \varepsilon_b = \varepsilon_0 - VQ_\theta + (V_s + V_q)Q_\theta^2 \quad (9)$$

According to equation (9) the departures from the linearity are thus *different* for a_{1g} ($\sim 3z^2 - r^2$) and b_{1g} ($\sim x^2 - y^2$) orbitals. Usually the isotropic term involving V_s in equation (7) is not considered in the description of the quadratic coupling [1,3,8] but included implicitly within the quadratic term of equation (1). Although both terms are formally equivalent, the removal of $V_s(Q_\varepsilon^2 + Q_\theta^2)\mathbf{I}$ term in equation (7) leads however to $\varepsilon_b - \varepsilon_0 - VQ_\theta = \varepsilon_0 - \varepsilon_a - VQ_\theta$, which is in general wrong.

If for simplicity only Q_θ variations are considered the validity of the series expansion gathered in equations (5)–(7) is favoured when phenomena happen in the region verifying

$$V_q Q_\theta \ll V, \quad V_s Q_\theta \ll V \quad (10)$$

Bearing in mind the present analysis the Q_θ dependence of the total energy can easily be written for the two possible electronic states

$$\begin{aligned} E(3z^2 - r^2; Q_\theta) &= E_0 - VQ_\theta + (1/2)KQ_\theta^2 - A_3Q_\theta^3 + (V_s - V_q)Q_\theta^2 \\ E(x^2 - y^2; Q_\theta) &= E_0 + VQ_\theta + (1/2)KQ_\theta^2 - A_3Q_\theta^3 + (V_s + V_q)Q_\theta^2 \end{aligned} \quad (11)$$

If, in a first approximation, the anharmonic and quadratic coupling terms are discarded the associated adiabatic minima, $Q_\theta^0(3z^2 - r^2)$ and $Q_\theta^0(x^2 - y^2)$, are found to occur at [1,3]

$$\begin{aligned} Q_\theta^0(3z^2 - r^2) &= Q_\theta^* = \frac{V}{K} \\ Q_\theta^0(x^2 - y^2) &= -Q_\theta^* = -\frac{V}{K} \end{aligned} \quad (12)$$

According to equation (4) the result collected in equation (12) is reasonable provided

$$|V/K| \ll \sqrt{12}R_0 \quad (13)$$

Typical values for the force constant lie in the $1\text{--}10 \text{ eV/\AA}$ range. Following results collected in Refs. [14,15] values in the $1\text{--}3 \text{ eV/\AA}$ range can be expected. The

symmetry conveyed by equation (12) is destroyed when, in a second step, the anharmonic and quadratic coupling terms are taken into consideration. In that case $Q_\theta^0(3z^2 - r^2)$ and $Q_\theta^0(x^2 - y^2)$ can be approximated by

$$\begin{aligned} Q_\theta^0(3z^2 - r^2) &= Q_\theta^* + \Delta(3z^2 - r^2) \\ Q_\theta^0(x^2 - y^2) &= -Q_\theta^* + \Delta(x^2 - y^2) \\ K\Delta(3z^2 - r^2) &= 3A_3(Q_\theta^*)^2 + 2Q_\theta^*(V_q - V_s) \\ K\Delta(x^2 - y^2) &= 3A_3(Q_\theta^*)^2 + 2Q_\theta^*(V_q + V_s) \end{aligned} \quad (14)$$

The anharmonic and quadratic coupling terms are also responsible for the different values of $E(3z^2 - r^2; Q_\theta^0)$ and $E(x^2 - y^2; Q_\theta^0)$

$$\begin{aligned} E(3z^2 - r^2; Q_\theta^0) &\cong E_0 - E_{JT} - A_3(Q_\theta^*)^3 + (V_s - V_q)(Q_\theta^*)^2 \\ E(x^2 - y^2; Q_\theta^0) &\cong E_0 - E_{JT} + A_3(Q_\theta^*)^3 + (V_s + V_q)(Q_\theta^*)^2 \end{aligned} \quad (15)$$

where the Jahn–Teller energy, E_{JT} , is given by [1–3]

$$E_{JT} = V^2/(2K) \quad (16)$$

Therefore the separation, δE , between the two minima of equation (15) is given by

$$\delta E \equiv E(x^2 - y^2; Q_\theta^0) - E(3z^2 - r^2; Q_\theta^0) = 2A_3(Q_\theta^*)^3 + 2V_q(Q_\theta^*)^2 \quad (17)$$

This result implies that the minimum associated with the $3z^2 - r^2$ electronic state is the lowest one if the anharmonic term dominates and $A_3 > 0$ or if the quadratic coupling is the leading term and V_q is positive. The curvature at the minimum of $E(3z^2 - r^2; Q_\theta)$ and $E(x^2 - y^2; Q_\theta)$ curves also depends on both the anharmonic and quadratic coupling terms

$$\begin{aligned} \left(\frac{\partial^2 E(3z^2 - r^2; Q_\theta)}{\partial Q_\theta^2} \right)_{Q_\theta^0} &\approx K - 6A_3Q_\theta^* - 2(V_q - V_s) \\ \left(\frac{\partial^2 E(x^2 - y^2; Q_\theta)}{\partial Q_\theta^2} \right)_{Q_\theta^0} &\approx K + 6A_3Q_\theta^* + 2(V_q + V_s) \end{aligned} \quad (18)$$

Therefore if quadratic coupling can be neglected and $A_3 > 0$ the curvature for the $3z^2 - r^2$ electronic state is softened, while that for the $x^2 - y^2$ state increases. Of course the same effect is produced if A_3 is negligible and $V_q > 0$. The present description can be applied to a good extent to the case of substitutional d^9 ions in cubic lattices with octahedral coordination. Under a Q_θ distortion there are two electronic states in D_{4h} : in B_{1g} the hole is in b_{1g} ($\sim x^2 - y^2$), while in A_{1g} it is placed in the a_{1g} ($\sim 3z^2 - r^2$) orbital. Bearing in mind this fact the $E(B_{1g}; Q_\theta)$ curve for d^9 ions looks similar to $E(3z^2 - r^2; Q_\theta)$ for d^7 ions.

3. DFT CALCULATIONS FOR RhCl_6^{4-} IN NaCl: EVALUATION OF PARAMETERS

Rhodium-centred clusters involving up to a total of 87 atoms have been used in order to investigate the properties of RhCl_6^{4-} embedded in NaCl. The use of finite clusters for describing the properties of $\text{NaCl}:\text{Rh}^{2+}$ is consistent with the highly localized character of the unpaired electron residing only in the RhCl_6^{4-} complex region [12]. Calculations have been carried out using the Amsterdam Density Functional (ADF) code [16] and the generalized gradient approximation (GGA). The effects of the electrostatic potential due to the rest of the ions in the host lattice upon the studied cluster have been considered in all calculations. Basis sets of the best quality in the ADF code have been employed. More details can be found elsewhere [12]. The equilibrium distance $R_0 = 2.53 \text{ \AA}$, obtained for the $(3z^2 - r^2)^{0.5}(x^2 - y^2)^{0.5}$ configuration keeping the octahedral geometry is found to be practically *independent* of the *cluster size*. This value means a 10% *inwards* relaxation with respect to the $\text{Na}^+ - \text{Cl}^-$ distance for the perfect NaCl lattice. As previously discussed, the RhCl_6^{4-} complex is found to be significantly decoupled from the rest of the lattice. In fact fourth shell Na^+ ions placed at $5.64 \text{ \AA}$ in the perfect NaCl lattice are calculated to be at $5.8 \text{ \AA}$ using either 39 or 87 atoms clusters. A picture of the 39 atoms cluster is given in Fig. 2. Keeping the octahedral geometry the $E(Q_\theta)$ curve for the $(3z^2 - r^2)^{0.5}(x^2 - y^2)^{0.5}$ electronic configuration has subsequently been explored.

Results reached for the $\text{RhCl}_6\text{Na}_{12}\text{Cl}_8\text{Na}_6\text{Cl}_6$ cluster are portrayed in Fig. 3. As expected the energy minimum is found for $Q_\theta = 0$ indeed and the curve is not symmetric with respect to the minimum thus revealing the existence of anharmonicity. From the $E(Q_\theta)$ curve displayed in Fig. 3 the following values of K and A_3 parameters, involved in equation (1) can be derived

$$K = 4.5 \text{ eV/\AA}^2, \quad A_3 = 0.86 \text{ eV/\AA}^3 \quad (19)$$

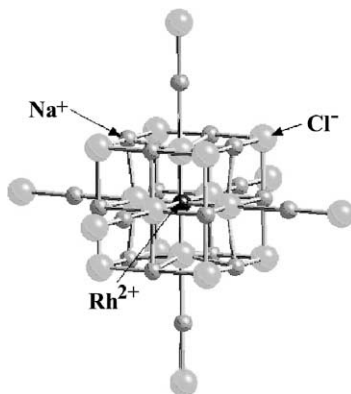


Fig. 2. Pictorial description of the 39 atoms $\text{RhCl}_6\text{Na}_{12}\text{Cl}_8\text{Na}_6\text{Cl}_6$ cluster.

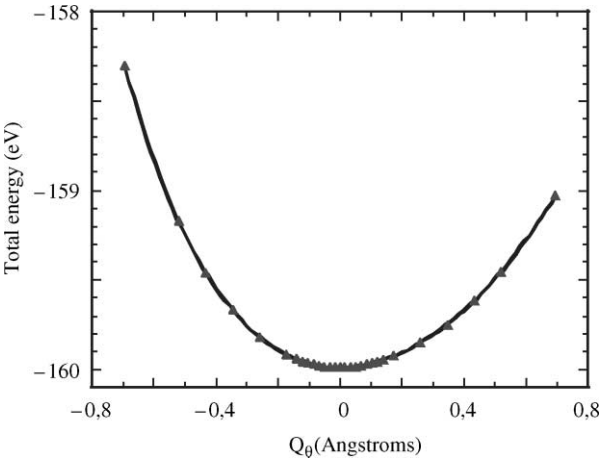


Fig. 3. $E(Q_\theta)$ curve for the $(3z^2 - r^2)^{0.5}(x^2 - y^2)^{0.5}$ electronic configuration corresponding to the $\text{RhCl}_6\text{Na}_{12}\text{Cl}_8\text{Na}_6\text{Cl}_6$ cluster.

These values are consistent with the estimation embodied in equation (3). Results obtained for $(3z^2 - r^2)^1$ or $(x^2 - y^2)^1$ electronic configurations under a Q_θ distortion (D_{4h} symmetry) are displayed in Figs 4 and 5. In Fig. 4 the dependence of the one-electron energies ε_a and ε_b on the distortion parameter $a \equiv Q_\theta/\sqrt{12}$ is shown. Both ε_a and ε_b exhibit a perfect linear behaviour at least in the 0–0.15 Å range. From

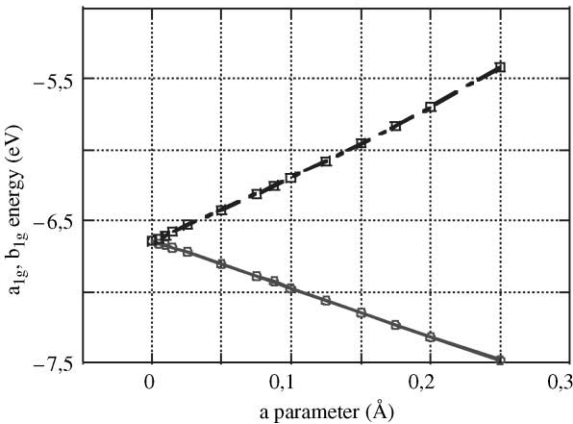


Fig. 4. Dependence of the one-electron energies ε_a and ε_b (associated with the antibonding a_{1g} ($\sim 3z^2 - r^2$) and b_{1g} ($\sim x^2 - y^2$) orbitals, respectively) on the distortion parameter $a \equiv Q_\theta/\sqrt{12}$.

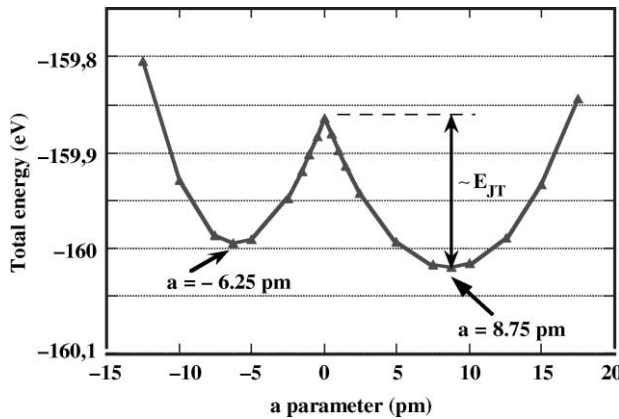


Fig. 5. Q_θ dependence of total energies corresponding to $(3z^2 - r^2)^1$ and $(x^2 - y^2)^1$ electronic configurations for the $\text{RhCl}_6\text{Na}_{12}\text{Cl}_8\text{Na}_6\text{Cl}_6$ cluster.

results collected in Fig. 4, a value

$$V = 1.1 \text{ eV}/\text{\AA} \quad (20)$$

is derived. Therefore, according to equations (12), (19), and (20) the following Q_θ^* value is obtained:

$$Q_\theta^* = V/K = 0.25 \text{ \AA} \quad (21)$$

This value verifies the inequality (13) and thus supports that, in the present case, the linear term should be the main responsible for the coupling between the electronic state and the vibrational E_g mode of the MX_6 complex. It is worth noting that to the value $Q_\theta^* = 0.25 \text{ \AA}$ corresponds $a^* \equiv Q_\theta/\sqrt{12} = 0.07 \text{ \AA}$ which is thus placed in the region where the a dependence of the one-electron energies ε_a and ε_b is fully linear as depicted in Fig. 4. Bearing in mind equations (16), (19), and (20), the following E_{JT} and $E_{\text{JT}}/\hbar\omega_E$ values can be expected:

$$E_{\text{JT}} = 0.135 \text{ eV}, \quad E_{\text{JT}}/\hbar\omega_E \approx 6 \quad (22)$$

and thus an EPR spectrum characteristic of a static Jahn–Teller effect is expected at low temperature. This conclusion is in agreement with experimental findings [10]. The Q_θ dependence of total energies corresponding to $(3z^2 - r^2)^1$ and $(x^2 - y^2)^1$ electronic configurations is displayed in Fig. 5. It can be seen that the energy minimum for the $(3z^2 - r^2)^1$ electronic state is the lowest one leading to an *elongated* octahedron as equilibrium geometry. This geometry is in agreement with reported EPR data. Such a minimum involves a stabilisation energy, $E_0 - E(3z^2 - r^2; Q_\theta^0) = 0.15 \text{ eV}$, while $E_0 - E(x^2 - y^2; Q_\theta^0) = 0.12 \text{ eV}$. At the same time the minimum for the $(3z^2 - r^2)^1$ state is found at $a_0 = 0.0875 \text{ \AA}$, while that for $(x^2 - y^2)^1$ is obtained at $a_0 = -0.0625 \text{ \AA}$, and so the two minima do not appear

at the same $|a|$ value. *Both* relevant facts can reasonably accounted for by: (i) equations (14) and (17); (ii) the values of $A_3 = 0.86 \text{ eV/\AA}^3$ and $Q_\theta^* = 0.25 \text{ \AA}$ derived from the present calculations; (iii) *neglecting* the effects coming from *quadratic* coupling. This result thus concurs with the findings reported in Fig. 4 showing that small non-linear effects in the $\varepsilon_a(Q_\theta)$ and $\varepsilon_b(Q_\theta)$ curves are visible *only* for $a > 0.15 \text{ \AA}$. As firstly suggested by Öpik and Pryce [7] the type of equilibrium geometry (elongated or compressed octahedron) is a direct consequence of the A_3 sign. Let us consider a Q_θ distortion for a MX_6 complex in an orbital singlet state decoupled from the rest of the host lattice. Let us also assume in a simple way that changes of total energy can be described in terms of those corresponding to six independent bonds. The energy variation, $E(\text{bond})$, of each one of such bonds is modelled by the expression

$$E(\text{bond}) \cong \frac{1}{2} \kappa (R - R_0)^2 - \frac{g}{6} (R - R_0)^3 \quad (23)$$

For an *isolated* MX_6 molecule the anharmonic constant g is *always* positive. Assuming equation (23) as a first approximation it is a simple matter to obtain the anharmonic energy for a Q_θ distortion leading to

$$A_3 = g/(6\sqrt{12}) \quad (24)$$

This simple argument suggests that A_3 should be positive when the MX_6 complex is *decoupled* from the rest of the host lattice. This simple fact can thus explain that the equilibrium geometry found experimentally for d^7 or d^9 ions placed substitutionally at *cubic* sites often corresponds to an *elongated* octahedron when the Jahn–Teller effect has a static character [2]. This statement cannot however be true when the interaction of ligands with metal in the complex becomes comparable to that of ligands with first neighbours belonging to the rest of lattice ions. Examples where this situation holds are given in Ref. [17]. Looking at Figs 4 and 5 it can be noted that the curvature $(\partial^2 E / \partial Q_\theta^2) \approx 3.5 \text{ eV/\AA}^2$ at the absolute minimum in Fig. 5 is smaller than $K = 4.5 \text{ eV/\AA}^2$ derived for the $(3z^2 - r^2)^{0.5}(\chi^2 - y^2)^{0.5}$ configuration. If the quadratic coupling is neglected one would expect that the curvature at the absolute minimum in Fig. 5 would be $(\partial^2 E / \partial Q_\theta^2) = 3.2 \text{ eV/\AA}^2$ using equations (18), (19), and (21).

Let us now say a few words about the separation among three equivalent minima (in the absence of local random strains) which appear once the two contributions (1) and (3) are considered together. Writing [1–3]

$$Q_\theta = \rho \cos \theta; \quad Q_\varepsilon = \rho \sin \theta \quad (25)$$

the three minima are described in a first approximation by the couple $(\rho_0; \theta_0)$ where

$$\rho_0 = Q_\theta^*, \quad \theta_0 = 0, 2\pi/3, 4\pi/3 \quad (26)$$

If the barrier, β , among three minima mainly comes from anharmonicity the θ dependence of the energy, E , in equation (1) is just given by the term [1–3,18]

$$-A_3 \rho_0^3 \cos 3\theta \quad (27)$$

and thus the barrier for passing from one minimum to another is

$$\beta \approx 2A_3\rho_0^3 \tag{28}$$

Treating the potential energy (27) in the harmonic approximation the corresponding angular frequency, ω^* , is just given by [18]:

$$(\omega^*)^2 = 9A_3\rho_0/M_L \tag{29}$$

Therefore the existence of at least one vibrational state in a given well is favoured if the following condition is fulfilled:

$$\hbar\omega^*/2 < \beta \tag{30}$$

Using now the values $A_3 = 0.86 \text{ eV/\AA}^3$ and $\rho_0 = Q_\theta^* = 0.25$ derived for RhCl_6^{4-} embedded in NaCl it is found that $\hbar\omega^*/2 = 8 \text{ meV}$, to be compared with $\beta = 27 \text{ meV}$.

4. OTHER JAHN–TELLER SYSTEMS EXPLORED THROUGH DFT

4.1. Cu^{2+} doped cubic oxides

For gaining a better insight into the properties of $\text{MO}:\text{Cu}^{2+}$ ($\text{M} = \text{Mg}, \text{Sr}$) systems [1–6] DFT calculations have also been carried out. First results obtained using a $\text{CuO}_6\text{M}_6^{2+}$ cluster including first M^{2+} cations of the host lattice along $\langle 1\ 0\ 0 \rangle$ directions are gathered in Table 1. Following a similar procedure to that described in Section 3 total energy calculations for the $(3z^2 - r^2)^{1.5}(x^2 - y^2)^{1.5}$ configuration have firstly been performed. It can be noted that R_0 values derived from such calculations are rather close to R_L corresponding to the perfect host lattice. This result means that the $\text{M}^{2+} \rightarrow \text{Cu}^{2+}$ substitution leads only to a small local lattice relaxation and thus the impurity–ligand distance is mainly governed by the host lattice constant. This situation, also encountered in previous Hartree–Fock calculations [19], is thus rather different to that found for 3d impurities in cubic fluorides where R_0 is determined, in a first approximation, by the ionic radius of the impurity and the coordination number [17]. This difference may reflect the high local bulk modulus of oxygen in oxides as discussed recently [20]. Bearing in mind that $R_0 = 2.1 \text{ \AA}$ for $\text{MgO}:\text{Cu}^{2+}$, while $R_0 = 2.5 \text{ \AA}$ for $\text{SrO}:\text{Cu}^{2+}$ (Table 1) it is not

Table 1. DFT results obtained for $\text{MO}:\text{Cu}^{2+}$ ($\text{M} = \text{Mg}, \text{Sr}$) systems using a $\text{CuO}_6\text{M}_6^{2+}$ cluster

Lattice	R_L (Å)	R_0 (Å)	a_0 (Å)	E_{JT} (cm ^{−1})	$\hbar\omega_E$ (cm ^{−1})	$E_{\text{JT}}/\hbar\omega_E$	K (eV/Å ²)
MgO	2.106	2.100	0.023	281	490	0.65	14.23
SrO	2.580	2.497	0.042	378	200	1.89	2.37

R_L is the M–O distance for the perfect MO lattice.

surprising that the force constant, K , for the former system is found to be about six times higher than that for $\text{SrO}:\text{Cu}^{2+}$. Variations of this kind albeit not so big have also been encountered in the case of Mn^{2+} -doped fluoroperovskites [17]. For $\text{MgO}:\text{Cu}^{2+}$ under a Q_θ distortion the present calculations lead to

$$\frac{\partial(\varepsilon_a - \varepsilon_b)}{\partial a} = 7.3 \text{ eV}/\text{\AA}, \quad V = \frac{1}{2\sqrt{12}} \frac{\partial(\varepsilon_a - \varepsilon_b)}{\partial a} = 1.05 \text{ eV}/\text{\AA} \quad (31)$$

Therefore, this value of V found for $\text{MgO}:\text{Cu}^{2+}$ is practically the same as that obtained for $\text{NaCl}:\text{Rh}^{2+}$. The big difference between $K = 4.5 \text{ eV}/\text{\AA}^2$ for $\text{NaCl}:\text{Rh}^{2+}$ and $K = 14 \text{ eV}/\text{\AA}^2$ for $\text{MgO}:\text{Cu}^{2+}$ is thus the main responsible for the small values of $a_0 = -0.023 \text{ \AA}$ and $E_{\text{JT}} = 0.035 \text{ eV}$ found in the latter case. It is worth noting that present calculations lead in fact to a ratio $E_{\text{JT}}/\hbar\omega_E = 0.65$ which favours the observation of low temperature EPR spectra displaying cubic angular pattern [4]. This value is thus more reasonable than the ratio $E_{\text{JT}}/\hbar\omega_E = 40$ previously estimated by Reynolds *et al.* [5]. Moreover the $\varepsilon_b - \varepsilon_a$ separation at equilibrium is just given by

$$\varepsilon_b - \varepsilon_a = 4E_{\text{JT}} \quad (32)$$

Thus from the present calculations it is derived $\varepsilon_b - \varepsilon_a = 0.14 \text{ eV}$ for $\text{MgO}:\text{Cu}^{2+}$. This figure concurs with the value [21] derived from the analysis of the temperature dependence of spin–lattice relaxation, T_1 . The value of the coupling coefficient for $\text{SrO}:\text{Cu}^{2+}$ is found to be $V = 0.47 \text{ eV}/\text{\AA}$. In comparison with $V = 1.05 \text{ eV}/\text{\AA}$ found for $\text{MgO}:\text{Cu}^{2+}$ this reduction reflects the increase of R_0 . Therefore, the big reduction undergone by force constant, K , on going from $\text{MgO}:\text{Cu}^{2+}$ to $\text{SrO}:\text{Cu}^{2+}$ is thus the main responsible for $E_{\text{JT}}/\hbar\omega_E = 1.9$ obtained for $\text{SrO}:\text{Cu}^{2+}$. This value, which is three times bigger than $E_{\text{JT}}/\hbar\omega_E = 0.65$ derived for $\text{MgO}:\text{Cu}^{2+}$ can explain the observation [22] of *static* EPR spectra for $\text{SrO}:\text{Cu}^{2+}$.

4.2. Cu^{2+} doped SrCl_2

Theoretical calculations can be particularly useful in cases where a description based in truncated series expansion is hardly meaningful. This situation can be encountered when the impurity or neighbouring ions experience displacements from their initial positions, which are comparable to interatomic distances. Representative examples of this behaviour are found experimentally [2] for some cubic lattices with CaF_2 structure doped with d^9 ions. Taking as a guide the case of $\text{SrCl}_2:\text{Cu}^{2+}$ EPR data demonstrate [2,11] that Cu^{2+} undergoes a big off-centre displacement along $\langle 001 \rangle$ directions from the initial substitutional position leading to a change of eightfold to practically fourfold coordination. The angle φ depicted in Fig. 6 is estimated to be around 10° . If the equilibrium position of the d^9 ion is at $(0, 0, z_0)$ then $z_0 \approx 1.4 \text{ \AA}$ for $\text{SrCl}_2:\text{Cu}^{2+}$, where the lattice constant, a' , is equal to $6.97 \text{ \AA}$. This big off-centre displacement involves a coupling with a T_{1u} mode which then cannot give rise to any linear coupling with the electronic ground state $T_{2g}(xy, xz, yz)$. In a first attempt Lacroix [23] tried to ascribe the big off-centre

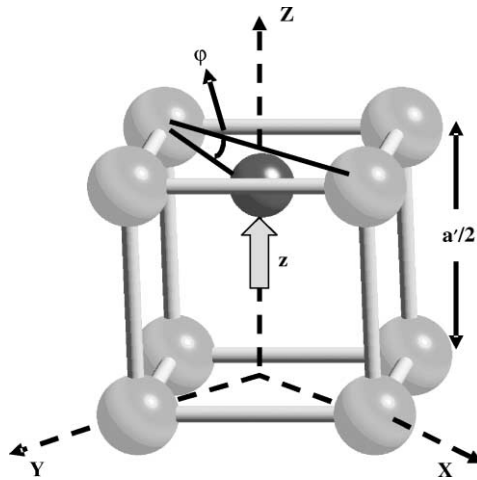


Fig. 6. Picture of the off-centre motion in $\text{SrCl}_2:\text{Cu}^{2+}$. The local axis X , Y , and Z are also indicated. The dark sphere represents the d^9 ion.

displacement considering only the quadratic Jahn–Teller coupling though z_0 being comparable to interatomic distances. When the parameters of that model were estimated it was found [23] that the displacement would occur along $\langle 111 \rangle$ directions. Searching to clarify this situation ADF calculations have been performed for a $\text{CuCl}_8\text{Sr}_{12}^{17+}$ cluster subjected to the electrostatic potential due to the rest of SrCl_2 lattice ions. In this process the 12 second neighbours are fixed at their positions in the SrCl_2 lattice.

Following a similar procedure to that described in Section 3 the $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ configuration has firstly been explored. If the cubic symmetry is kept one finds $R_0 = 2.82 \text{ \AA}$ implying a 6% inwards relaxation. This value is reasonably consistent with the eightfold coordination of the copper ion. The variation of the total energy, $E(z)$, for different $(0, 0, z)$ positions of Cu^{2+} and the same $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ configuration, is depicted in Fig. 7. According to this figure the energy minimum for this electronic configuration is $z_0 = 0$ implying that if orbital degeneracy is excluded Cu^{2+} wants to be on-centre. We have verified that the barrier for the $(xy)^{5/3}(xz)^{5/3} \times (yz)^{5/3}$ configuration depicted in Fig. 7 mainly comes from the electrostatic field on copper due to the rest of ions. Results reached when the unpaired electron is fully located in the $b_{2g} \sim xy$ orbitals are also displayed in Fig. 7. In comparison to results obtained for the $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ configuration drastic changes can be noticed. The energy minimum for the $(xy)^1(xz)^2(yz)^2$ configuration is found to occur not at $z = 0$ but at $z_0 = 1.4 \text{ \AA}$ which is thus in agreement with that inferred from EPR data [11]. As a salient feature the results collected in Fig. 7 for the $(xy)^1(xz)^2(yz)^2$ configuration stress the lack of barrier for reaching the off-centre position from $z = 0$. Therefore this result supports that the off-centre situation can be reached spontaneously once the Cu^+ ion,

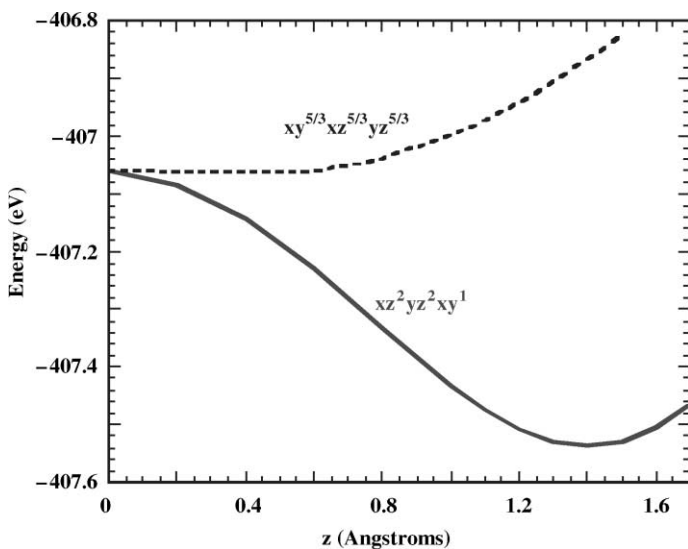


Fig. 7. $E(z)$ curves for $\text{SrCl}_2:\text{Cu}^{2+}$ in the $(xy)^{5/3}(xz)^{5/3}(yz)^{5/3}$ and $(xy)^1(xz)^2(yz)^2$ configurations.

introduced as impurity in SrCl_2 , traps a hole released by X-ray irradiation [11]. From a microscopic viewpoint the hindrance for the off-centre motion in the $(xy)^{5/3}(xz)^{5/3} \times (yz)^{5/3}$ configuration is removed by the gain in electronic energy which happens in the $(xy)^1(xz)^2(yz)^2$ open shell configuration. In fact bonding effects are stronger for the xy hole when Cu^{2+} exhibits a square planar rather than a cubic coordination. It is worth noting however that in the equilibrium situation described by Figs 6 and 7 Cu^{2+} does not reach the plane formed by the four Cl^- ligands. This fact together with the energy raise for $z > 1.4 \text{ \AA}$ in Fig. 7 reflects the progressive increase of the repulsive electrostatic field on Cu^{2+} due to the rest of lattice ions. Further work along this line is now under way.

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REFERENCES

- [1] I. Bersuker and V. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, Berlin, 1989.
- [2] H. Bill, in *The Dynamical Jahn–Teller Effect in Localized Systems* (eds Yu. E. Perlin and M. Wagner), Elsevier, Amsterdam, 1984.

- [3] F. S. Ham, in *Electron Paramagnetic Resonance, I* (ed. S. Geschwind), Plenum Press, New York, 1972.
- [4] R. E. Coffman, *Phys. Rev.*, 1968, **48**, 609.
- [5] R. W. Reynolds, L. Boatner, M. Abraham and Y. Chen, *Phys. Rev. B*, 1974, **10**, 3802.
- [6] M. C. M. O'Brien and C. C. Chancey, *Am. J. Phys.*, 1993, **61**, 688.
- [7] U. Öpik and M. H. M. Pryce, *Proc. R. Soc. A*, 1957, **238**, 425.
- [8] D. Reinen and M. Atanasov, *Magn. Reson. Rev.*, 1991, **15**, 167.
- [9] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989, p. 1.
- [10] H. Vercammen, D. Schoemaker, B. Briat, F. Ramaz and F. Callens, *Phys. Rev. B*, 1999, **59**, 11286.
- [11] H. Bill, *Phys. Lett.*, 1973, **44**, 101.
- [12] M. T. Barriuso, P. García-Fernández, J. A. Aramburu and M. Moreno, *Solid State Commun.*, 2001, **120**, 1.
- [13] C. J. Ballhausen, *Ligand Field Theory*, 73, McGraw-Hill, New York, 1962.
- [14] M. T. Barriuso, J. A. Aramburu and M. Moreno, *Phys. Stat. Sol. b*, 1996, **196**, 193.
- [15] K. Wissing, M. T. Barriuso, J. A. Aramburu and M. Moreno, *J. Chem. Phys.*, 1999, **111**, 10217.
- [16] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. Van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comp. Chem.*, 2001, **22**, 931.
- [17] M. T. Barriuso, M. Moreno and J. A. Aramburu, *Phys. Rev. B*, 2002, **65**, 064441-1.
- [18] M. C. M. O'Brien, *Proc. R. Soc. A*, 1964, **281**, 323.
- [19] J. L. Pascual, L. Seijo and Z. Barandiarán, *J. Chem. Phys.*, 1993, **98**, 9715.
- [20] A. Martín Pendás, A. Costales, M. A. Blanco, J. M. Recio and V. Luaña, *Phys. Rev. B*, 2000, **62**, 13970.
- [21] U. Höchli, K. A. Müller and P. Wyssling, *Phys. Lett.*, 1965, **15**, 5.
- [22] Yu. N. Tolparov, G. L. Bir, L. S. Sochava and N. N. Kovalev, *Sov. Phys. Solid State*, 1974, **16**, 573.
- [23] R. Lacroix, *Helv. Phys. Acta*, 1974, **47**, 689.

Analysis of the EPR and Raman Scattering of Copper(II) Doped CaO

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Abstract

A numerical procedure is described to calculate Raman and electron paramagnetic resonance (EPR) spectra, as well as the magnetic and geometrical properties, of octahedrally coordinated copper(II) complexes, directly from the eigenvalues and eigenfunctions of the vibronic Hamiltonian. The suite of programs is employed to model the available experimental data for the copper(II) impurity doped into CaO; a system for which widely different values for the Jahn–Teller stabilization energy, E_{JT} , have been proposed. It is shown that a satisfactory account of the experimental data can be obtained within the framework of the model of O'Brien with $\hbar\omega = 216\text{ cm}^{-1}$ and $E_{JT}/\hbar\omega \sim 8$. Further experiments are suggested that would assist in the elucidation of the vibronic structure.

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1. INTRODUCTION

The author of this contribution is of the opinion that experimental investigations into the vibronic structure of copper(II) doped CaO ($\text{CaO}:\text{Cu}^{2+}$), and related materials, constitute some of the most rigorous and instructive studies ever performed on Jahn–Teller active systems. Raman measurements on $\text{CaO}:\text{Cu}^{2+}$ by Guha and Chase [1] have yielded the vibronic spectrum from ~ 3 to 250 cm^{-1} as a function of applied stress and temperature using just a Spex 1400 double monochromator. As an experimentalist, with some experience in the collection and analysis of electronic Raman data, the author can state that this is a remarkable experimental achievement. Electron paramagnetic resonance (EPR) studies on these systems have been no less illuminating. The 1.3 K EPR spectrum of $\text{CaO}:\text{Cu}^{2+}$ exhibits a high degree of structure [2,3], interpreted as arising from a vibronic ${}^2E$ ground state with appreciable random-strain coupling to a low lying A_1 or A_2 vibronic singlet [3]. We find the theoretical analysis of the spectra by Reynolds and Boatner to be particularly definitive [4]. They showed that a good reproduction of the low temperature EPR spectrum of $\text{CaO}:\text{Cu}^{2+}$ could be obtained using a three-state model. They were not able to simulate adequately the spectrum of $\text{MgO}:\text{Cu}^{2+}$ however, which, they suggested, might be a consequence of the limitation of the perturbation model [3].

Guha and Chase estimated the Jahn–Teller coupling frequency to be in the range $300\text{--}350\text{ cm}^{-1}$ for $\text{CaO}:\text{Cu}^{2+}$ with $E_{\text{JT}} = 5500\text{ cm}^{-1}$, thus the ratio $E_{\text{JT}}/\hbar\omega$, commonly regarded as a measure of the strength of the Jahn–Teller interaction, is ~ 17 . For $\text{MgO}:\text{Cu}^{2+}$, a value of $E_{\text{JT}}/\hbar\omega \sim 40$ was suggested [3], which implies a Jahn–Teller effect of heroic magnitude. More recent *ab initio* [5] and DFT [6] calculations suggest that much smaller values of E_{JT} pertain to $\text{CaO}:\text{Cu}^{2+}$ and related systems, with $E_{\text{JT}}/\hbar\omega$ estimated to be only 0.65 for $\text{MgO}:\text{Cu}^{2+}$ [6]. The energy level structure of $\text{CaO}:\text{Cu}^{2+}$ has also been considered in detail by O'Brien [7]. She showed that the electronic Raman spectrum of $\text{CaO}:\text{Cu}^{2+}$ is characteristic of multi-mode coupling giving rise to sharp low energy features, characteristic of coupling with a local mode, and broad bands at higher energy typical of impurity-assisted scattering from a spectrum of phonons. She interpreted the Raman spectra [7] using vibronic coupling parameters similar to values suggested for the copper(II) ion in molecular systems [8].

This work has two objectives. First, we attempt to model the available experimental data using a single phonon mode coupling model with the variety of parameter sets proposed, and show that a satisfactory account can be obtained only with a rather limited range of parameters. Secondly, a number of various experimental quantities are calculated and further experiments proposed that would assist in defining the nature of the vibronic interaction in these intriguing systems. In particular, it is shown that it should be possible to determine the tunnelling splitting directly from a high-field, high-frequency EPR experiment.

2. THEORY

2.1. The vibronic Hamiltonian

The Hamiltonian of the problem is written as the sum,

$$\hat{H} = \hat{H}_{\text{CF}} + \hat{H}_{\text{SO}} + \hat{H}_{\text{Zee}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{JT}} + \hat{H}_{\text{st}} + \hat{H}_{\text{hyp}} \quad (1)$$

where the terms designate the cubic crystal field, spin–orbit coupling, Zeeman, phonon, Jahn–Teller, low symmetry crystal field (strain), and hyperfine contributions to the energy, respectively. The matrix representation of the terms $\hat{H}_{\text{CF}} + \hat{H}_{\text{SO}} + \hat{H}_{\text{Zee}}$ in the real cubic bases, is given in Appendix A, where the g -factor for the free electron has been set to two for clarity.

$\hat{H}_{\text{ph}}$ and $\hat{H}_{\text{JT}}$ are written as:

$$\begin{aligned} H_{\text{ph}} &= [0.5\hbar\omega(P_\theta^2 + P_\varepsilon^2 + Q_\theta^2 + Q_\varepsilon^2) + A_3(3Q_\theta Q_\varepsilon^2 - Q_\theta^3)]U_\tau \\ H_{\text{JT}} &= A_1^E(Q_\theta U_{E\theta} + Q_\varepsilon U_{E\varepsilon}) + A_2^E((Q_\varepsilon^2 - Q_\theta^2)U_{E\theta} + 2Q_\theta Q_\varepsilon U_{E\varepsilon}) \\ &\quad + A_1^T(Q_\theta U_{T\theta} + Q_\varepsilon U_{T\varepsilon}) \end{aligned} \quad (2)$$

where $\hbar\omega$ is the energy of the two-dimensional harmonic oscillator, A_3 the anharmonic coupling constant, A_1^E, A_2^E the first- and second-order $E \otimes e$ Jahn–Teller coupling constants, and A_1^T the linear $T \otimes e$ Jahn–Teller coupling constant. U_τ is the unitary matrix; $U_{E\theta}, U_{E\varepsilon}, U_{T\theta}, U_{T\varepsilon}$ are electronic operators having the form:

$$\begin{aligned} U_{E\theta} &= \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}; & U_{E\varepsilon} &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; & U_{T\theta} &= \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \\ U_{T\varepsilon} &= \begin{pmatrix} \sqrt{3}/2 & 0 & 0 \\ 0 & -\sqrt{3}/2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (3)$$

where we have used the Clebsh–Gordan coefficients as listed by Sugano, Tanabe, and Kamimura [9]. The orbital basis functions are $\psi_\theta \sim 2z^2 - x^2 - y^2$; $\psi_\varepsilon \sim \sqrt{3}(x^2 - y^2)$ for the U_E operators and $\psi_\xi \sim yz$, $\psi_\eta \sim zx$, and $\psi_s \sim xy$ for the U_T operators. $\hat{Q}_i$ and $\hat{P}_i$ are dimensionless operators, related to the observables for position and momentum, $\hat{q}_i, \hat{p}_i$ by [10],

$$\hat{Q}_i = \sqrt{\frac{\mu\omega}{\hbar}}\hat{q}_i; \quad \hat{P}_i = \frac{1}{\sqrt{\mu\hbar\omega}}\hat{p}_i \quad (4)$$

where μ is the reduced mass of the phonon mode.

Within an octahedral E term, two parameters are required to describe the splitting of the electronic states due to a low symmetry ligand field,

$$\hat{H}_{\text{st}} = S_{\theta}U_{E\theta} + S_{\varepsilon}U_{E\varepsilon} \quad (5)$$

where S_{θ} and S_{ε} are the tetragonal and orthorhombic components of the low symmetry strain. The inclusion of these terms breaks the cubic symmetry of the Hamiltonian. Two vibrational energies and further vibronic coupling constants are formally required. However, the values of the parameters S_{θ} and S_{ε} are so small that the inclusion of further parameters is unwarranted. S_{θ} and S_{ε} are related to the strain splitting parameter, ∂ , by the relations,

$$S_{\theta} = \partial \cos \phi; \quad S_{\varepsilon} = \partial \sin \phi \quad (6)$$

where ϕ is the angular co-ordinate in the θ, ε space. Throughout this work we shall refer frequently to the quantities, $\bar{\partial}$ and 3Γ , which denote the mean random-strain and tunneling splitting parameters respectively, after Reynolds and Boatner [4]. A Gaussian distribution about the mean strain splitting may be chosen in the suite of programs described; the full width at half height of the strain distribution is given by the parameter σ . Where a random-strain splitting is specified, ϕ was varied between 0 and 360°, in one-degree steps, and the quantity summed and averaged over all values of ϕ . For certain parameter sets it was sufficient to sum over a limited range of values of ϕ . For example, for the calculation of the magnetic moment with $\vec{B} \parallel [1\ 1\ 1]$, the C_{3v} symmetry of the θ, ε co-ordinate space is preserved, with co-kernel points at 0, 120, and 240°. In this instance ϕ need only be varied between 0 and 60°.

For the calculation of the EPR spectra, the basis functions were extended to include the four spin functions of copper nuclei, and the following expression for the nuclear hyperfine interaction added to the Hamiltonian:

$$\hat{H}_{\text{hyp}} = P \left[\hat{l} \cdot \hat{l} - \kappa \hat{s} \cdot \hat{l} + \frac{1}{7} \hat{a} \cdot \hat{l} \right]$$

where

$$\hat{a} = 4\hat{s} - (\hat{l} \cdot \hat{s})\hat{l} - \hat{l}(\hat{l} \cdot \hat{s}) \quad (7)$$

Free ion values for the parameter P are: $^{63}\text{Cu(II)}$ (69.2%) = 0.03928 cm^{-1} , $^{65}\text{Cu(II)}$ (30.8%) = 0.04204 cm^{-1} [11]. For all the EPR simulations presented, P was fixed at 0.036 cm^{-1} . The isotropic Fermi contact parameter, κ , was varied to obtain the best agreement with the EPR data. The nuclear quadrupole interaction was not included.

The eigenvalues and eigenvectors of the Hamiltonian were found by setting it up as a matrix in a basis of products of electronic states and the states of the $\{Q_{\theta}, Q_{\varepsilon}\}$ harmonic oscillator of dimension $N = 1/2(n_v + 1)(n_v + 2)$, up to the level n_v . The matrix was brought to diagonal form using a fast Lanczos diagonalization routine for

real symmetric matrices. This meant a further doubling of the size of the original complex matrix. All the software described was written by the author with the exception of the Lanczos diagonalization routine. This was written by the late, great Mary O'Brien and passed on to the author by Mark Riley, with minor modifications.

The vibronic eigenfunctions of the Hamiltonian, Ψ , are expressed as linear combinations of the basis functions,

$$\Psi = \sum_i \sum_j \sum_k \sum_{l+m=0}^{n_v} a_{ijklm} |\psi_i, M_{sj}, M_{lk}, n_{\theta l}, n_{em}\rangle \quad (8)$$

where ψ_i spans the five orbital components of the real 3d functions, M_s and M_l are the electron and nuclear spin quantum numbers, and n_{θ} and n_e the quantum numbers of the harmonic oscillators.

2.2. Calculation of the experimental quantities

2.2.1. Raman spectra

The zeroth-order electronic Raman cross-section, I , for a transition from state i to state f , was calculated according to,

$$I \propto E_s^4 \exp\left(\frac{-E_i}{kT}\right) \langle \Psi | \hat{\alpha}_{I\gamma} | \Psi' \rangle \langle \Psi' | \hat{\alpha}_{I\gamma} | \Psi \rangle \delta(E_f - E_i - E_0 + E_s) \quad (9)$$

where E_0 and E_s are the energies of the incident and scattered radiation, E_i , E_f the energies of the states Ψ and Ψ' relative to E_0 , and $\hat{\alpha}_{I\gamma}$ is the component of the Raman polarizability tensor, transforming as the γ th component of the I th irreducible representation of the O_h point group. The experimental spectra were recorded with an excitation frequency of $E_0 = 514.5$ nm [1] and this value was used in the calculation of all the spectra presented.

Guha and Chase reported that a Raman spectrum could be observed only in experiments that select a component of the polarizability tensor transforming as E_{θ} or E_{ε} [1]. The electronic matrix elements in these polarization geometries are [1]

$$\begin{aligned} \langle \Psi | \hat{\alpha}_{E_{\theta}} | \Psi' \rangle &= \sum_{l+m=0}^{n_v} \sum_{l'+m'=0}^{n'_v} (-a_{\theta lm}^* a'_{\theta l' m'} + a_{\varepsilon lm}^* a'_{\varepsilon l' m'}) \delta_{ll'} \delta_{mm'} \\ \langle \Psi | \hat{\alpha}_{E_{\varepsilon}} | \Psi' \rangle &= \sum_{l+m=0}^{n_v} \sum_{l'+m'=0}^{n'_v} (a_{\theta lm}^* a'_{\varepsilon l' m'} + a_{\varepsilon lm}^* a'_{\theta l' m'}) \delta_{ll'} \delta_{mm'} \end{aligned} \quad (10)$$

where we have omitted the expansion in terms of the electron and nuclear spin, as these co-ordinates have no effect on the calculated intensity. The calculated electronic Raman transitions were folded with a Lorentzian or Gaussian bandwidth, with constant width across the whole spectrum.

2.2.2. Magnetic data

The effect of dynamic Jahn–Teller coupling on the magnetic properties of a complex has been considered by Sasaki and Obata [12] and Ham [13]. These authors derived closed-form expressions for the paramagnetic susceptibility using perturbation theory. Later, O’Brien outlined how the paramagnetic susceptibility may be calculated from the eigenvalues obtained from two numerical diagonalizations of the vibronic Hamiltonian [14]. Tregenna-Piggott and Güdel discussed the magnetic properties of the $[\text{Ti}(\text{OH}_2)_6]^{3+}$ cation, in the high-field low temperature limit [15]. The magnetization was calculated by fitting the calculated energies to a power series in field, from which the Zeeman coefficients of the states were derived to third-order. This procedure, although instructive, is rather laborious, requiring numerous diagonalizations of the vibronic Hamiltonian. In this work, the magnetic moment of the copper(II) complex was calculated using the full thermodynamic equation,

$$M_{\text{ion}} = \frac{\sum_n \left(-\frac{dE_n}{dB} \right) \exp\left(\frac{-E_n}{kT} \right)}{\sum_n \exp\left(\frac{-E_n}{kT} \right)} \quad (11)$$

where the sum is over the n eigenstates of the Hamiltonian (those with a significant population) and the derivatives found using the Hellman–Feynman theorem,

$$\begin{aligned} \frac{dE_n}{dB} &= \left\langle \Psi_n \left| \frac{d\hat{H}}{dB} \right| \Psi_n \right\rangle \\ &= \sum_i \sum_{i'} \sum_j \sum_{j'} \sum_{l+m=0}^{n_v} \sum_{l'+m'=0}^{n'_v} a_{ijlm}^* a_{i'j'l'm'} \left\langle \psi_i, M_{sj} \left| \frac{d\hat{H}}{dB} \right| \psi_{i'}, M_{sj'} \right\rangle \delta_{ll'} \delta_{mm'} \quad (12) \end{aligned}$$

This method allows the magnetic moment at a given field to be calculated exactly from one numerical diagonalization of the vibronic Hamiltonian.

2.2.3. EPR spectra

The EPR spectrum of $\text{CaO}:\text{Cu}^{2+}$ and related systems has been calculated by Reynolds and Boatner [4] using a three-state perturbation model [16]. The work of these authors has provided considerable insight into the underlying physics determining the anomalous EPR spectra of a number of quasicubic systems. Riley has outlined a procedure to calculate the temperature dependence of the g values of Cu(II) systems from the numerical diagonalization of the vibronic Hamiltonian [8]. This approach treats the Zeeman interaction as a perturbation within each of the resulting Kramers doublets; and is valid only when the splitting of the degeneracy of the vibronic states due to low symmetry ligand fields is large compared to the Zeeman interaction. This approximation is legitimate for the copper(II) tutton salt

systems, for which his software was derived, but is inappropriate for $\text{CaO}:\text{Cu}^{2+}$ and related systems, where deviations from cubic symmetry are minimal. Furthermore, the hyperfine interaction was not included. The EPR spectra presented in this paper are calculated directly from the full vibronic Hamiltonian, which includes the nuclear hyperfine interaction. This unique approach was motivated by the reported inability to simulate the EPR spectrum of $\text{MgO}:\text{Cu}^{2+}$ from the three-state perturbation model [3]; and, by the desire to investigate whether it might be possible to observe EPR transitions between states split by the tunnelling effect, in instances where the states are not strongly localized in one of the three potential minima resulting from the warping of the Mexican-hat potential energy surface. As far as we are aware this is the first time that EPR resonant fields and intensities have been calculated directly from the full vibronic Hamiltonian, which is not altogether surprising given the time required to compute a single spectrum. The intensity of a transition between states Ψ and Ψ' of energy E_i and E_f , was calculated according to:

$$I \propto \exp\left(\frac{-E_i}{kT}\right) \langle \Psi | \hat{\mu}_\perp | \Psi' \rangle \langle \Psi' | \hat{\mu}_\perp | \Psi \rangle \delta(E_f - E_i - \nu_e) \quad (13)$$

where $\hat{\mu}_\perp$ is the magnetic moment operator in the direction of the oscillating magnetic field, H_1 , of frequency ν_e , which is perpendicular to the steady magnetic field B . From equation (8) we obtain:

$$\begin{aligned} \langle \Psi | \hat{\mu}_\perp | \Psi' \rangle &= \sum_i \sum_{i'} \sum_j \sum_{j'} \sum_k \sum_{k'} \sum_{l+m=0}^{n_v} \sum_{l'+m'=0}^{n_v} \\ &\times a_{ijklm}^* a_{i'j'k'l'm'}^l \langle \psi_i, M_{sj} | \hat{\mu}_\perp | \psi_{i'}, M_{sj'} \rangle \delta_{kk'} \delta_{ll'} \delta_{mm'} \end{aligned} \quad (14)$$

With the number of phonon levels, n_v , set to 20, the total dimension of the matrix needed to be diagonalized is 18 480, which is not trivial. The resonant fields of the transitions were found using a simple but powerful algorithm, the essence of which was dictated to the author over the telephone by the celebrated Faroese chemist Høgni Weihe. This algorithm allows one to find the resonant fields in the field range of 1000 – 120 000 G, to within 1 G using an average of only three diagonalizations. Nevertheless, the generation of a single spectrum requires a considerable amount of computation, particularly when the spectrum is calculated as a superposition of spectra corresponding to different strain parameters, as is the case here. A less rigorous, though faster method would be to generate a matrix representation of the Zeeman interaction in a basis consisting of just the low energy vibronic states, from which an EPR spectrum could be generated at sufficiently low temperatures and fields. The current version of the program takes no account of spin–lattice relaxation. Work in this area is currently in progress. The calculated EPR transitions were folded with a first-derivative Lorentzian or Gaussian bandwidth, with constant width across the whole spectrum.

2.2.4. Bond lengths

Finally, the mean values of the bond lengths, that would be determined by crystallography, were calculated assuming coupling to the $\nu_2(\text{CuO}_6)$ vibration only with components $Q_\theta \sim 2\Delta z^2 - \Delta x^2 - \Delta y^2$ and $Q_\varepsilon \sim \sqrt{3}(\Delta x^2 - \Delta y^2)$. This was achieved by first evaluating the expectation values of $\hat{q}_\theta$ and $\hat{q}_\varepsilon$ in each of the thermally populated vibronic wavefunctions, as outlined by Riley and co-workers [17]:

$$\begin{aligned}
 \langle \hat{q}_\theta \rangle &= \sqrt{\frac{\hbar}{\mu\omega}} \langle \Psi | \hat{Q}_\theta | \Psi \rangle \\
 &= \sqrt{\frac{\hbar}{\mu\omega}} \sum_i \sum_{i'} \sum_j \sum_{j'} \sum_{l+m=0}^{n_v} \sum_{l'+m'=0}^{n'_v} a_{ijlm}^* a'_{i'j'l'm'} \langle n_\theta | \hat{Q}_\theta | n'_\theta \rangle \delta_{ii'} \delta_{jj'} \delta_{mm'} \\
 &= \sqrt{\frac{\hbar}{\mu\omega}} \sum_i \sum_{i'} \sum_j \sum_{j'} \sum_{l+m=0}^{n_v} \sum_{l'+m'=0}^{n'_v} \\
 &\quad \times \left(a_{ij(l+1)m}^* a'_{i'j'l'm'} \sqrt{\frac{l'+1}{2}} + a_{ij(l-1)m}^* a'_{i'j'l'm'} \sqrt{\frac{l'}{2}} \right) \delta_{ii'} \delta_{jj'} \delta_{mm'} \quad (15)
 \end{aligned}$$

and similarly for $\langle \hat{q}_\varepsilon \rangle$. The mean displacements of the oxygen atoms along each of the six Cu–O_i bond vectors [18] is then given by,

$$\begin{aligned}
 \Delta r_1 &= \Delta r_4 = \frac{1}{\sqrt{12}} (2\langle \hat{q}_\theta \rangle) \\
 \Delta r_2 &= \Delta r_5 = \frac{1}{\sqrt{12}} (-\langle \hat{q}_\theta \rangle + \sqrt{3}\langle \hat{q}_\varepsilon \rangle) \\
 \Delta r_3 &= \Delta r_6 = \frac{1}{\sqrt{12}} (-\langle \hat{q}_\theta \rangle - \sqrt{3}\langle \hat{q}_\varepsilon \rangle) \quad (16)
 \end{aligned}$$

The bond lengths were calculated as the Boltzmann average of the geometric properties of the individual vibronic energy levels.

3. ANALYSIS OF THE EXPERIMENTAL DATA OBTAINED FOR $\text{CaO}:\text{Cu}^{2+}$ AND $\text{MgO}:\text{Cu}^{2+}$

3.1. Raman data

In Fig. 1(a) is shown the 4.2 K Raman spectrum of $\text{CaO}:\text{Cu}^{2+}$, recorded by Guha and Chase [1], who assigned the low energy region of the spectrum lines to

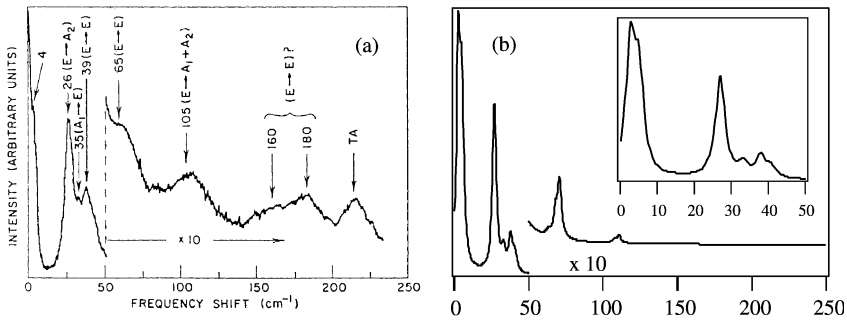


Fig. 1. Experimental and theoretical electronic Raman Spectra of $\text{CaO}:\text{Cu}^{2+}$. The experimental spectrum (a), is reproduced from the work by Guha and Chase [1] and was collected at ~ 4.2 K in a polarization geometry which facilitates the observation of transitions of E_g symmetry only. The theoretical spectrum was calculated using equation (9) employing the following parameters: $\hbar\omega = 330 \text{ cm}^{-1}$, $A_1^E = -1900 \text{ cm}^{-1}$, $A_2^E = -0.65 \text{ cm}^{-1}$, $S_\theta = 3 \text{ cm}^{-1}$, $S_e = 3 \text{ cm}^{-1}$, $n_v = 40$, $T = 7$ K.

transitions within the hindered rotational levels, characteristic of the $E \otimes e$ vibronic problem, depicted in Fig. 2, where the quantities α and β are defined by O'Brien [19]. The spectrum is referred to as 'the E_g spectrum', the polarization of the incoming and scattered radiation are not specified. From careful reading of their paper, however, we can assume that the transitions are of E_g symmetry [20]. In Fig. 1(b) is shown a theoretical spectrum calculated in E_g geometry, with $\hbar\omega$ set to 330 cm^{-1} , the value suggested by Guha and Chase, and the remaining parameters adjusted to yield the best fit to the experimental spectrum. Anharmonicity and quadratic coupling both lead to a warping of the Mexican-hat potential energy surface. To limit the number of adjustable parameters A_3 was set to zero and all the warping absorbed into the second-order coupling constant A_2^E .

As the linear coupling is increased, the $\{A_1, A_2\}$ first excited states ($j = 3/2$) approach the E ($j = 1/2$) ground state. The experimental spectrum is characteristic of these states being $\sim 10 \text{ cm}^{-1}$ wavenumbers above the ground state, split by a small warping term. With $\hbar\omega = 330 \text{ cm}^{-1}$, it is found that good agreement with experiment can be obtained with $A_1^E = -1900 \text{ cm}^{-1}$, $A_2^E = -0.65 \text{ cm}^{-1}$, from which $E_{JT} \sim 5500 \text{ cm}^{-1}$, in accordance with the value deduced by Guha and Chase. Better agreement was obtained with the spectrum calculated at 7 K, rather than at the reported temperature of 4.2 K. This can be attributed to heating of the crystal by the incident laser. The electronic Raman spectrum exhibits a strong temperature dependence, the essence of which can also be reproduced using these parameters. The calculated profile is also very sensitive to the magnitude of the strain parameters, and the best reproduction of the energies and intensities was found with S_θ and S_e both set to 3 cm^{-1} . A poorer reproduction of the experimental spectrum was obtained if a random-strain distribution was assumed. This is contrary to

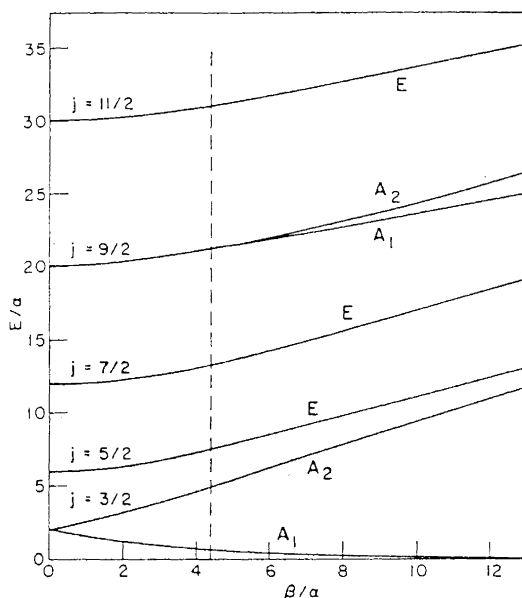


Fig. 2. Eigenvalues of the hindered-rotational levels of the $E \otimes e$ vibronic problem, reproduced from the work of Guha and Chase [1]. The broken line corresponds to the value of β/α , which best fits the $\text{CaO}:\text{Cu}^{2+}$ data.

the findings of Reynolds and Boatner [4] who showed that the EPR spectrum of $\text{CaO}:\text{Cu}^{2+}$ is indicative of random strain. This apparent discrepancy may be due to differences in the way the crystal is mounted. In an X-band EPR experiment, it is normally sufficient to fix the crystal, weighing several milligrams, onto the face of a sample holder using just a coating of silicon grease. For a Raman experiment it is beneficial to use larger crystals, which must be glued onto a goniometer head. As the sample is cooled, directional strains in the crystal can be induced due to the different thermal expansion coefficients of glue and crystal. In Fig. 3 are shown experimental and calculated Raman spectra of $\text{CaO}:\text{Cu}^{2+}$ with stress applied along the $\langle 001 \rangle$ direction. It is seen that very good agreement with experiment is obtained in E_g geometry but not in E_θ geometry. This was also found by Guha and Chase, who suggested that the discrepancy might be due to the inaccuracy of the cluster-model eigenfunctions. O'Brien suggested that there might be a cancellation between two sets of effective operators in the polarizability tensor, one set operating on the electronic co-ordinates, the other on the vibrational co-ordinates [7]. The latter is responsible for the high-energy broad band scattering and is not included in our treatment [equation (9)].

The data may also be reproduced with alternative choices for the effective phonon frequency, as the energy spacing is an approximate function of $\hbar\omega^3/A_1^{E^2}$. The lower

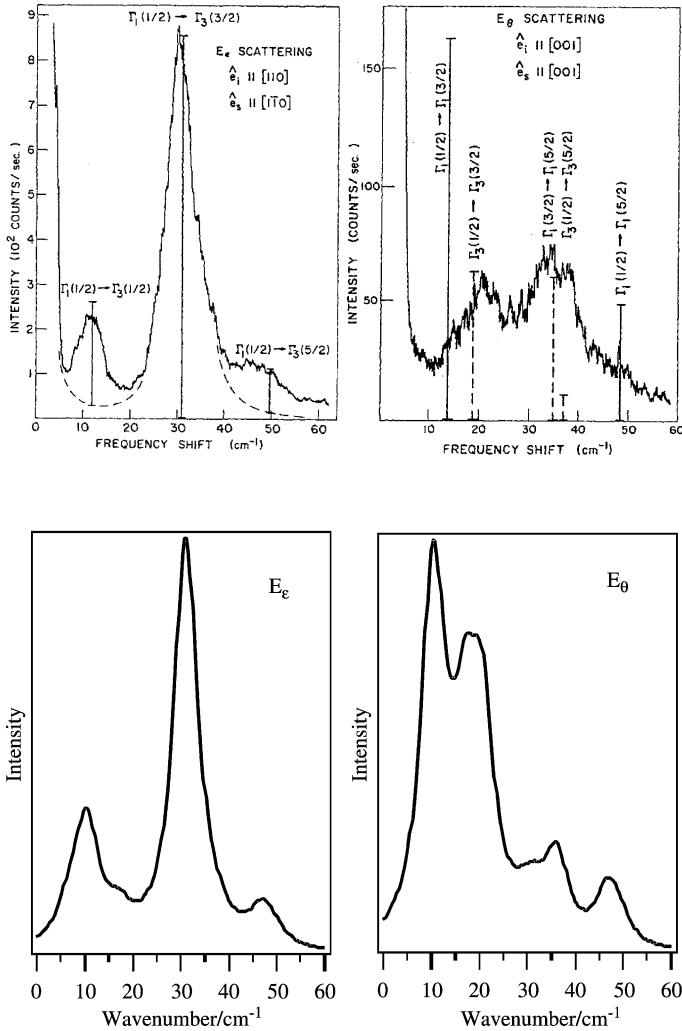


Fig. 3. Experimental and theoretical electronic Raman Spectra of $\text{CaO}:\text{Cu}^{2+}$ in polarization geometries which facilitate the observation of transitions of E_e or E_θ symmetry only. The experimental spectra are reproduced from the work by Guha and Chase [1] and were collected at ~ 4.2 K. The relative intensities calculated by the authors are shown as vertical bars. The theoretical spectra shown below were calculated with the following parameters: $\hbar\omega = 330 \text{ cm}^{-1}$, $A_1^E = -1900 \text{ cm}^{-1}$, $A_2^E = -0.65 \text{ cm}^{-1}$, $S_\theta = 10 \text{ cm}^{-1}$, $S_e = 4 \text{ cm}^{-1}$, $n_v = 40$, $T = 7 \text{ K}$.

the value of $\hbar\omega$, the smaller the value of A_1^E needed for the energy of the $\{A_1, A_2\}$ first excited states to come to within $\sim 10 \text{ cm}^{-1}$ of the ground state. O'Brien deduced an effective frequency of $\hbar\omega = 216 \text{ cm}^{-1}$ from the broad-band Raman scattering [7]. Using this frequency, we have also been able to obtain

Table 1. Calculated values of E_{JT} and $\hbar\omega$ reported for $\text{MgO}:\text{Cu}^{2+}$ and related systems

	$\text{MgO}:\text{Cu}^{2+}$	$\text{CaO}:\text{Cu}^{2+}$	$\text{SrO}:\text{Cu}^{2+}$
$E_{JT} \text{ (cm}^{-1}\text{)}$	335 [5]; 281 [6]	450 [5]	440 [5]; 378 [6]
$\hbar\omega \text{ (cm}^{-1}\text{)}$	400 [5]; 490 [6]	235 [5]	185 [5]; 200 [6]

These values are reproduced from Refs. [5,6].

a good reproduction of the experimental Raman spectrum with $A_1^E = -1030$, $A_2^E = -1.0 \text{ cm}^{-1}$. Finally, we consider the parameters proffered on the basis of *ab initio* [5] and DFT [6] calculations by various Spanish groups. The calculated values of E_{JT} and $\hbar\omega$ for $\text{MgO}:\text{Cu}^{2+}$ and related systems are compiled in Table 1, derived assuming coupling to the $\nu_2(\text{CuO}_6)$ vibration only.

The values of E_{JT} are in the range $281\text{--}450 \text{ cm}^{-1}$, whilst $\hbar\omega$ spans $185\text{--}490 \text{ cm}^{-1}$. For $\text{CaO}:\text{Cu}^{2+}$, Pascual *et al.* calculate $E_{JT} = 450$ and $\hbar\omega = 235 \text{ cm}^{-1}$. It is not possible to obtain agreement with the electronic Raman data with these parameters. For such low values of E_{JT} , $\hbar\omega$ must be reduced substantially. Using the following parameters, corresponding to $E_{JT} \sim 285 \text{ cm}^{-1}$, fair agreement is obtained: $\hbar\omega = 70 \text{ cm}^{-1}$, $A_1^E = -200 \text{ cm}^{-1}$, $A_2^E = -2.3 \text{ cm}^{-1}$, $S_\theta = 3 \text{ cm}^{-1}$, $S_e = 3 \text{ cm}^{-1}$, $T = 7 \text{ K}$.

3.2. UV–vis data

Although the nature of the strain interaction may be different in crystals examined by EPR, electronic, and Raman spectroscopies, one would expect the remaining parameters to vary little. A given model must be able to account for all the experimental data.

Crystals of $\text{CaO}:\text{Cu}^{2+}$ and $\text{MgO}:\text{Cu}^{2+}$ are green in color, implying absorption in the red and blue. As far as we are aware, electronic spectra have been reported for $\text{MgO}:\text{Cu}^{2+}$ only. Schmitz-Du Mont recorded spectra as a function of Cu^{2+} concentration [21] and identified the tail end of an intense transition in the blue/UV region of the spectrum, and two weaker broad bands at ~ 5500 and $\sim 11\,500$, in all the samples examined. The lower energy bands may be assigned to the intra- E and $E \rightarrow T_2$ d–d transitions, respectively, with energies $\sim 4E_{JT}(= 2\hbar\omega(A_1^E/\hbar\omega)^2)$ and $(2E_{JT} + 10\text{Dq})$, giving $E_{JT} \sim 1400$ and $10\text{Dq} \sim 8750 \text{ cm}^{-1}$. On the basis of these assignments, the theoretical values for E_{JT} in Table 1 are too low. Similar values for E_{JT} and 10Dq would be expected for $\text{CaO}:\text{Cu}^{2+}$, though the trend in Table 1 suggests that E_{JT} may be a little higher. In the previous section we showed that the Raman data can be modelled with $\hbar\omega = 330$, $E_{JT} = 5500 \text{ cm}^{-1}$ or $\hbar\omega = 70$, $E_{JT} = 285 \text{ cm}^{-1}$. These parameters must be rejected as they imply that the energy of the $4E_{JT}$ transition would be substantially different to that observed for $\text{MgO}:\text{Cu}^{2+}$. Finally we consider O’Brien’s multimode model [7]. According to her

analysis, multimode coupling gives rise to low energy structure which approximates to that calculated using a single mode $E \otimes e$ vibronic Hamiltonian, but that the effective coupling constant inferred is too high. In O'Brien's notation, the effect of multimode coupling in CaO:Cu^{2+} is such that the value of $\langle \omega \rangle / k_{\text{eff}}^2$ deduced from a single-mode theory should be reduced by $\sim 30\%$; this quantity corresponds to $\langle \hbar \omega \rangle / (A_1^E / \hbar \omega)^2$ in our notation. The Raman data may be modelled using $\hbar \omega = 216 \text{ cm}^{-1}$, as suggested by O'Brien, with $\langle \hbar \omega \rangle / (A_1^E / \hbar \omega)^2 \sim 9.5 \text{ cm}^{-1}$. Taking into account the compression of the energy scale in the low energy region by multimode effects, the value for $\langle \hbar \omega \rangle / (A_1^E / \hbar \omega)^2$ should be replaced by $\sim 13.57 \text{ cm}^{-1}$ ($A_1^E \sim -860 \text{ cm}^{-1}$) from which $2\langle \hbar \omega \rangle (A_1^E / \hbar \omega)^2 \sim 6850 \text{ cm}^{-1}$. This value is in accordance with the first transition energy that would be expected for CaO:Cu^{2+} , based on the MgO:Cu^{2+} data.

3.3. EPR data

The EPR spectrum of CaO:Cu^{2+} is quite exquisite. The 1.3 K spectrum is undoubtedly that of a Γ_8 ground state split by low symmetry strain, the spin-Hamiltonian parameters being precisely defined [2,3]. Two sets of resonances are located with $\vec{B} \parallel [1\ 0\ 0]$, one centred at $g \sim 2$, the other at $g \sim 2.34$. With $\vec{B} \parallel [1\ 1\ 1]$ a complex spectrum is obtained with a number of resonances observed centred at ~ 2.22 . The deviation of the g value from the free electron value increases as a function of λ/Δ , where Δ is the energy gap between the ground state and the levels of the higher lying ${}^2T_{2g}$ term, which is of the order of $2E_{\text{JT}} + 10\text{Dq}$. Using the parameters $\hbar \omega = 216 \text{ cm}^{-1}$, $A_1^E = -860 \text{ cm}^{-1}$, $A_2^E = -1.0 \text{ cm}^{-1}$, we are able to obtain good agreement with the observed g values by setting λ to -700 cm^{-1} , 10Dq to 8000 cm^{-1} and the orbital reduction factor, k , to 0.88. The value for 10Dq is in keeping with expectations based on the value determined for MgO:Cu^{2+} . The g values can also be reproduced with $\hbar \omega = 330 \text{ cm}^{-1}$, and $E_{\text{JT}} = 5500 \text{ cm}^{-1}$, but the value of $\lambda/10\text{Dq}$ implied is not realistic. Reynolds *et al.* suggested that the hyperfine coupling constants obtained are consistent with $\kappa \sim 0.002$ [3]. We find better agreement is obtained with $\kappa \sim 0.2$.

For all the parameter sets used to model the Raman data, the calculated tunnelling splitting, 3Γ , is $\sim 3 \text{ cm}^{-1}$. The energies and wavefunctions of states within ca 5 cm^{-1} of the ground state cannot be probed by Raman spectroscopy due to the problem of elastic scattering, but have been inferred from the low temperature EPR spectra. In Fig. 4 are shown the experimental and simulated EPR spectra of CaO:Cu^{2+} reproduced from Ref. [3]. Good agreement between theory and experiment is obtained using a three-state perturbation model [16] assuming random-strain coupling between the ground state and an excited state singlet, with $3\Gamma \sim 3 \text{ cm}^{-1}$ and $\bar{\delta}/3\Gamma \sim 0.67$.

From the work of O'Brien [7] we infer that it should be possible to simulate the EPR spectra of CaO:Cu^{2+} using a single-mode vibronic model, but in doing so the values for the parameters should be regarded as effective quantities.

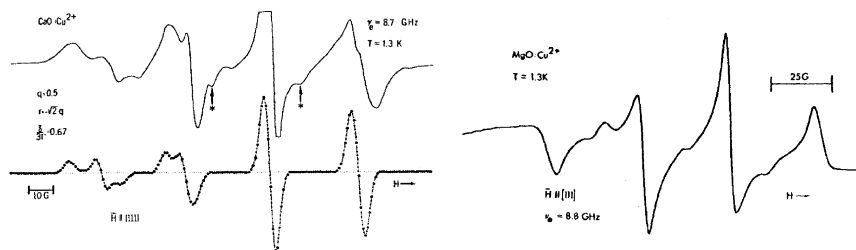


Fig. 4. Experimental and Calculated EPR spectra of $\text{CaO}:\text{Cu}^{2+}$ and $\text{MgO}:\text{Cu}^{2+}$ reproduced from the work of Reynolds, Boatner, Abraham, and Chen [3]. The X-band spectra were recorded at 1.3 K with $\vec{B} \parallel [1\ 1\ 1]$. The calculated spectrum was generated using a three-state perturbation model described in detail in Refs. [4,16].

In Fig. 5 are shown EPR simulations as a function of the magnitude of the random-strain parameter, $\bar{\delta}$, calculated from repeated numerical diagonalizations of the single mode Hamiltonian given in equation (1), where we have employed parameters pertaining to $\hbar\omega = 70\text{ cm}^{-1}$. In doing so we are not sanctioning this frequency. For a given value of $\bar{\delta}$, the profile of the spectrum depends on the value of 3Γ , and on the reduction factor $q \approx \frac{1}{2}[1 + (\hbar\omega/4E_{\text{JT}})^2]$ [4]; and these quantities are very similar for all three parameter sets used to model the Raman data. The calculation of an EPR spectrum with $\hbar\omega = 70\text{ cm}^{-1}$, as opposed to 216 cm^{-1} , requires considerably less computation, as satisfactory convergence can be obtained with smaller values of n_v . In these calculations, we have chosen the values of A_1^E and A_2^E that reproduce the vibronic Raman spectrum, and adjusted the remaining parameters to best reproduce the reported values of the g and A parameters. The calculated hyperfine splitting with $\vec{B} \parallel [1\ 1\ 1]$ is a little greater than the experimentally determined value.

The calculated spectra provide a poignant illustration of the expected change in the profile as a function of $\bar{\delta}/3\Gamma$. The physical origin of the curious line shapes is well understood, and has been discussed in detail by Reynolds and Boatner [4]. The effect of random-strain coupling is to distribute the resonance positions between limits corresponding to the dynamic and static Jahn–Teller effect. These authors classified ‘quasidynamic’ to the general range of $\bar{\delta}/3\Gamma$ values given by $0.1 < \bar{\delta}/3\Gamma < 0.8$ and ‘quasistatic’ to the general region of $\bar{\delta}/3\Gamma$ values given by $0.3 < \bar{\delta}/3\Gamma < 5.0$. A fair reproduction of the experimental profile is found for $\bar{\delta}/3\Gamma \sim 0.67$, but is admittedly not as impressive as that produced by Reynolds and Boatner shown in Fig. 4. Further modelling of the data should be attempted; the trouble being that it takes rather a long time to calculate a single spectrum. It should be noted, however, that the simulation with $\bar{\delta}/3\Gamma \sim 0.1$ bears some resemblance to the spectrum of $\text{MgO}:\text{Cu}^{2+}$, also shown in Fig. 5, which Reynolds and Boater were unable to simulate though a value of $\bar{\delta}/3\Gamma \sim 0.12$ was inferred from the angular dependence of the spectrum [3].

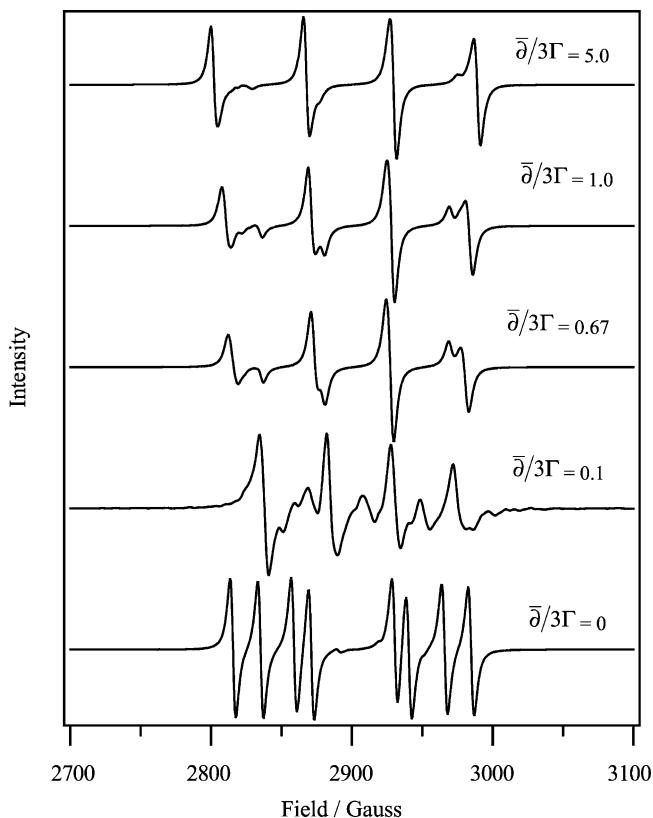


Fig. 5. EPR simulations calculated as described in Section 2 with the following parameters: $\hbar\omega = 70 \text{ cm}^{-1}$, $A_1^E = -200 \text{ cm}^{-1}$, $A_2^E = -2.3 \text{ cm}^{-1}$, $A_1^T = -50 \text{ cm}^{-1}$, $10Dq = 10\,000 \text{ cm}^{-1}$, $\lambda_z = -700 \text{ cm}^{-1}$, $P = 0.036 \text{ cm}^{-1}$, $\kappa = 0.17$, $n_v = 20$, $\nu_e = 9.0 \text{ GHz}$, $T = 1.3 \text{ K}$, $\vec{B} \parallel [1\ 1\ 1]$. These parameters equate to $3\Gamma \sim 3.22 \text{ cm}^{-1}$. The spectra were calculated for different ratios of $\bar{\partial}/3\Gamma$, displayed in the figure, with $\sigma = 0.1\bar{\partial}$.

4. SUGGESTED EXPERIMENTS FOR THE CHARACTERIZATION OF THE LOW ENERGY VIBRONIC STRUCTURE

The nature of the Jahn–Teller interaction is such as to yield several vibronic states, within just a few wave numbers of the ground state. These states have very different expectation values for the electronic and nuclear co-ordinates, and we shall now examine how the low-lying vibronic structure may be elucidated by the followings modern physical techniques: high-field, multifrequency electron paramagnetic resonance (HFMF EPR); magnetic circular dichroism (MCD), and extended X-ray absorption fine structure spectroscopy (EXAFS). The recent advent of HFMF EPR

technique [22] allows one to employ excitation frequencies typically ranging from 95 to 575 GHz in conjunction with magnetic fields up to 20 T or more. MCD and EXAFS are selective spectroscopic techniques that can be used to study the magnetic properties and local geometries of impurity ions in crystals.

From modelling of the experimental data, it has been established that the warping of the potential minimum is small, and that random strain is comparable in magnitude to the tunnelling splitting. Thus, the three lowest lying Kramers doublets are not strongly localized in the three minima produced by the warping. In order to investigate whether it might be possible to observe transitions between states belonging to different Kramers doublets, we have calculated spectra at very high fields and high frequencies, using the same parameter set used to calculate the spectrum in Fig. 5, with $\bar{\delta}/3\Gamma = 0.67$. In Fig. 6 is shown the calculated EPR spectrum at 190.0 GHz between 0.1 and 12 T at 5 K. Compared to the X-band simulation, the higher frequency spectrum displays a far greater degree of structure and therefore affords a more precise characterization of the electronic structure of the copper(II) impurity. Additional resonances are observed at other regions of the spectrum, and are ca 3000 times less intense. These resonances do indeed correspond to transitions between the three lowest lying Kramers doublets and should be observable on a sufficiently sensitive instrument, providing they are not smeared out due to relaxation effects. Relaxational averaging of the X-band EPR spectrum is reported to occur for CaO:Cu²⁺ [2,3] upon increasing the temperature from 1.3 to 5 K. Recording the spectrum at 190 as opposed to 9 GHz does, however, afford a 20-fold increase in the time resolution.

The electronic Raman data can be modelled with $\bar{\delta} \sim 4.2 \text{ cm}^{-1}$ and $\phi = 45^\circ$, whereas the EPR data are consistent with $\bar{\delta} \sim 2.2 \text{ cm}^{-1}$, and a random-strain

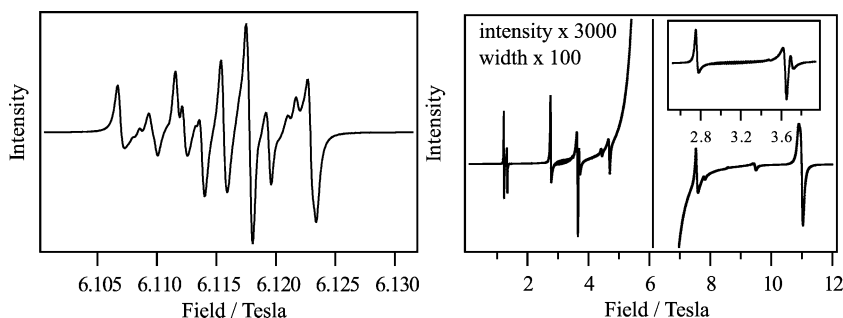


Fig. 6. EPR simulation of an octahedrally co-ordinated copper(II) centre in the field range 0.1–12 T, calculated with the following parameters: $\hbar\omega = 70 \text{ cm}^{-1}$, $A_1^E = -200 \text{ cm}^{-1}$, $A_2^E = -2.3 \text{ cm}^{-1}$, $A_1^T = -50 \text{ cm}^{-1}$; $10Dq = 10\,000 \text{ cm}^{-1}$, $\lambda = -700 \text{ cm}^{-1}$, $\bar{\delta} = 2.23 \text{ cm}^{-1}$, $P = 0.036 \text{ cm}^{-1}$, $\kappa = 0.17$, $n_v = 15$, $\nu_e = 190.0 \text{ GHz}$, $T = 5 \text{ K}$ with $\vec{B} \parallel [1\ 1\ 1]$.

distribution. The execution and interpretation of both these experiments is challenging. We suggest that they should be complemented by MCD measurements, from which the magnetic moment at high fields and low temperatures can be determined. The high-field, low temperature magnetization curves provide a sensitive measure of the strain distribution in the crystal. This can be seen in Fig. 7 where we plot the magnetic moment vs. B/T , for $\vec{B} \parallel [1\ 0\ 0]$, and fixed ϑ , but various values of ϕ . For $\phi = 0^\circ$ and 180° , the electronic part of the ground state wavefunction is $\sim 3z^2 - r^2$ and $\sim x^2 - y^2$, respectively (for $\delta > \beta$), giving rise to very different values for the saturation magnetization. Other values of ϕ will give rise to saturation values of the magnetic moment within these limits.

It is conceivable that a strong magnetic field might change the strain distribution in the crystal to favor the stabilization of the Kramers doublet with the larger g value. This would give rise to magnetic hysteresis.

Perhaps the most elegant experiment would be to monitor the nuclear coordinates as a function of the orientation of a crystal of $\text{CaO}:\text{Cu}^{2+}$ in a magnetic field. If the temperature is sufficiently low, and the strain splitting sufficiently small, it should be possible to exert a significant influence over the geometry of the complex

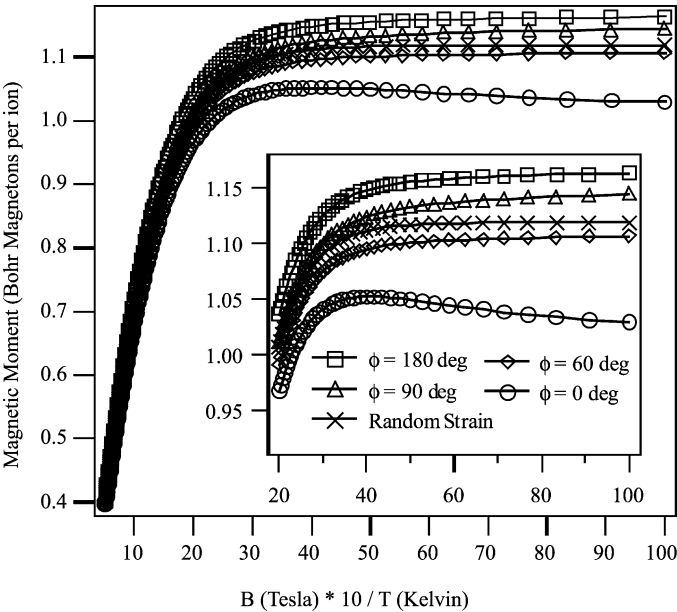


Fig. 7. Theoretical calculations of the magnetic moment vs. B/T , with $\vec{B} \parallel [1\ 0\ 0]$. The parameters common to all the calculated curves are: $B = 10\text{ T}$, $\hbar\omega = 70\text{ cm}^{-1}$, $A_1^E = -200\text{ cm}^{-1}$, $A_2^E = -2.3\text{ cm}^{-1}$, $10Dq = 10\ 000\text{ cm}^{-1}$, $\lambda = -700\text{ cm}^{-1}$, $\vartheta = 2.23\text{ cm}^{-1}$. The curves differ in terms of the anisotropy of the strain splitting, as indicated in the figure.

Table 2. Vibronic energy levels and bond lengths for the $[\text{CuO}_6]^{10-}$ entity calculated using the parameters listed in the caption of Fig. 8 with the angle of $\vec{B}$ from the $[1\ 0\ 0]$ direction in the $(1\ 0\ 0)$ plane set to 45°

Energy (cm^{-1})	Cu–O(1) ($\text{\AA}$)	Cu–O(2) ($\text{\AA}$)	Cu–O(3) ($\text{\AA}$)
0	2.1257	1.8325	2.0418
0.9	1.9411	2.1144	1.9445
3.9	1.9369	2.0495	2.0136
10.2	2.1012	1.8030	2.0958
11.4	1.9330	2.1360	1.9310
14.2	1.9682	2.0563	1.9755
24.9	2.0161	1.9838	2.0001
34.8	1.9980	1.9915	2.0105
35.0	2.0055	2.0081	1.9864
35.4	2.0002	1.9867	2.0131

by applying a strong magnetic field. In Table 2 are shown the calculated bond lengths for the low-lying vibronic states of $\text{CaO}:\text{Cu}^{2+}$ in a field of 10 T.

In a diffraction experiment one would observe the Boltzmann average of the geometric properties of the vibronic energy levels. This quantity is plotted in Fig. 8,

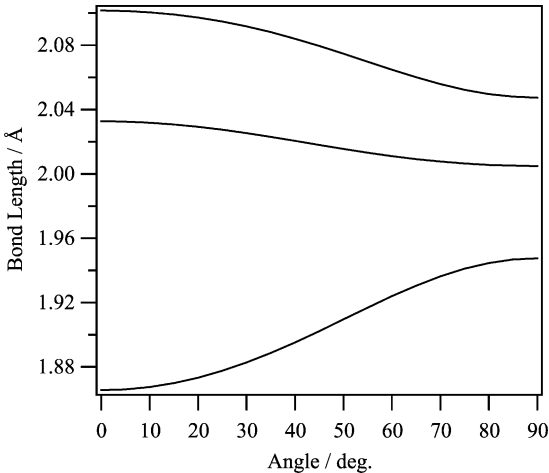


Fig. 8. Calculated Cu–O bond lengths vs. angle of $\vec{B}$ from the $[1\ 0\ 0]$ direction in a $(1\ 0\ 0)$ plane. The bond lengths were calculated with the following parameters: $B = 10\ \text{T}$, $\hbar\omega = 70\ \text{cm}^{-1}$, $A_1^E = -200\ \text{cm}^{-1}$, $A_2^E = -2.3\ \text{cm}^{-1}$, $10Dq = 10\ 000\ \text{cm}^{-1}$, $\lambda = -700\ \text{cm}^{-1}$, $\partial = 1\ \text{cm}^{-1}$, $\phi = 135^\circ$, $T = 1.2\ \text{K}$, average Cu–O bond length = $2.0\ \text{\AA}$, reduced mass = 18 atomic units.

as a function of the angle of $\vec{B}$ from the $[1\ 0\ 0]$ direction in a $(1\ 0\ 0)$ plane. The apparent change in the observed bond lengths is quite pronounced and the relationship is very sensitive to the parameters of the vibronic Hamiltonian, in particular to λ and Δ , as the ratio of these parameters governs the g values of the Kramers doublets. In practice it would be easier to conduct an EXAFS experiment, in which case one obtains information about the local copper–oxygen bond lengths. As shown in the seminal study of the ammonium copper tutton salt [17], the EXAFS signal at a given temperature will be a Boltzmann-weighted superposition of the geometric properties of the individual vibronic levels.

5. CONCLUSION

In this work we have attempted to model the available experimental data for $\text{CaO}:\text{Cu}^{2+}$ using a variety of parameter sets taken from the literature. We conclude that only O'Brien's multimode model [7], for which $\hbar\omega \sim 216\text{ cm}^{-1}$ and $E_{\text{JT}}/\hbar\omega \sim 8$, can satisfactorily account for all the data. These systems are particularly attractive to both the theoretician and experimentalist fascinated by Jahn–Teller funny business in that the states pertaining to $j = 1/2$ and $3/2$ span just a few wave numbers. We have demonstrated how a number of modern physical techniques can be employed to elucidate further the low-lying vibronic structure. In particular it should be possible to obtain a direct measure of the tunnelling splitting from a high-field, high-frequency EPR experiment.

ACKNOWLEDGEMENTS

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APPENDIX A

Hamiltonian matrix for the cubic ligand field, spin–orbit coupling and the electronic Zeeman interaction in the real cubic bases of a ${}^2D$ term. The g -factor for the free electron has been set to two for clarity (Table A.1).

Table A.1.

	$\theta +$	$\theta -$	$\varepsilon +$	$\varepsilon -$	$yz +$	$yz -$	$zx +$	$zx -$	$xy +$	$xy -$
$\theta +$	$B_z\beta - E$	$B_x\beta - iB_y\beta$	0	0	$+B_x\beta k\sqrt{3}i$	$\lambda i\sqrt{3}/2$	$-B_y\beta k\sqrt{3}i$	$-\lambda\sqrt{3}/2$	0	0
$\theta -$	$B_x\beta + iB_y\beta$	$-B_z\beta - E$	0	0	$\lambda i\sqrt{3}/2$	$+B_x\beta k\sqrt{3}i$	$\lambda\sqrt{3}/2$	$-B_y\beta k\sqrt{3}i$	0	0
$\varepsilon +$	0	0	$B_z\beta - E$	$B_x\beta - iB_y\beta$	$+B_x\beta ki$	$\lambda i/2$	$B_y\beta ki$	$\lambda i/2$	$-\lambda i - B_z\beta k2i$	0
$\varepsilon -$	0	0	$B_x\beta + iB_y\beta$	$-B_z\beta - E$	$\lambda i/2$	$+B_x\beta ki$	$-\lambda i/2$	$B_y\beta ki$	0	$-\lambda i - B_z\beta k2i$
$yz +$	$-B_x\beta k\sqrt{3}i$	$-\lambda i\sqrt{3}/2$	$-B_x\beta ki$	$-\lambda i/2$	$10Dq + B_z\beta - E$	$B_x\beta - iB_y\beta$	$\lambda i/2 + B_z\beta ki$	0	$-B_y\beta ki$	$-\lambda i/2$
$yz -$	$-\lambda i\sqrt{3}/2$	$-B_x\beta k\sqrt{3}i$	$-\lambda i/2$	$-B_x\beta ki$	$B_x\beta + iB_y\beta$	$10Dq - B_z\beta - E$	0	$-\lambda i/2 + B_z\beta ki$	$\lambda i/2$	$-B_y\beta ki$
$zx +$	$+B_y\beta k\sqrt{3}i$	$\lambda\sqrt{3}/2$	$-B_y\beta ki$	$-\lambda i/2$	$-\lambda i/2 - B_z\beta ki$	0	$10Dq + B_z\beta - E$	$B_x\beta + iB_y\beta$	$+B_x\beta ki$	$-\lambda i/2$
$zx -$	$-\lambda\sqrt{3}/2$	$+B_y\beta k\sqrt{3}i$	$\lambda i/2$	$-B_y\beta ki$	0	$\lambda i/2 - B_z\beta ki$	$B_x\beta + iB_y\beta$	$10Dq - B_z\beta - E$	$\lambda i/2$	$+B_x\beta ki$
$xy +$	0	0	$\lambda i + B_z\beta k2i$	0	$+B_y\beta ki$	$\lambda i/2$	$-B_y\beta ki$	$-\lambda i/2$	$10Dq + B_z\beta - E$	$B_x\beta - iB_y\beta$
$xy -$	0	0	0	$-\lambda i + B_z\beta k2i$	$-\lambda i/2$	$+B_y\beta ki$	$-\lambda i/2$	$-B_x\beta ki$	$B_x\beta + iB_y\beta$	$10Dq - B_z\beta - E$

REFERENCES

- [1] S. Guha and L. L. Chase, *Phys. Rev. B*, 1975, **12**, 1658.
- [2] R. E. Coffman, D. L. Lyle and D. R. Mattison, *J. Phys. Chem.*, 1968, **72**, 1392.
- [3] R. W. Reynolds, L. A. Boatner, M. M. Abraham and Y. Chen, *Phys. Rev. B*, 1974, **10**, 3802.
- [4] R. W. Reynolds and L. A. Boatner, *Phys. Rev. B*, 1975, **12**, 4735.
- [5] J. L. Pascual, L. Seijo and Z. Barandiarán, *J. Chem. Phys.*, 1993, **98**, 9715.
- [6] J. A. Aramburu, M. T. Barriuso, P. García Fernández, M. Moreno, *Advances in Quantum Chemistry*, 2003, **44**, 445–459.
- [7] M. C. M. O'Brien, *J. Phys. C. Solid State Phys.*, 1983, **16**, 85.
- [8] M. J. Riley, *Top. Curr. Chem.*, 2001, **214**, 57.
- [9] S. Sugano, Y. Tanabe and H. Kamimura, *Multiplets of Transition Metal Ions in Crystals*, Academic Press, New York, 1970.
- [10] C. Cohen-Tannoudji, B. Diu and F. Laloe, *Quantum Mechanics*, 1977, Vol. 1, Chapter V, p. 488.
- [11] F. E. Mabbs and D. Collison, *Electron Paramagnetic Resonance of Transition Metal Compounds*, Elsevier, 1992, p. 359.
- [12] K. Sasaki and Y. Obata, *J. Phys. Soc. Jpn*, 1970, **28**, 1157.
- [13] F. S. Ham, *J. Phys. Colloq.*, 1971, **32**, 952.
- [14] P. L. W. Tregenna-Piggott, M. C. M. O'Brien, J. R. Pilbrow, H-U. Güdel, S. P. Best and C. Noble, *J. Chem. Phys.*, 1997, **107**, 8275.
- [15] P. L. W. Tregenna-Piggott and H-U. Güdel, *Inorg. Chem.*, 2001, **40**, 5497.
- [16] F. S. Ham, Jahn–Teller effects in electron paramagnetic resonance spectra. in *Electron Paramagnetic Resonance* (ed. S. Geshwind), Plenum Press, New York, 1972.
- [17] V. M. Masters, M. J. Riley and M. A. Hitchman, *Inorg. Chem.*, 2001, **40**, 843.
- [18] With the metal centre at the origin of a Cartesian co-ordinate system, the positions of the six oxygen atoms are as follows: O(1), O(2), ... are as follows: O(1) = x, y, z ; O(2) = z, x, y ; O(3) = y, z, x ; O(4) = $-x, -y, -z$; O(5) = $-z, -x, -y$; O(6) = $-y, -z, -x$.
- [19] M. C. M. O'Brien, *Proc. R. Soc., A*, 1964, **281**, 323.
- [20] The authors [1] report (p. 1670) that the calculated intensities for the E_θ geometry are in very poor agreement with the data shown in Fig. 10. This spectrum is an order of magnitude weaker than the E_θ spectrum. We believe that there is a typographical error here and that the last three words of the quote should read the E_e spectrum. This would be consistent with the absolute intensity scales in Figs 8 and 10 of their work
- [21] O. Schmitz-Du, Mont, *Monatshefte für Chemie*, 1968, **99**, 1285.
- [22] F. Muller, A. Hopkins, N. Coron, M. Grynberg, L. C. Brunel and G. Martinez, *Rev. Sci. Instrum.*, 1989, **60**, 3681; A. L. Barra, L. C. Brunel and J. B. Robert, *Chem. Phys. Lett.*, 1990, **165**, 107.

The Mechanisms of Jahn–Teller Complex Reorientations

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Abstract

The process of reorientations of the Jahn–Teller (JT) complex with trigonal site symmetry as well as slightly elongated and compressed ones are studied by X-band and Q-band electron paramagnetic resonance (EPR). The observed phenomena of the resonance line broadening and the dispersion of the resonance signal followed by its coalescence are discussed taking into consideration the increase in the transition rate with a rise in temperature. We conclude that even for a complex located at low symmetry sites the transitions between JT conformations can have a tunneling character.

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1. INTRODUCTION

The temperature dependence of the magnetic complex conformation is known to be one of the distinguishable features of Jahn–Teller (JT) dynamics [1]. Keeping in mind electron paramagnetic resonance (EPR) as one of the most effective methods of studying the JT effect, we shall consider the problem of the transition from the low temperature, static JT situation to the high temperature, dynamic, motional averaged JT situation. The results of such processes are discussed in the literature [1–4]. At the same time, some important features – the nature of the transitions

between JT conformations, the energy of the excited vibronic levels involved in the process and the transition rates are problems which still require consideration. More than that, the role of the singlet vibronic level, when the isotropic high temperature spectrum EPR is observed, also gives rise to uncertainties [4]. We consider the mechanisms of the transitions between the possible JT conformations as applied to examples of the Cu^{2+} ion in sixfold coordination. An adiabatic approach in the framework of the $E \times e$ JT problem will be used. Discussion of the JT complex reorientations will thus be provided using the simple adiabatic potential surface scheme. This allows us to simplify the visualization of the discussed phenomena and use known parameters.

X- and Q-band EPR in the temperature range 4.2–300 K were used to obtain data for the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ JT complex. The cases of the JT complexes in a site of cubic (or trigonal) symmetry (*a*), tetragonal elongated symmetry (*b*), and tetragonal compressed symmetry (*c*) are analyzed. The crystallo-hydrates are suitable and convenient objects for investigation, as representatives of this class of compounds:

- All the above three situations are realized.
- The same chromophore – the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ octahedron – presents a JT complex which is very convenient from the point of view of studying the influence of different perturbing effects.
- A large set of this class of compounds is available and local JT properties as well as the effects of the cooperative interactions can be investigated.

2. THE EXPERIMENTAL RESULTS AND DISCUSSION

2.1. JT complex in a site of cubic (trigonal) symmetry

The $^{63}\text{Cu}^{2+}$ doped $\text{ZnZrF}_6 \cdot 6\text{H}_2\text{O}$ was used as the representative of the cubic (trigonal) structure. This is known to be an analogue of $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$, which allowed the first observation by Bleaney *et al.* in 1955 [5] of the unusual temperature dependence of the EPR spectrum, due to the JT effect. $\text{ZnZrF}_6 \cdot 6\text{H}_2\text{O}$ was studied several times over the years (see Ref. [6] for example). We reinvestigate now $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{ZrF}_6 \cdot 6\text{H}_2\text{O}$ to emphasize some features not mentioned before [7].

The $\text{ZnZrF}_6 \cdot 6\text{H}_2\text{O}$ crystal structure belongs to the $R\bar{3}m$ space group, so that the guest $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complexes are subjected to the influence of the octahedral crystal field with a small trigonal symmetry component. The adiabatic potential surface has three minima of equal energy (the energy intervals δ_{ij} between minima, $\delta_{12} = \delta_{13} = \delta_{23} = 0$ neglecting random strains). The potential barrier between minima has been estimated as $2\beta \approx 600\text{--}450\text{ cm}^{-1}$ [8,9]. At low temperatures this allows the observation of the static JT conformations corresponding to the octahedron elongated along one of the three C_4 axes, and the averaging of the conformations with temperature increase can be studied directly.

The changes of the X-band spectrum over the temperature range 4–120 K at the stationary magnetic field $H \parallel \langle 1\ 0\ 0 \rangle$ (C_4) axes are shown in Fig. 1. The parameters of the spin Hamiltonian describing the spectrum are provided in Table 1.

As seen distinctly in Fig. 1, there are the three distinguishable temperature intervals. Below ~ 40 K spectra corresponding to the low temperature values of $g_{\parallel}$ and $g_{\perp}$ are detected. At temperatures between 40 and 55 K the spectrum in the parallel orientation (magnetic field H parallel to a C_4 -axis of the complex) is not observed. Above ~ 55 K a quasi-isotropic spectrum with $\langle g \rangle = 2.22$ and $\langle A \rangle = 24 \times 10^{-4} \text{ cm}^{-1}$ is observed. It can be mentioned also, that in the T -interval 4.2–40 K the EPR lines for $H \parallel C_4$ broaden with increasing T without changing, in the limit of the experimental errors, their position in the magnetic field (a small displacement of the signals in perpendicular orientations is observed). The same is true for the parameter of hyperfine interaction $A_{\parallel}$. Any distinctions of the line widths corresponding to different m_I are absent in this T -interval.

Such behavior of the spectrum fully corresponds to the predictions of the theories of motional narrowing of Anderson, Kubo and Tomita and others [10,11]. With temperature increase the transition rate between different JT conformations ν_{tr}

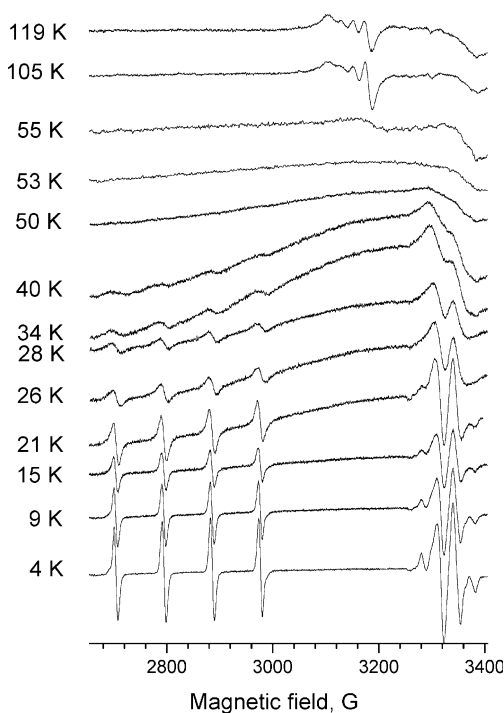


Fig. 1. Temperature dependence of the single crystal X-band spectrum of $\text{ZnZrF}_6 \cdot 6\text{H}_2\text{O}:\text{Cu}^{2+}$ with $H \parallel \langle 1\ 0\ 0 \rangle (C_4)$.

Table 1.

T (K)	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel} \times 10^{-4}$ (cm $^{-1}$)	$A_{\perp} \times 10^{-4}$ (cm $^{-1}$)
300	2.234	2.221		
77	2.233	2.221	– 22	– 26
4.2	2.471	2.101	– 105	+ 17

changes gradually from the condition $\nu_{\text{tr}} < (\nu_1 - \nu_2) \equiv (g_{\parallel} - g_{\perp})\beta H/h$, allowing observation of the different JT conformations, to the condition $\nu_{\text{tr}} > (g_{\parallel} - g_{\perp})\beta H/h$, corresponding to the motional averaged conformation. The relatively low temperature $T \approx 40$ K ($kT = 28$ cm $^{-1}$, much less than the potential barrier height 2β), at which different conformations become averaged shows that the transitions between conformations have a tunneling character. Considering these transitions as tunneling controlled process [12], we can attempt to determine the energy of the intermediate vibronic states involved. With this aim we consider the Q-band EPR results [6]. The main features of the spectral changes were the same as in X-band, but the disappearance of the static spectrum was observed at the higher temperature of $T \approx 55$ K. In order to use these data for the estimation of the energy of vibronic levels participating in the tunneling controlled process, we have assumed that it takes place through a single excited vibronic level (we shall return to consideration of the validity of such a supposition later).

Let us use Heisenberg's uncertainty principle:

$$\Delta\nu\tau \sim 1/2\pi \quad (1)$$

considering $\Delta\nu$ as the frequency interval between the vibronic states of the JT complex to be averaged and τ as the shortest time allowing the states ν_1 and ν_2 to be distinguished. Then:

$$\nu_{\text{tr}}^{\text{X}} = \Delta\nu_{\text{X}} \text{ (in X-band)} \approx 1/2\pi \tau_{\text{X}}^{-1} = \nu_{\text{tun}} \exp(-E_{\text{v}}/kT_{\text{X}})$$

$$\text{with} \quad \Delta\nu_{\text{X}} = \Delta g\beta H/h \approx 1.8 \times 10^9 \text{ Hz}; \quad T_{\text{X}} = 40 \text{ K}$$

and

$$\nu_{\text{tr}}^{\text{Q}} = \Delta\nu_{\text{Q}} \text{ (in Q-band)} \approx 4\Delta\nu_{\text{X}} = 1/2\pi \tau_{\text{Q}}^{-1} = \nu_{\text{tun}} \exp(-E_{\text{v}}/kT_{\text{Q}})$$

$$\text{with} \quad \Delta\nu_{\text{Q}} = \Delta g\beta H/h \approx 7.2 \times 10^9 \text{ Hz}; \quad T_{\text{Q}} = 55 \text{ K}$$

The structure of the pre-exponential parameter ν_{tun} in the expression:

$$\nu_{\text{tr}} = \nu_{\text{tun}} \exp(-E_{\text{v}}/kT) \quad (2)$$

obtained by Sussmann [12], was analyzed by Vikhnin [13]. It is important for the present consideration that ν_{tun} presents the frequency of 'tunneling' across the potential barrier *via* the vibronic level in question. This allows us to estimate the value of $E_{\text{v}} \approx 140$ cm $^{-1}$. We found $\nu_{\text{tun}} \approx 3.0 \times 10^{11}$ Hz from the X-band

experiment using the estimated value of E_v and for Q-band the value of $\nu_{\text{tun}} \approx 3.6 \times 10^{11}$ Hz. The discrepancy between these estimates is not large and taking into account that in a thermodynamic equilibrium the reciprocal lifetime of the vibronic state inside a well is of the order of magnitude of 10^{13} s^{-1} [12] we can consider that both values are reasonable.

An estimation of ν_{tr} can be also obtained, using the formula [14]:

$$\nu_{\text{tr}}(T) \sim 0.86\gamma_e\Delta H(T) \quad (3)$$

describing the temperature dependence of the line width ΔH below 40 K, when $\nu_{\text{tr}} < (g_{\parallel} - g_{\perp})BH/h$. With $\Delta H \sim 100$ G extrapolated for $T \sim 40$ K (X-band) one obtains $\nu_{\text{tr}} = 1.5 \times 10^9$ Hz.

It is interesting to note that the observation of the averaged EPR spectrum at $T \geq 60$ –65 K at X-band and at $T \geq 80$ –85 K in Q-band is not suggested by population of the excited vibronic singlet level. It is known that such A_1 (A_2) vibronic singlets will produce an isotropic EPR spectrum. More than that, in the strong JT effect approach, energy separations $\Delta E(^2A_2 - ^2E) = 0.3 \text{ cm}^{-1}$ and $\Delta E(^2A_1 - ^2E) = 200 \text{ cm}^{-1}$ have been estimated for $\text{Cu}^{2+}:\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ crystallo-hydrate at $T < 20$ K [15]. This urged Abragam and Bleaney to note [4] that it is impossible to find the true reason for the appearance of an isotropic spectrum upon temperature increase, as the population of the vibronic singlet and the increasing rate of reorientations of a JT complex lead to the same result. However, the averaging of the EPR spectrum due to population of this singlet vibronic state should not depend on the frequency. The experimental observation of this dependence allows us to assume that the vibronic singlet state does not participate in the present process. The silence of the excited singlet in EPR seems to be a general problem. Possibly this is connected with a broadening of this level, the reasons for which were analyzed by Bersuker and Polinger [1], who concluded that it should be attributed to higher order JT coupling and to the multimode JT effect.

The temperature interval in which the spectrum vanishes is large enough to increase the population of the necessary vibronic level and of ν_{tr} in order to switch from the condition of slow motion to those of fast motion without taking into consideration excited vibronic levels of higher energy.

In the present case any deformations of the JT complex position due to external strain are random and close to zero. We take into account the directed ones by the addition of deforming components of tetragonal, Δ_{θ} , or rhombic, Δ_{ε} , symmetry, or their combination, to the vibronic Hamiltonian. Now we move to the situation of the slightly elongated host octahedron, i.e., to the case $\Delta_{\theta} < 0$; $\Delta_{\theta} < 2\beta$.

2.2. A site strain according to an elongated octahedron; $\Delta_{\theta} < 0$, $\Delta_{\varepsilon} = 0$

We started with the crystal of high symmetry where the host position of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ octahedron is not deformed (the trigonal distortions do not affect the JT behavior and can be ignored). Due to the strong coupling of the JT complex with the crystal lattice, even a very slight deformation of the order of 10^{-3} – 10^{-4} nm, results

in such a strong decrease in energy of one of the JT conformations $\delta E_{1,2(1,3)} \sim 2\beta$ that the JT dynamics is suppressed. Perhaps the only possible situation where the manifestations of JT dynamics in EPR remain for the case where the host octahedron is elongated, is when these result from a crystal phase transition.

The above conditions are realized for $\text{Zn}_{1-x}\text{Cu}_x\text{GeF}_6 \cdot 6\text{H}_2\text{O}$ single crystals [16,17]. The ^{63}Cu isotope was used now in the single crystal synthesis. A phase transition of the ferroelastic type takes place at $T_c = 191$ K in this crystal when $x = 0.01$. ($T_c = 186$ and 172 K for $x = 0.1$ and 0.2 , respectively; in a powder sample T_c is lower by ~ 5 K). On cooling, the crystal switches from trigonal symmetry $R\bar{3}$ to the monoclinic space group $P2_1/C$. Above T_c a single line with $\langle g \rangle = 2.223$ and a temperature dependent width ΔH is observed. Below T_c the spectrum is strongly anisotropic and its parameters $g_x = g_y$ and g_z (as well as the A_i) depend on temperature (Figs 2 and 3). At $T = 4.2$ K one obtains $g_{\parallel} = 2.472$, $g_{\perp} = 2.103$; $A_{\parallel} = -108.9 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\perp} = 18.1 \times 10^{-4} \text{ cm}^{-1}$. This reflects the

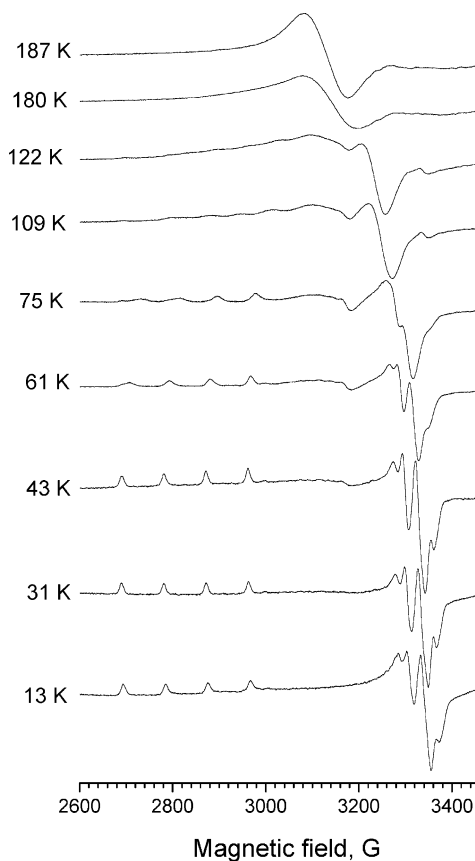


Fig. 2. The powder X-band EPR spectra of $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{GeF}_6 \cdot 6\text{H}_2\text{O}$.

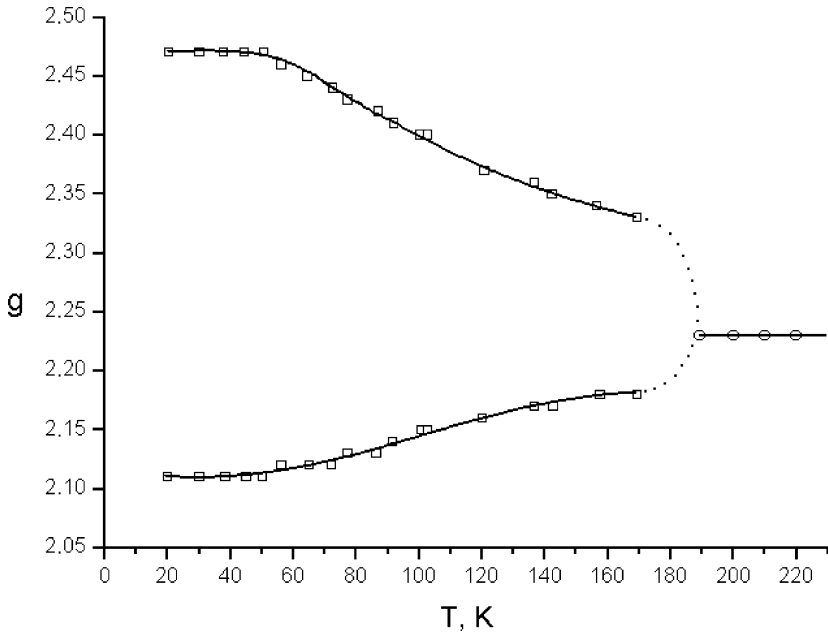


Fig. 3. Temperature dependence of g -factors for $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{GeF}_6 \cdot 6\text{H}_2\text{O}$.

tetragonal deformation of the water octahedron below T_c . It makes the potential wells corresponding to the three JT conformation of the water octahedron energetically inequivalent.

The temperature dependence of the g_i and A_i parameters definitely shows that rapid reorientations of the water octahedron, i.e., the rapid transitions between JT conformations, take place [18]. As a result, an averaged conformation is observed. The observed parameters can be written as follows:

$$\begin{aligned}
 g_z(T) &= K_1 g_z^{(1)} + K_2 g_y^{(2)} + K_3 g_y^{(3)}, \\
 g_y(T) &= K_1 g_y^{(1)} + K_2 g_z^{(2)} + K_3 g_x^{(3)}, \\
 g_x(T) &= K_1 g_x^{(1)} + K_2 g_x^{(2)} + K_3 g_z^{(3)}
 \end{aligned} \tag{4}$$

Here $g_i^{(j)}$ presents the i th g -component in the j th well and K_i is the temperature dependent Boltzmann population of the i th well. Analysis of the spectra shows that the tetragonal deformation appears abruptly at $T_c = 191$ K corresponding to the separation energy $\delta E_{1,2(3)} \sim 130 \text{ cm}^{-1}$. $\delta E_{1,2(3)}$ gradually increases to $\sim 150 \text{ cm}^{-1}$ as the temperature decreases to $T \approx 60$ K. The corresponding adiabatic potential calculated for the vibronic parameters of cubic symmetry to which the $\Delta_\theta \cos \varphi$ component ($\Delta_\theta = \delta E_{1,2(3)}$) is added, is shown in Ref. [20]. The energy difference between the deepest and the two higher wells is equal to 140 cm^{-1} and the potential barrier between the wells is about 400 cm^{-1} .

The energy of the vibronic level(s) allowing a phonon-induced averaging of the JT conformations can be derived from the temperature dependence of the line widths of the hyperfine components $\Delta(m_I)$ of the EPR spectrum in the monoclinic phase. These are shown in Fig. 4. An observed m_I -dependence allows the use of theories describing the motional averaging of magnetic resonance spectra. This was done [17] with the formula obtained for such an analysis by Silver and Getz [18] and adopted for the case of the three wells adiabatic potential with the two equal wells of higher energy:

$$\nu_{tr} = 4K'/(K' + 2)^3 \cdot (\nu_1 - \nu_2)^2/\Delta\nu \quad (5)$$

where $K' = K_1/K_2$, $\nu_1 = (g_1\beta H_0 + A_1m_I)/h$, and $\nu_2 = (g_2\beta H_0 + A_2m_I)/h$. In the conditions of our experiment $g_1 = g_z$ and $g_2 = g_x = g_y$. H_0 is the resonance field at which the line would be observed at ν_1 and ν_2 . $\Delta\nu$ is the contribution to the line width due to transitions between wells 1 and 2 ($= 3$). The experimental line width is the sum of a reorientation independent part (which we accept as the line width for temperature interval 4.2–34 K) and a contribution from jumping. A plot of $\ln \nu_{tr}$ vs. $(kT)^{-1}$ is shown in Fig. 5.

It follows from Fig. 5 that in the temperature interval from 35 up to ~ 60 K the jumping rate follows a simple exponential law

$$\nu_{tr} = \nu_0 \exp(-\Delta/kT)$$

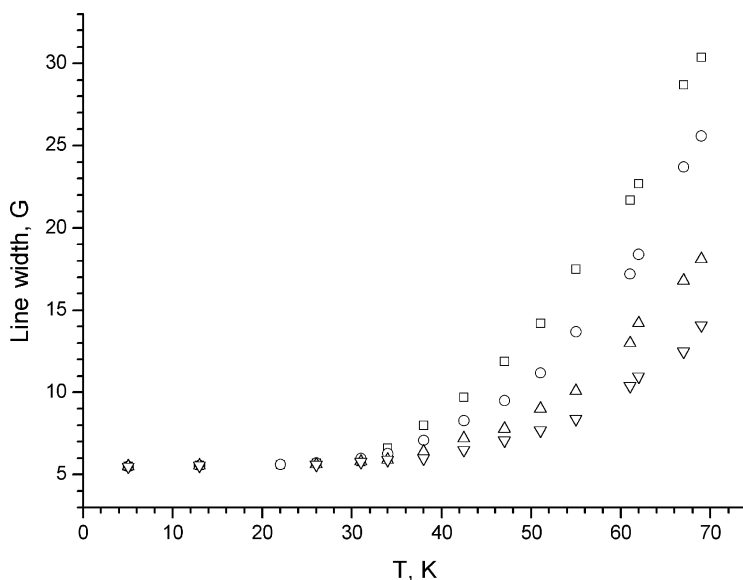


Fig. 4. Temperature dependence of $\Delta H(m_I)$ for $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{GeF}_6 \cdot 6\text{H}_2\text{O}$: (□) $m_I = 3/2$; (○) $m_I = 1/2$; (△) $m_I = -3/2$; (▽) $m_I = -1/2$.

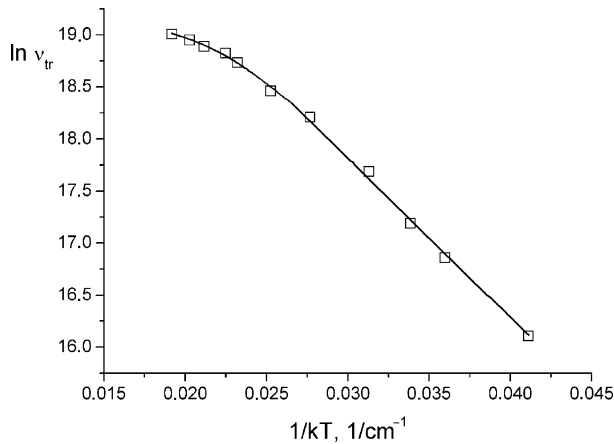


Fig. 5. Temperature dependence of $\ln \nu_{tr}$ for $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{GeF}_6 \cdot 6\text{H}_2\text{O}$.

with $\Delta \approx 160 \text{ cm}^{-1}$. This value practically coincides with the energy interval $\delta E_{1,2(3)}$ between the ground and excited JT conformations. Taking into account the high energy barrier, 400 cm^{-1} , between wells 1 and 2(3) we note that passing over the barrier is not effective in this case and conclude that JT complex reorientations occur as a tunneling controlled process. One should consider it as a tunneling between an excited vibronic state in the well 1 and the ground vibronic state in the well 2(3). There is thus a distinction between the tunnel jumping for the present situation of the very slightly elongated octahedron, and the situation of the regular octahedron considered above. It is interesting to compare the rates of tunneling in these cases. Following the Sussmann–Vikhnin approach [12,13] used in the previous section, we obtain $\nu_{\text{tun}} \approx 5 \times 10^9 \text{ Hz}$.

2.3. Complex subjected to an axial compression; $0 < \Delta_\theta \ll 2\beta$, $\Delta_\epsilon \ll \Delta_\theta$

Such a situation is realized, for example, in the Tutton salt $\text{A}_2\text{Zn,Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (I) [19,20] and in its structural analogues $\text{A}_2\text{Zn,Cu}(\text{ZrF}_6)_2 \cdot 6\text{H}_2\text{O}$ (II) with $\text{A} = \text{K, Rb, NH}_4$, and Cs [19], as well as in the $\text{K}_2\text{Zn,CuF}_4$ crystal (III) [21,22]. In (III), due to a large Δ_θ deformation, the separation between the high-energy conformation and the two low-energy ones is greater than the thermal vibration energy, $\Delta E_\theta > kT$ at $T \sim 300 \text{ K}$. The potential barrier $2\beta_{1,2}$ between the two low-energy conformations ($\Delta_\epsilon = 0$) is of order of kT at $T = 4.2 \text{ K}$ and these conformations are averaged just by zero-point vibrations.

In (I) and most of the (II) crystals $\Delta_\epsilon \neq 0$ and the ratio between Δ_θ and Δ_ϵ takes such values that though $2\beta_{1,2} > \delta E_{1,2}$, transitions between JT conformation were shown to have over-barrier character. Even in $\text{K}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ with the smallest distortion of the $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ octahedron ($\text{Zn}-\text{O}_7 = 2.132 \text{ \AA}$; $\text{Zn}-\text{O}_8 = 2.126 \text{ \AA}$; $\text{Zn}-\text{O}_9 = 2.028 \text{ \AA}$) and a relatively small energy difference between the two lower

JT wells of the doped $\text{Cu}(\text{H}_2\text{O})_6$ ion ($\delta E_{1,2} = 75 \text{ cm}^{-1}$; $2\beta_{1,2} = 120 \text{ cm}^{-1}$), the transitions are over-barrier ones. (The reason is the large value of $\delta E_{1,3} > 600 \text{ cm}^{-1}$ accompanied by the small value of the barrier $2\beta_{1,2} = 120 \text{ cm}^{-1}$).

An interesting case is presented by the $\text{Cs}_2\text{Zn,Cu}(\text{ZrF}_6)_2 \cdot 6\text{H}_2\text{O}$ crystal [23,24]. The values of Δ_θ and Δ_ε in the zinc compound are the smallest among (I) and (II) crystals, in agreement with the spacings $\text{Zn}-\text{O}_1 = 2.099 \text{ \AA}$; $\text{Zn}-\text{O}_2 = 2.105 \text{ \AA}$; $\text{Zn}-\text{O}_3 = 2.096 \text{ \AA}$ (oxygen numbering according to Ref. [24]) in this crystal and the resulting δE_{ij} ($\delta E_{1,2} = 30 \text{ cm}^{-1}$; $\delta E_{1,3} = 165 \text{ cm}^{-1}$ for 300 K and 84 cm^{-1} and 190 cm^{-1} for 30 K, respectively). All these made possible the detection and study of the phonon controlled tunneling for a potential surface with unequal wells. The detailed description of the dynamic behavior of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ in this crystal is given in Ref. [25]. Here we shall present the analysis of the temperature behavior of the conditions and mechanisms of the inter-conformation transitions.

We have studied samples doped with 1% $^{63}\text{Cu}(\text{H}_2\text{O})_6^{2+}$ by EPR both in X- and Q-band. X-band spectra of the single crystal for $H \parallel Z$ -axis [see equation (4)] are shown in Fig. 6. The EPR signal is observed for all temperature intervals. All three components of g -tensor are temperature dependent: g_z and g_y starting at $T \sim 30 \text{ K}$,

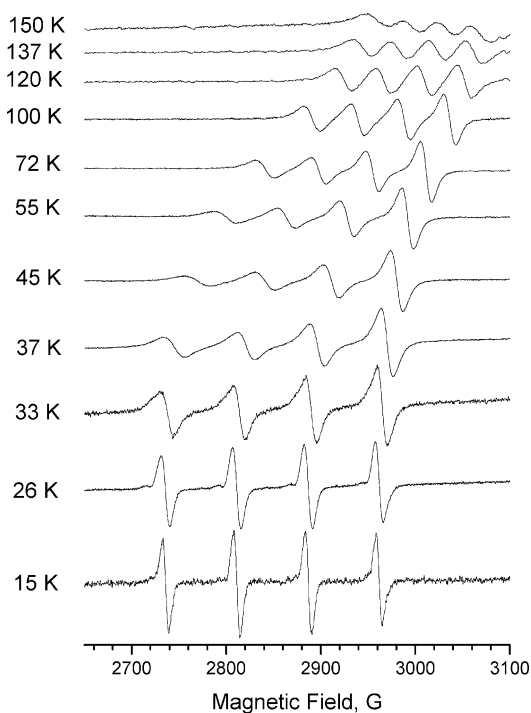


Fig. 6. The temperature evolution of the single crystal spectra ($H \parallel Z$ -axis) of $\text{Cs}_2\text{Zn}_{0.99}\text{Cu}_{0.01}(\text{ZrF}_6)_2 \cdot 6\text{H}_2\text{O}$.

g_x above ~ 65 K. In accordance with equation (4) this confirms the population of all wells of the adiabatic potential and averaging of the Boltzmann weighted JT conformations. In this respect the temperature dependence of the widths of the hyperfine structure components (Fig. 7) is very interesting. It starts at very low temperatures, 10–15 K, when the broadening of all m_I components is the same. But already at 26 K the low-field component becomes broader. With the temperature increase, the dependencies of $\Delta H(T, m_I)$ on temperature and on m_I become more pronounced, with a very unusual character. The line widths increase up to $T \sim 45$ K, then decrease up to about 100 K and finally increase again. In this last T -interval the differences between $\Delta H(m_I)$ gradually disappear. This corresponds to the conditions of a fast exchange; ΔH includes an increasing contribution from spin–lattice relaxation, which predominates at $T > 100$ K. Two factors should be mentioned. An averaging mechanism commences at $T \sim 25$ K with a rate higher than the frequency difference between the JT complexes in the neighboring wells. (This is the usual feature of the EPR spectra of all slightly distorted JT complexes for which conformation depends on the temperature.) What distinguishes the situation in

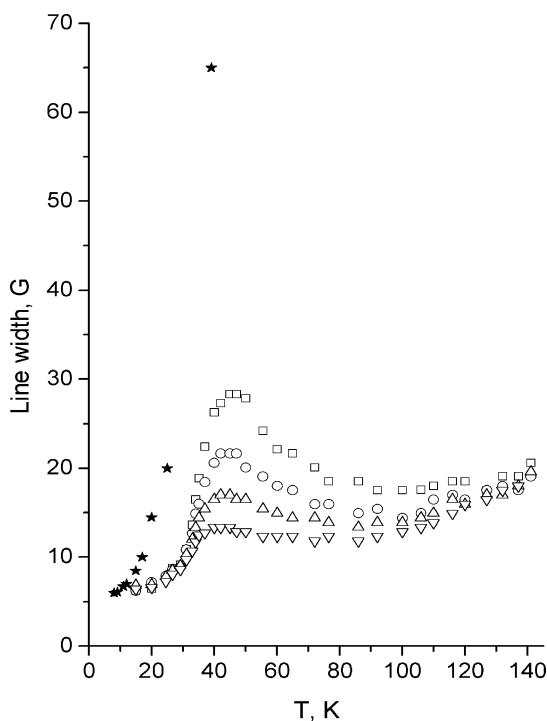


Fig. 7. Temperature dependencies of the $\Delta H(m_I)$ in $\text{Cs}_2\text{Zn}_{0.99}\text{Cu}_{0.01}(\text{ZrF}_6)_2 \cdot 6\text{H}_2\text{O}$ at X-band: ($\square$) $m_I = 3/2$; ($\circ$) $m_I = 1/2$; ($\triangle$) $m_I = -3/2$; (∇) $m_I = -1/2$ and ($\star$) Q-band (all $\Delta H(m_I)$ are equal).

$\text{Cs}_2\text{Zn}_{0.99}\text{Cu}_{0.01}(\text{ZrF}_6)_2 \cdot 6\text{H}_2\text{O}$ crystal is the unexpected change of the average rate in the T -interval 40–45 K. One can suppose that the observed decrease of $\Delta H(T)$ and the $\Delta H(m_l)$ dependence is determined by an increase of the rate of averaging. Usually this occurs at higher temperatures and is masked by the fast spin–lattice relaxation processes. The latter can explain the line broadening taking place in our case at $T > 100$ K.

The peculiarities of the X-band spectra are more pronounced in the Q-band experiment. The corresponding powder spectra are shown in Fig. 8. (We have also measured single crystals spectra but there were some difficulties in signal detection at intermediate temperatures, between ~ 35 and 50 K.) The Q-band temperature dependence of the line widths at $T < 40$ K is included in Fig. 7.

It is interesting that the behavior of the spectra shows similarities both to the trigonal and to the Tutton salt crystals. The three temperature intervals, mentioned above, can be distinguished here also. In the first, from the lowest T up to ~ 40 K, only an increase of the line widths without their positions changing is observed. It is followed by the disappearance of the signal in the parallel orientation (as observed for the $\text{Zn,CuZrF}_6 \cdot 6\text{H}_2\text{O}$ spectrum). Finally, after recovery, a very strong temperature dependence of the line widths and positions is observed (as in the cases of the JT centers with the three adiabatic potential wells of different depths). Each of these intervals has its own peculiarity: (i) very sharp lines broadening;

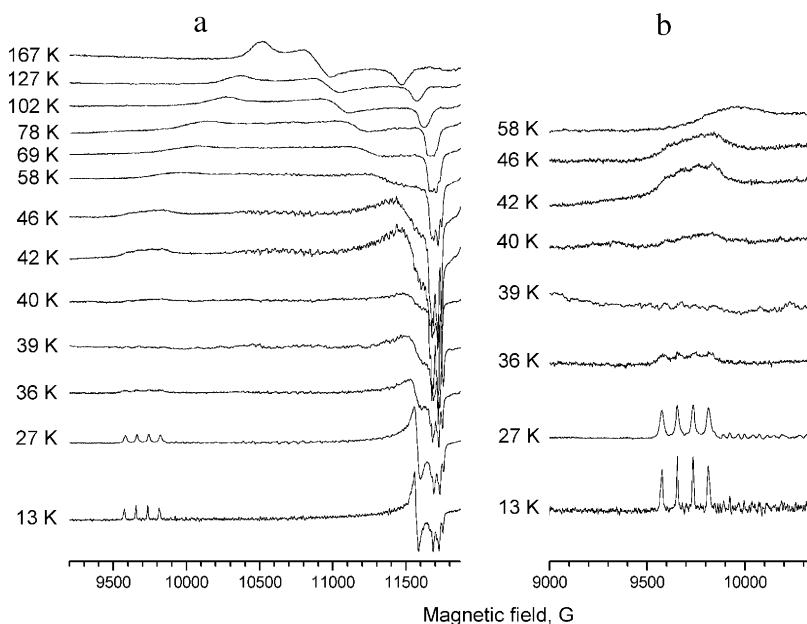


Fig. 8. (a) The temperature dependence of the Q-band EPR powder spectra for $\text{Cs}_2\text{Zn}_{0.99}\text{Cu}_{0.01}(\text{ZrF}_6)_2 \cdot 6\text{H}_2\text{O}$; (b) selected spectra amplified four times.

(ii) extremely narrow interval in which the spectrum is not observed; (iii) rapid coalescence of previously dispersed resonance lines followed by a strong $\Delta H(m_l)$ -dependence and temperature-induced broadening which prevents the observation of hyperfine structure. The details of these peculiarities relate to the Cs_2Zn , $\text{Cu}(\text{ZrF}_6)_2 \cdot 6\text{H}_2\text{O}$ crystal and should be analyzed specially. Now we emphasize the main feature: the spectral behavior fully corresponds to transformations producing motional narrowing. The existence of a temperature region where the rate of averaging, $\nu_{\text{av}} \equiv \nu_{\text{tr}}$, is comparable with the frequency differences of the signals, $\Delta g\beta H/h$, is especially important. This proves directly the tunneling character of the inter-conformation transitions and allows the estimation of the rate of tunneling. Accepting $\nu_{\text{av}} \approx 9.6 \times 10^9$ Hz for Q-band at $T = 40$ K, we obtain $\nu_{\text{tun}} \approx 1.8 \times 10^{11}$ Hz.

The picture observed in X-band indicates that the rate of averaging the JT conformations ν_{av} always exceeds $\Delta g\beta H/h$ in the X-band EPR time scale. Using the estimate $\nu_{\text{tun}} \approx 1.8 \times 10^{11}$ Hz one can see that even for $T = 30$ K the value of $\nu_{\text{av}} = 3.6 \times 10^9$ Hz satisfies this condition. We should point out that attempts to obtain ν_{av} using Silver and Getz's expressions lead to a poor result. Up to $T \sim 80$ K this yields values of ν_{av} less than 10^9 Hz. Our estimates are therefore based on the comparison of ν_{av} and $\Delta g\beta H/h$. The only deficiency of such an approach is its relative inaccuracy. But at the same time, it seems likely that the estimates are of the correct order of magnitude.

3. CONCLUSIONS

Our analysis of the conditions governing the transition of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex from the localized JT conformation to the motional averaged one has shown that even for low symmetry sites (but only tiny geometric distortions) in the host crystal the transitions between JT conformations can have a tunneling character. The lattice-induced distortions cause energy differences between JT conformations not larger than $100\text{--}200\text{ cm}^{-1}$. The questions concerning the relative energies of the excited vibronic states populated by phonons, which give rise to the tunneling, merit some comments.

It is clear that in the crystal site of trigonal symmetry the vibronic states of the JT complex have equal energy in all wells. In this case the transition probability is determined by the tunneling matrix element, by the interactions of the complex with phonons and by the temperature, as analyzed theoretically [12,13]. If the wells have different energies, the energy interval between the levels and the width of levels become especially important, and it is not obvious *a priori* that the probability of tunneling is not zero. Our experiments do not allow an exact determination of both the energies of the excited overlapping levels making possible the tunneling transitions, and their separations. We can only estimate the energies of the vibronic states expected to give rise to non-zero tunneling matrix elements. More exact information on the energies and separations of the vibronic levels in question needs

to be obtained. The evidence for JT tunneling transitions in the present crystals gives an additional stimulus for such work.

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REFERENCES

- [1] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, Berlin, 1989.
- [2] F. S. Ham, in *Electron Paramagnetic Resonance 1* (ed. S. Geshwind), Plenum Press, New York, 1972.
- [3] R. Englman, *The Jahn–Teller Effect in Molecules and Crystals*, Wiley-Interscience, London, 1972.
- [4] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Metal Ions*, Clarendon, Oxford, 1970.
- [5] B. Bleaney, K. D. Bowers and D. I. E. Ingram, *Proc. R. Soc.*, (London), 1955, **A225**, 147.
- [6] A. M. Ziatdinov, Doct. Thesis, Kazan University, Kazan, 1979; A. M. Ziatdinov, M. M. Zaripov, Yu. V. Yablokov and R. L. Davidovich, *Ref. J. Physica*, (in Russian), 1978, **N 1**, 1D734, VINITI, Dep. N 3550-77 on 30.08.1977.
- [7] M. A. Augustyniak-Jablokow, S. Kiczka and Yu. V. Yablokov, to be published.
- [8] U. Öpik and M. H. L. Pryce, *Proc. R. Soc.*, (London), 1957, **A238**, 425.
- [9] M. A. Hitchman, W. Maaskant, J. van der Plas, C. J. Simmons and H. Stratemeier, *J. Am. Chem. Soc.*, 1999, **121**, 1488.
- [10] P. W. Anderson, *J. Phys. Soc. Jpn*, 1954, **9**, 316.
- [11] A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon, Oxford, 1961.
- [12] J. A. Sussmann, *J. Phys. Chem. Solids*, 1967, **28**, 1643.
- [13] V. S. Vikhnin, *Solid State Phys.*, (in Russian), 1978, **20**, 1340.
- [14] J. A. Pople, W. G. Schneider and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance*, New York, 1959.
- [15] D. P. Breen, D. C. Krupka and F. I. B. Williams, *Phys. Rev.*, 1969, **179**, 241.
- [16] Yu. V. Yablokov, M. M. Zaripov, A. M. Ziatdinov and R. L. Davidovich, *Chem. Phys. Lett.*, 1977, **48**, 443.
- [17] A. M. Ziatdinov, R. L. Davidovich, V. Ya. Shevchenko and Yu. V. Yablokov, *Koordinatsionnaya Khimija*, 1983, **9**, 1644.
- [18] B. Silver and D. Getz, *J. Chem. Phys.*, 1974, **61**, 638.
- [19] V. E. Petrashen, Yu. V. Yablokov and R. L. Davidovich, *Phys. Stat. Sol. (b)*, 1980, **101**, 117.
- [20] M. J. Riley, M. A. Hitchman and A. W. J. Mohammed, *J. Chem. Phys.*, 1987, **87**, 3766.
- [21] M. V. Eremin, Yu. V. Yablokov, T. A. Ivanova and R. M. Gumerov, *Sov. Phys. JETPh*, 1984, **60**, 128.
- [22] M. J. Riley, M. A. Hitchman and D. Reinen, *Chem. Phys.*, 1986, **102**, 11.
- [23] M. V. Eremin, A. Yu. Zavidonov, V. S. Petrashen, Yu. V. Yablokov and R. L. Davidovich, *Solid State Phys.*, (in Russian), 1987, **29**, 3426.
- [24] M. A. Hitchman, Yu. V. Yablokov, V. E. Petrashen, M. A. Augustyniak-Jablokow, H. Stratemeier, M. J. Riley, K. Łukaszewicz, P. E. Tomaszewski and A. Pietraszko, *Inorg. Chem.*, 2002, **41**, 229.

Diffusion in Concentrated Jahn–Teller Systems

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Abstract

The effect of strontium on the diffusion coefficients D of oxygen tracers in the $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$, temperature dependence of the oxygen tracer diffusion coefficient in $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ ($y = 0.025$) were determined. The D values were measured using ^{18}O tracers and the nuclear microanalysis method. Analysis of the concentration dependences of the diffusion coefficients D was made using the approach, which takes into account variation of the number of orbitally degenerate (JT) states of 3d-ions during non-isovalent alloying.

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1. INTRODUCTION

The study of oxygen diffusion in oxides with mixed-valence 3d-ions presents great interest both in theoretical and practical terms. Such systems with Jahn–Teller (JT) 3d-cations are suitable model objects for analysis of the diffusion process in degenerate or pseudo-degenerate condensed systems. The mechanism of multi-well potential formation has been explored well for JT ions [1,2] and it is possible to give a simple microscopic description of the inter-center interactions and different properties of these systems. The practical interest paid to diffusion properties of the

said oxides (including the $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ compound with a perovskite structure) is determined by the use of mixed-conductivity oxides in separators to convert available hydrocarbons into more desirable products, in electrochemical reactors, for the separation of oxygen from mixed gases, in chemical sources of current, to utilize materials for many catalysis applications, etc. It was found that the oxygen self-diffusion coefficients can be changed by several orders of magnitude by alloying of the cation sublattice of perovskites (see, for example, Ref. [3]).

Unfortunately, theoretical concepts, which would allow the prediction of variation regularities of the oxygen diffusion coefficients, have not been formulated so far. This situation is explained to a large extent by the lack of experimental data, which can be related reliably to the effect of JT interactions on the diffusion coefficients. Let us clarify this statement in terms of a universally acknowledged model when the diffusion activation energy Q is viewed as the sum of the energy of vacancy formation in the oxygen subsystem Q_f and the migration energy Q_m . It is known that alloying of the metal sublattice with lower-valence cations may lead to formation or an increase in the concentration of structural vacancies and, correspondingly, an increase in the oxygen diffusion coefficients. This process is observed, for example, in $\text{Sm}_{1-y}\text{Sr}_y\text{CoO}_{3-\delta}$, $\text{Sm}_{1-y}\text{Cd}_y\text{CoO}_{3-\delta}$ [4], $\text{La}_{1-y}\text{Sr}_y\text{CoO}_{3-\delta}$ [5] and $\text{La}_{1-y}\text{Sr}_y\text{FeO}_{3-\delta}$ [6]. When Sr^{2+} or Cd^{2+} ions are added instead of Sm^{3+} , Fe^{3+} or La^{3+} , some oxygen sites (proportional to $\delta = y/2$) become vacant and the contribution of Q_f to Q decreases or reduces to zero. Such substitution should have a strong effect on the diffusion coefficients, because the activation energy $Q \cong Q_m$ usually is ~ 1 eV for oxygen self-diffusion in oxide structures with anion structural vacancies and $Q > 2$ eV for diffusion with thermal vacancies [7]. Other weaker mechanisms, through which substitutional atoms (including JT ones) influence the activation energy and the oxygen diffusion coefficients, can hardly be distinguished against this background.

Remarkably, the above examples refer to systems, in which only one mechanism of charge compensation, that is, formation of structural vacancies, can be realized during alloying. It is known that an alternative mechanism of charge compensation, which is related to appearance of different valence states of 3d-cations, operates in some other systems upon alloying. One of such valence states of the cation in an octahedral configuration is, as a rule, orbitally degenerate. The number of these orbitally degenerate (JT) states of 3d-ions is changed during non-isovalent alloying. This is accompanied by a rearrangement of the crystal structure and variation of magnetic conduction, and other properties. One of the systems, in which all these effects are pronounced most, is $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ (see, for example, Refs. [8–10]). Therefore, it may be expected that variation regularities of the diffusion coefficients in strontium-alloyed $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ will differ from those observed in other perovskite systems. Unfortunately, experimental evidence obtained for the $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ system proved to be contradictory. Firstly, the oxygen self-diffusion coefficients D , which were determined by the secondary ion mass spectroscopy (SIMS method), differed by several orders of magnitude from those evaluated from the chemical diffusion coefficients [5] (the latter were

measured using a potentiostatic step technique). Secondly, strontium had an absolutely different effect on the diffusion coefficients: D increased with growing strontium concentration in SIMS experiments and decreased in potentiostatic experiments.

Considering what has been said above, the main goals of this study were as follows: obtain reliable data concerning the effect of strontium on the diffusion coefficients D of oxygen tracers in the $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ system; analyze concentration dependences of the diffusion coefficients D using the approach, which takes into account variation of the number of orbitally degenerate (JT) states of 3d-ions during non-isovalent alloying. In view of the theoretical nature of this study (analysis of the effect of JT displacements on the oxygen diffusion coefficients), we thought it was reasonable to take strontium-diluted solutions. The D values were measured using ^{18}O tracers and the nuclear microanalysis method, which provides, similarly to SIMS, a direct determination of concentration profiles of diffusing atoms.

2. EXPERIMENTAL: SAMPLES AND METHODS

Powders of $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ oxides ($y = 0, 0.025, \text{ and } 0.075$) were prepared by annealing of a mixture of pure initial reagents La_2O_3 , Mn_2O_3 and SrCO_3 at 900°C for 20 h, at 1000°C for 50 h and at 1300°C for 15 h, one after the other. The powders were mixed thoroughly before and after the annealings. X-ray diffraction indicated that the samples had perovskite structure. The concentrations of metal components in the samples were not controlled. They were calculated by weighing the initial powders. The powder was pressed in cylinders 10 mm in diameter and 3 mm high. The durability of the samples was provided by their annealing at 1300°C for 6 h. The samples were cooled in air to 650°C , were homogenized additionally at this temperature for 6 h, and were cooled slowly to room temperature. Special tests for porosity and microcracks were not performed, but relevant qualitative information was obtained from the analysis of concentration profiles $c(x)$ of ^{18}O tracers after diffusion annealing. The samples contained some quantity of pores or microcracks. This circumstance in combination with some other factors narrowed considerably the temperature interval for measurement of the volume diffusion coefficients in the present study. At temperatures below 500°C , the profiles $c(x)$ generally were not connected with the volume diffusion, but were due to diffusion of oxygen atoms along pores and microcracks or grain-boundary diffusion. Therefore, the study was performed only in the temperature interval from 850 to 950°C . The volume diffusion zone was identified reliably for this interval.

Diffusion annealings were performed in a quartz tube under an oxygen atmosphere enriched to 70% with the ^{18}O isotope at a pressure of 0.21×10^5 Pa. The isotope composition of the gaseous phase was maintained constant throughout

the annealing time. Immediately before the diffusion annealing, the samples were annealed in the same quartz tube in air. The latter annealing process was longer than the diffusion annealing, while temperatures of the two annealing processes were equal. When changing to the diffusion annealing, the air atmosphere in the quartz tube was replaced quickly by the oxygen atmosphere with the ^{18}O isotope. This procedure eliminated an oxygen concentration gradient ($^{16}\text{O} + ^{18}\text{O}$) in the diffusion zone throughout the annealing time. The annealed samples were cooled for about 1 min. A chromel–alumel thermocouple measured the temperature to within $\pm 1^\circ\text{C}$. The quartz tube was placed in a bulky metal cylinder during annealing. As a result, the zone with the samples had no temperature gradients within the measurement accuracy.

The concentration of oxygen isotopes in the samples was measured using the nuclear microanalysis technique [11,12]. A 2-MV Van der Graaf accelerator was used. The sample was fitted in an evacuated chamber and was exposed to a beam of accelerated deuterons or protons having an energy of 900 and 762 keV, respectively. The flat surface of the samples was perpendicular to the axis of the primary beam. The recording angle of nuclear reaction products was 160° . Energy spectra of reaction products were measured using a surface-barrier silicon detector about 10 mm in diameter having an energy resolution of 20 keV. The detector was covered with an absorber (a mylar film) of backscattered deuterons and protons 16 and 10 μm thick, respectively. The diameter of the incident beam was 1–2 mm, i.e., the measured concentrations were averaged over a large number of crystallites. The number of the incident beam ions was determined using a secondary monitor [13] to within 0.5%. The oxygen concentration was measured to a depth of $\sim 1.5 \mu\text{m}$ without destruction of the samples. The $^{16}\text{O}(\text{d},\text{p}_1)^{17}\text{O}$ and $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ reactions were used. Profiles of the ^{16}O isotope were measured only to check the total ($^{16}\text{O} + ^{18}\text{O}$) oxygen concentration in the diffusion zone. The corresponding data are not reported below. The concentration profile was calculated by comparing the spectra of the test sample and a standard sample containing a constant oxygen concentration (the Fe_3O_4 oxide was used). The concentrations were determined using data on the hydrogen and helium stopping powers in elements. The stopping powers for the test oxides were calculated using tabulated data for pure components and Bragg's additive rule [14]. The mean-root-square measurement error of the oxygen concentrations did not exceed a few percent. The method for calculation of the concentration profiles was described in more detail elsewhere [15–17].

A typical concentration profile of ^{18}O oxygen is shown in Fig. 1. It is characterized by some specific features as compared to a simple case of the diffusion equation for a constant source. Firstly, it is seen that the concentration c_s on the surface of the sample is lower than the equilibrium concentration in the test samples. Therefore, a solution of the diffusion equation depending on the boundary conditions must be used [18]. Secondly, the concentration c_1 of the ^{18}O isotope was almost constant at a large depth x and was much higher than the initial concentration of the ^{18}O isotope in samples. It is not improbable that this

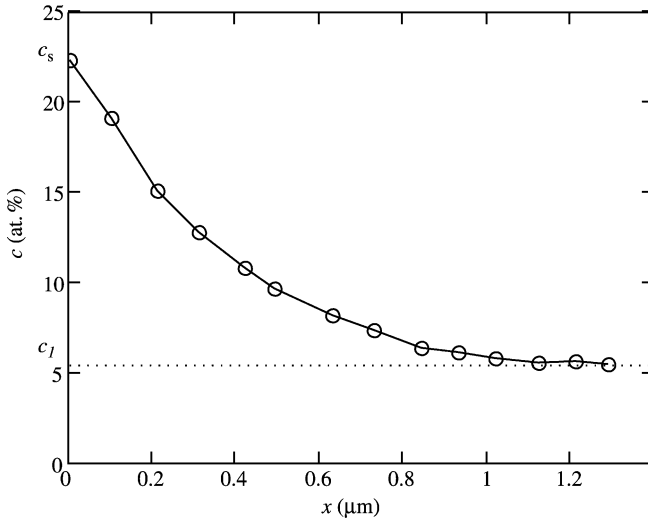


Fig. 1. Penetration plot obtained after 1.23 h anneal at 900 °C for $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ ($y = 0.025$). c_l is the concentration of ^{18}O at a large depth; c_s is the surface concentration of ^{18}O .

feature of the profile $c(x)$ was determined not only and not so much by the grain-boundary diffusion as by the presence of pores and cracks in the samples. Correctly substantiated methods for processing of experimental data are lacking in this case. Therefore, in what follows, the c_l values were subtracted from the experimental profiles $c(x)$ and the data $C(x) \equiv c(x) - c_l$ were fit to theoretical solutions of the diffusion equations in order to calculate the diffusion parameters. Such solutions were for a constant source:

$$C = C_0 \operatorname{erfc}\left[\frac{x}{2\sqrt{Dt}}\right] \quad (1)$$

and a solution of the diffusion equation depending on boundary conditions:

$$C = C_0 \left[\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) - \exp(Hx + H^2Dt) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + H\sqrt{Dt}\right) \right] \quad (2)$$

where C_0 is an equilibrium ^{18}O concentration in the samples if an oxygen enriched to 70% with the ^{18}O isotope to use; H is a fitting parameter, accounting the influence of surface potential barriers on diffusion.

From general considerations, the use of equation (2) seems to be more reasonable. However, we used both approximations (1) and (2) to understand how the choice of boundary conditions affected the D value. The data in Fig. 2 (these data were sufficiently typical) and in Table 1 show that boundary conditions had a weak effect on the diffusion coefficients. Therefore, results obtained with the approximation (2) will be discussed below. It may be noted, however, that the approximation

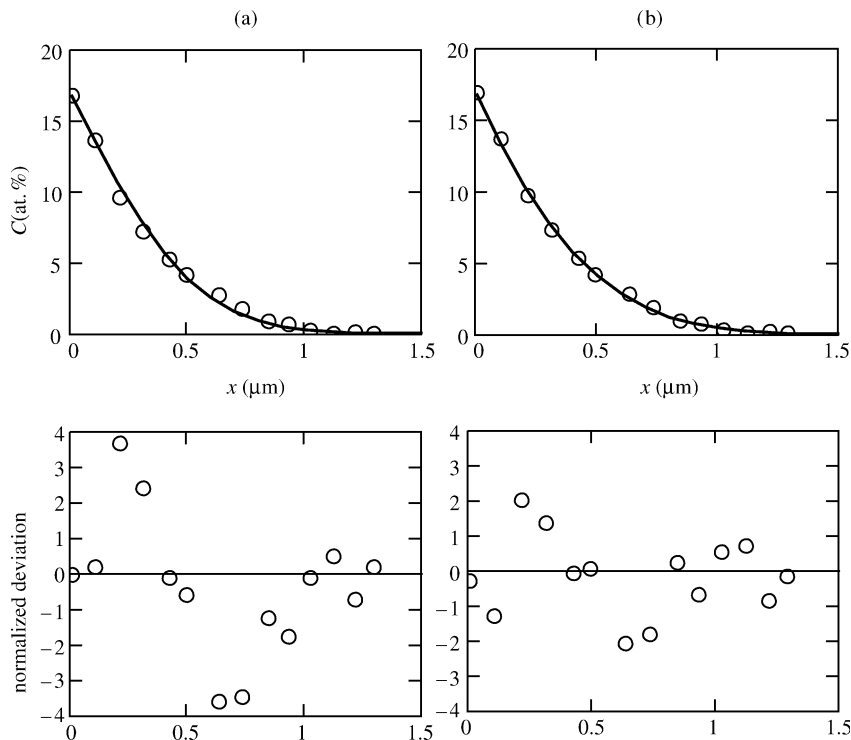


Fig. 2. (a) Penetration plot (top) obtained after 1.23 h anneal at 900 °C for system $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ ($y = 0.025$). Solid line represents a fit to solution of diffusion equation, accounting for volume (equation (1)). (b). Penetration plot (top) obtained after 1.23 h anneal at 900 °C for system $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ ($y = 0.025$). Solid line represents a fit to solution of diffusion equation, accounting for volume and surface exchange limited (equation (2)).

Table 1. Oxygen diffusion experimental results for $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$

Composition $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$	Temperature (°C)	Time (h)	D^a (cm^2/s)	D^b (cm^2/s)
$y = 0$	900	2	2.21×10^{-13}	3.22×10^{-13}
$y = 0.025$	850	2	7.87×10^{-14}	1.28×10^{-13}
	850	3.72	6.58×10^{-14}	9.94×10^{-14}
	870	1.82	1.68×10^{-13}	2.24×10^{-13}
	900	1.23	1.96×10^{-13}	2.87×10^{-13}
	900	3.23	1.24×10^{-13}	1.97×10^{-13}
	950	0.48	5.47×10^{-13}	8.27×10^{-13}
$y = 0.075$	900	2	9.64×10^{-14}	1.49×10^{-13}

^aCalculated from equation (1).

^bCalculated from equation (2).

(2) described the experimental results more adequately. This fact showed up as a lower value of the normalized average deviation from the analytical curve in the case of equation (2).

3. EXPERIMENTAL RESULTS

As was already noted in the foregoing discussion, diffusion coefficients of oxygen atoms in perovskites, which were measured in various studies, differ by several orders of magnitude and, therefore, cannot be systematized. Let us consider this problem more comprehensively in connection with the obtained results. From Fig. 3 and Table 1 it is seen that a discrepancy between results of two independent measurements on samples having the same compositions at 1173 and 1123 K is systematic: a longer annealing time t corresponds to a lower D value. Moreover, in both cases the D_1t_1/D_2t_2 ratios are very close (indices 1 and 2 correspond to two independent measurements at one and the same annealing temperature).

On one hand, the observed differences (1.46 times at 1173 K and 1.3 times at 1123 K) may be viewed as standard for ceramic samples [5]. On the other hand, they

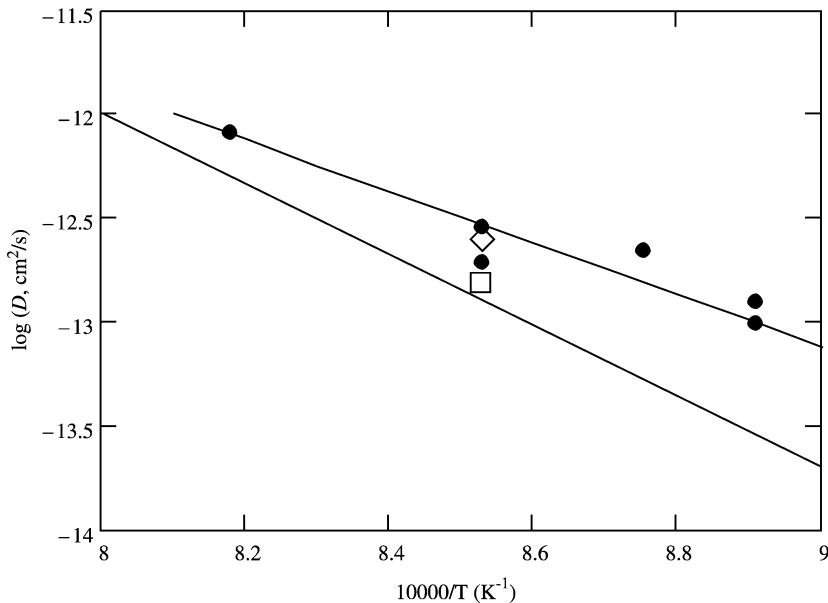


Fig. 3. Temperature dependence of the oxygen tracer diffusion coefficient in the crystals $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ ($y = 0.025$ —circle). Also shown are this work data for $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ ($y = 0.075$ —square) and SIMS data for $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_{3-\delta}$ (diamond) [21] and extrapolated Arrhenius diffusivity plot for $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_{3-\delta}$ (lower line) [22].

are much larger than the expected scatter of experimental D values if one takes into account a high accuracy of the concentration profiles, which were measured using the nuclear microanalysis technique. We believe that the systematical scatter of the diffusion coefficients is due to an improper fulfillment of boundary conditions of the diffusion equations. In turn, an improper fulfillment is connected with a poor quality of ceramic samples. Considering these factors, we thought it was possible to use different criteria for comparison of diffusion measurement results. If the diffusion coefficients are measured at largely different annealing times and, more so, in samples of different quality, a 2-fold difference of the measured values is quite regular and reasonable for ceramic samples. Otherwise, in this study it was reasonable to head for the measurement accuracy of the diffusion coefficients equal to a few percent. In terms of these criteria, the D values determined in this study agree well with all literature data known to us, which were obtained for ceramic samples with a similar composition using the SIMS method (Fig. 3). Therefore, this group of data on the volume diffusion coefficients of oxygen tracers in $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ may be assumed to be reliable.

The main result of the experimental part of the study, which is shown in Fig. 4, confirms the supposition, which was made in the Introduction above, that one cannot expect formation of structural vacancies in the oxygen sublattice of strontium-alloyed $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ perovskites and, correspondingly, a considerable increase

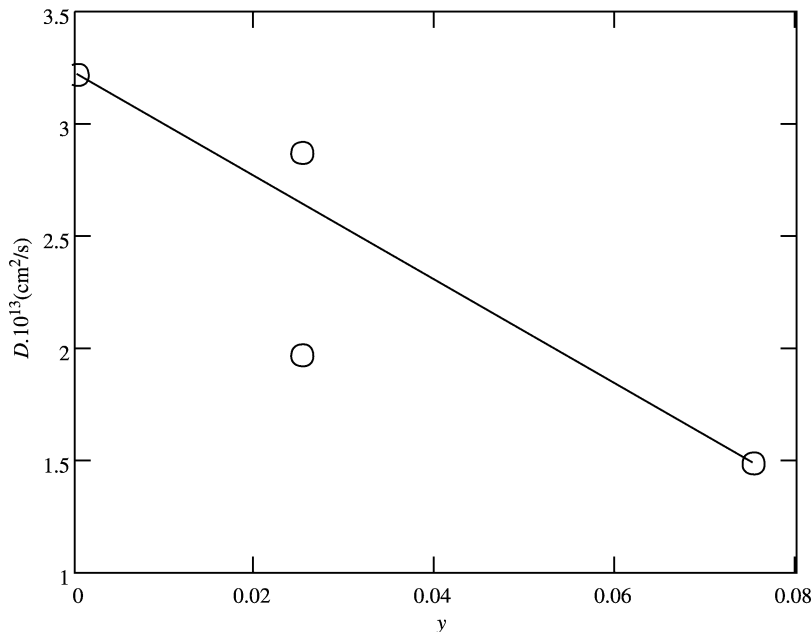


Fig. 4. Variation of the oxygen diffusion coefficient D with y in $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$.

in the diffusion coefficients of oxygen tracers. Moreover, it may be viewed as a reliably established fact that D values decrease with growing concentration of strontium. Let us note two additional factors pointing to reliability of this result. The samples with $y = 0$ and $y = 0.075$ were annealed simultaneously ($t = 2$ h), i.e., these data are free of systematic errors caused by different temperatures and annealing times. The scatter of the D values for the compound with $y = 0.025$ will be much smaller if we take into account a different duration of the diffusion anneal of these samples in accordance with the condition $D_1 t_1 / D_2 t_2 \cong \text{const.}$

Thus, the result obtained for $D(y)$ is due only to a decrease in the concentration of JT ions in the strontium-alloyed samples (some Mn^{3+} ions change their valence to Mn^{4+}). It will be used below when we discuss the effect of JT deformations on the oxygen diffusion coefficients.

4. THEORY

Considering the experimental findings presented above, we shall assume that when Sr^{2+} is substituted for La^{3+} , the mechanism of charge compensation is connected with a change in the valence of Mn^{3+} ions to Mn^{4+} , rather than formation of structural vacancies. In this case, the effect of alloying on the diffusion coefficients and the diffusion activation energy is not related to the vacancy formation energy and is determined largely by the variation of the concentration ratio of Mn^{3+} and Mn^{4+} ions.

In high-temperature crystalline $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ the mean (quantum-statistical) value of JT deformations of the nearest oxygen neighbors of Mn^{3+} ions is zero in the absence of random crystalline fields. In this case, a multi-well character of the potential at a JT ion may be reflected in the diffusion process if the oxygen neighbors of JT ions – a multi-level system – do not manage to relax (average themselves thermodynamically) during the time of a diffusion jump. This ratio between the relaxation time of a degenerate center and the diffusion jump time is possible only if splitting of degenerate levels is relatively small. If, on the contrary, splitting energies are large and, correspondingly, the ratio between the said times is reverse, the JT characteristics are lost to a large extent.

A relevant theoretical analysis of the diffusion coefficients of anions in crystals was performed on the assumption that an equilibrium occupancy of degenerate levels is not established during a diffusion jump in the JT subsystem [18]. In this case, the symmetry of the anion environment of the diffusing atom at the saddle point is determined by a random configuration of vibronic states of the nearest JT centers. Displacements of anions from symmetric sites, which correspond to these states, cause changes in the form of the diffusion potential barrier and, hence, the activation energy of jump frequencies. Consequently, configurations appear, leading to both a decrease and an increase in the activation energy as compared to the case

when JT displacements of anions in the crystal lattice are absent:

$$D = D^0 \sum_i W_i \exp\{-\Delta E_i/k_B T\} \cong D^0 \exp\{(\Delta/2k_B T)^2\} \quad (3)$$

where W_i is the probability of an i th configuration of vibronic states of JT centers nearest to the saddle point; ΔE_i is a change of the potential barrier height in the i th configuration caused by displacements of anions; Δ is the dispersion of the distribution ΔE_i , D^0 is the diffusion coefficient in the absence of JT interactions. For simplicity, we shall restrict ourselves to analysis of changes in the activation energy ΔE_i in terms of the elastic model of diffusion potential barriers [19,20]:

$$\Delta E_i = K_{\text{eff}} v_{\text{eff}} [(R_{\text{pol}}^i - R_{\text{anion}})^2 - (R_{\text{pol}}^0 - R_{\text{anion}})^2] / R_{\text{anion}}^2 \quad (4)$$

where R_{pol}^i is the passage radius in an i th configuration; R_{pol}^0 is the same radius in a configuration not distorted by JT displacements; R_{anion} is the radius of a diffusing anion; K_{eff} and v_{eff} denote effective values of the elastic modulus and the volume describing the deformation work during the diffusion migration.

If the difference between dimensions of the anion and the passage at the saddle point, $R_{\text{anion}} - R_{\text{pol}}^0$ is comparable with local JT displacements $u_{\text{JT}} \sim (10^{-1} - 10^{-2})R_{\text{anion}}$, the D value should increase considerably as compared to D^0 at temperatures $k_B T \leq \Delta$ ($\Delta \geq 10^{-1}$ eV).

Let us turn to the possibility of observing this effect. Most frequently, the diffusion of anions may be observed in high-symmetry phases of cooperative JT systems having a relatively high temperature of the JT transition $T_D \sim (10^2 - 10^3)$ K. The cooperative JT effect ensures diffusion in a crystal through fast channels of the anion migration, while a relatively high temperature of the structural JT transition provides local JT displacements, which are large enough.

One may expect that non-isovalent substitutions in these systems should cause a considerable decrease in the diffusion coefficients. This is due to a drop in the total number of degenerate centers and a simultaneous decrease in the concentration of degenerate centers having a relatively long relaxation time. Then for dilute systems with $y \ll 1$ the following value of ratio between the diffusion coefficients $D(y)/D(0)$ takes place: $D(y)/D(0) \cong 1 - yz$, where z is some coordination number. As is seen from Fig. 4, for $y = 0.075$ that value agrees fairly well with an experimental result $D(y = 0.075)/D(y = 0) = 0.46$ at a reasonable values of z (for example, $D(0.075)/D(0) = 0.4$ at $z = 8$).

When some critical concentration of substitutional centers is reached, the percolation through centers (saddle points) with a relatively small potential barrier should stop. This change of the diffusion coefficient with the concentration should correlate with the inhibition of the structural phase transformation during alloying. It is not inconceivable that similar situation took place at temperatures higher than the temperature of the structural phase transformation in a pseudo-JT perovskite-like $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ system [3], where in the region of critical concentration for structural phase transition the oxygen diffusion coefficient was changing anomalously.

5. CONCLUSIONS

1. The obtained diffusion data confirmed the existing ideas about mechanisms of charge compensation in oxides with 3d-ions. When the cation sublattice is alloyed with lower-valence ions, formation of anion structural vacancies and a large increase in the diffusion coefficients of oxygen atoms should be observed only if the cation sublattice is free of ions whose valence may increase upon alloying. Otherwise, the diffusion coefficients should not increase considerably upon alloying in the region of dilute solutions.
2. It was shown that the presence of degenerate or pseudo-degenerate states in the systems may have a considerable effect on the oxygen diffusion coefficients in oxides. In the high-temperature (high-symmetry) crystalline phase this effect is due to the influence of random JT deformations on parameters of diffusion potential barriers. In terms of the elastic model of formation of potential barriers, the effect is determined by a change (caused by JT deformations) of the size of the cavity, through which a diffusing atom passes at the saddle point. If dimensions of the cavity and the diffusing atom differ little, even small deformations may considerably influence the diffusion coefficients.
3. A correlation was predicted in terms of this model between the behavior of the concentration dependence of the temperature of the JT (or pseudo-JT) structural phase transition and the concentration dependence of the oxygen diffusion coefficient.

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REFERENCES

- [1] F. S. Ham, Jahn–Teller effects in electron paramagnetic resonance spectra, in *Electron Paramagnetic Resonance* (ed. S. Geshwind), Plenum Press, New York, 1972.
- [2] M. D. Sturge, *Solid State Phys.*, 1967, **20**, 91.
- [3] S. J. Rothman, J. L. Routbort, J. L. Novicki, K. C. Goretta, L. J. Thompson, J. N. Mundy and J. E. Baker, *Def. Diff. Forum*, 1989, **66–69**, 1081.
- [4] R. Doshi, J. L. Routbort and C. B. Alcock, *Def. Diff. Forum*, 1995, **127 and 128**, 39.
- [5] J. L. Routbort, R. Doshi and M. Krumpelt, *Solid State Ionics*, 1996, **90**, 21.
- [6] T. Ishigaki, S. Yamauchi, K. Kishio, J. Mizusaki and K. Fueki, *J. Solid State Chem.*, 1988, **73**, 179.
- [7] M. Runde, J. L. Routbort, J. N. Mundy, S. J. Rothman, C. L. Wiley and X. Xu, *Phys. Rev.*, 1992, **B46**, 3142.
- [8] (a) V. E. Naish, *Fiz. Met. Metalloved.*, 2001, **92** (5), 5; (b) V. E. Naish, *Fiz. Met. Metalloved.*, 1998, **85** (6), 5.
- [9] E. L. Nagaev, *Uspehi Fizicheskikh Nauk*, 1996, **166** (8), 833.
- [10] V. M. Loktev and Yu. G. Pogorelov, *Fiz. Nizkikh Temp.*, 2000, **26**, 231.

- [11] G. Amsel and D. Samuel, *Anal. Chem.*, 1967, **39**, 1689.
- [12] J. M. Mayer and E. Rimini, *Ion Beam Handbook for Materials Analysis*, Academic Press, New York, 1977.
- [13] V. N. Volkov, V. B. Vykhodets, I. K. Golubkov, S. M. Klotsman, P. V. Lerkh and V. A. Pavlov, *Nucl. Instr. Methods*, 1983, **205**, 73.
- [14] V. B. Vykhodets, S. M. Klotsman and A. D. Levin, *Fiz. Met. Metalloved.*, 1987, **64**, 920.
- [15] J. F. Ziegler (ed.), *The Stopping and Ranges of Ions in Matter*, Pergamon Press, New York, 1977.
- [16] V. B. Vykhodets, S. M. Klotsman, T. E. Kurennykh, L. D. Kurmaeva, A. D. Levin, V. A. Pavlov, M. A. Plekhanov and L. V. Smirnov, *Fiz. Met. Metalloved.*, 1987, **63**, 974.
- [17] V. B. Vykhodets, I. K. Golubkov, S. M. Klotsman, T. E. Kurennykh, G. N. Tatarinowa and A. N. Timofeer, *Fiz. Met. Metalloved.*, 1988, **66**, 303.
- [18] M. A. Ivanov, E. A. Pastukhov and A. Ya. Fishman, *Doklady Akademii Nauk*, 2002, **387**, 1.
- [19] Y. A. Bertin, J. Parisot and J. L. Gacougnolle, *J. Less-Common Met.*, 1980, **69**, 121.
- [20] J. D. Eshelby, *Solid State Phys.*, 1956, **3**, 79.
- [21] S. Carter, A. Selcuk, R. J. Chater, J. Kajda, J. A. Kilner and C. H. Steel, *Solid State Ionics*, 1992, **53–56**, 597.
- [22] J. L. Routbort, J. Wolfenstine, K. C. Goretta, R. E. Cook, T. R. Armstrong, C. Clauss and A. Dominguez-Rodriguez, *Diff. Dif. Forum*, 1997, **143–147**, 1201.

Spectral Intensities in Cubic Stoichiometric Elpasolites: The $\text{Cs}_2\text{NaSmCl}_6$ and $\text{Cs}_2\text{NaEuCl}_6$ Systems

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Abstract

We report theoretical studies regarding the optical properties of the $\text{Cs}_2\text{NaSmCl}_6$ and the $\text{Cs}_2\text{NaEuCl}_6$ systems, based upon new and updated experimental data from linear and non-linear optics. Vibronic intensity calculations are carried out for a series of selected transitions for which a number of superpositions of various spectral features derived from different excitations are most likely to take place and, as a consequence to play a significant role in both the observed oscillator strengths and in particular, the relative vibronic intensity distributions for a number of selected electronic transitions in these systems. Models and calculation methods are put forward, within the framework of a generalized vibronic model (VCF-LP). Our model calculation is based upon a minimum set of adjustable parameters (six parameters model, without including the force constants needed to build up a short-range interacting vibrational force field to modulate the normal modes of vibrations for the system). The model is developed within the assumption of either a small or a negligible coupling between the internal and the external vibrations for the crystal. In spite of the limitations and assumptions involved, it is shown that this model shows some utility and flexibility to advance our understanding of these complex radiative processes. For the sake of completeness, we discuss the most likely sources for improvement and the latest development in this field of research.

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1. INTRODUCTION

Following, Mason [1], the Laporte-forbidden $f \rightarrow f$ electronic transitions of lanthanide systems, acquire an electric-dipole probability by two mechanisms in the general independent system model (ISM), whereby overlap between the charge distributions of the metal ion and the ligand is neglected. A first-order electric-dipole transition dipole moment arises, either from the mixing of the $f \rightarrow f$ with $f \rightarrow d$ and $f \rightarrow g$ electron promotion under the electrostatic field of the ligands or from transient dipole induced by an allowed even-multipole electric moment of the $f \rightarrow f$ excitation, with the cooperation of the odd parity normal modes of vibrations for the system. It has been observed that the electrostatic field and the ligand polarization mechanisms make complementary intensity contributions to the $f \rightarrow f$ transitions of a given Ln(III) complex, depending upon the rank of the leading electric multipole moments. It is currently accepted that the polarization mechanism contributes essentially to the intensities of the ligand-hypersensitive 2^2 -pole $f \rightarrow f$ transitions, whereas the electrostatic mechanism is predominant for the 2^6 -pole transition intensities and makes the more important contribution in the 2^4 -pole cases. Also, Malta [2] in a more recent paper developed a model for the theory of vibronic transitions in rare earth compounds based upon a more reliable representation for the ligand field Hamiltonian than the crude electrostatic model. A set of general expressions for both the forced electric-dipole and dynamic coupling mechanisms was derived for the vibronic intensity parameters, including additional terms, from charge and polarizability gradients, which were not considered in previous research works. This paper is particularly interesting and a general discussion is given to account for the sensitivity of the calculated intensities to the values of the radial integrals, inter-configurational energy differences and ligand field parameters that may, in principle, be employed to undertake the spectral intensities calculations. Additionally, vibronic transitions in rare earth compounds have been studied based on the theoretical approaches by Faulkner and Richardson [3], Judd [4] and Stavola and co-workers [5]. These approaches have in common the basic idea in which the small deviation, during a vibration motion, from the equilibrium symmetry leads to additional ligand interactions that may be able to admix opposite parity configurations of the rare earth ion, as pointed out by Dexpert-Ghys and Auzel [6]. This is particularly important when the rare ion occupies a centrosymmetric site. A substantial amount of experimental data on vibronic intensities in rare earth compounds has been reported over the last three decades, and most of this data have been reviewed by Blasse [7]. Also, Reid and co-workers [8,9] have performed several analyses of spectral data and comparative energy level parameterizations for Ln^{3+} in cubic elpasolite crystals and also based upon a supra-parameterization

scheme have worked out vibronic intensity parameters for Er^{3+} in $\text{Cs}_2\text{NaErCl}_6$. Acevedo *et al.* [10], using a combined vibronic crystal field-closure-ligand polarization model carried out a full vibronic intensity calculation, using a six-parameter model with reference to the PrCl_6^{3-} and UBr_6^{2-} ions in cubic hosts. In addition, several recent calculations have been reported in the literature [10–15] dealing with systems such as: $\text{Cs}_2\text{NaTmCl}_6$, $\text{Cs}_2\text{NaErCl}_6$, $\text{Cr}(\text{CN})_6^{3-}$, and $\text{Cs}_2\text{NaScCl}_6\text{:MoCl}_6^{3-}$. Notwithstanding the simplicity of the approximations and assumptions involved in this approach, the results are good as could be expected, resulting that the overall oscillator strengths and most of the vibronic intensity distributions for a series of excitation in both absorptions and emissions, in different hosts, have been reproduced with a fair degree of success. The most likely sources for improvements have been discussed and our results to a certain extent agree with those of Malta [2], with reference to the sensitivity of the calculated intensities on the available set of the radial integrals and the choice of the inter-configurational energy differences between the terminal electronic states and the most likely intermediate states, which will probably influence mostly the observed spectral intensities. We have also discussed [16, and reference therein], the importance in considering the coupling among the vibrational modes of the same symmetry of the cluster to the analogous symmetry species of that of the counter ions in the host. This coupling, defined in this way, will include the effect of both the short- and the long-range interaction terms to the dynamic matrix and will, eventually produce a better description of the ‘true modes’ of vibrations for the crystal.

2. EXPERIMENTAL SECTION

We have carried out a thorough experimental study for the series of the $\text{Cs}_2\text{NaLnCl}_6$, elpasolite type systems [17–20]. The synthesis and, both the structural and spectroscopic characterization for $\text{Ln} = \text{Sm}, \text{Eu}$ elpasolites have been re-studied so as to enlarge the database and the accuracy of the experimental data reported for these two systems. These crystals belong to the $Fm\bar{3}m$ -space group and, to the best of our knowledge, their crystallographic data, X-ray powder diffraction and derived values for the lattice parameters have not yet been reported in the International Center for Diffraction Data (J.C.P.D.S). It has been very well established that these systems exhibit remarkable properties with significant applications to new luminescent devices and also to the laser industry. It is also worth mentioning that a fairly complete set of experimental data from linear and non-linear optics is needed to make possible to undertake sound and realistic calculations of these and related systems, to gain understanding in the optical properties and to advance the state-of-the-art in the lattice dynamic for these stoichiometric and non-stoichiometric elpasolite systems. With regards to the spectroscopic data, the reader is referred to the work of Richardson and co-workers [21] and Tanner [22,23]. In a series of articles, the synthesis of these and related crystals may be found [17–19], thus we will only report, the structural data needed for vibronic intensity calculations, to be

undertaken using a generalized version of the vibronic crystal field-closure-ligand polarization model (VCF-LP). The two crystals show the following nuclear equilibrium positions, $4\text{Ln}^{3+}(0,0,0)$, $4\text{Na}^{+}(1/2,1/2,1/2)$, $8\text{Cs}^{+}(1/4,1/4,1/4)$, and $24\text{Cl}^{-}(1/4,0,0)$, and correspond to closed cubic packing of $\text{Cs}^{+} + 3\text{Cl}^{-}$, with both ions Na^{+} and $\text{Ln}^{3+}(\text{Sm}^{3+}, \text{Eu}^{3+})$, filling octahedral holes. The refined lattice parameters, using the method put forward by Rietveld [20] are: 10.8342 Å (Sm^{3+}) and 10.8096 Å (Eu^{3+}).

3. THEORETICAL MODEL

The theory put forward by Judd and Ofelt [24,25] requires a generalization to become applicable to centrosymmetric complexes of the lanthanide ions in cubic hosts. The need for a generalization has become relevant, when considering the huge amount of experimental data from linear and non-linear optics, available in the literature [1,2,5–28]. Several attempts have been made in the literature, to deal with the most likely intensity sources so as to explain on a semi-quantitative way, the observed vibronic intensities in both centrosymmetric and non-centrosymmetric complex ions. These calculations have been carried out, using an increasing number of parameters to be fitted from the experimental data, using as a convergence test the minimization of the mean error deviation between the observed and the calculated energy gaps for a variety of transitions involving different terminal electronic states in various cubic hosts. The complexity of the spectra associated with the lanthanide type crystals is indeed formidable and, it should be expected to find difficulties in both the assignments and the identification of the various observed peaks in the spectra of these highly relativistic systems. In this research work, we introduce a symmetry-adapted formalism to account for the observed spectral intensities of the various peaks, with particular reference to two selected stoichiometric elpasolite type crystals in centrosymmetric environments. The current formalism will be applied with reference to the $\text{Cs}_2\text{NaSmCl}_6$ and $\text{Cs}_2\text{NaEuCl}_6$ crystals, for which we have a fair number, though incomplete, of well-determined experimental data from linear and non-linear optics. Due to complexity of the calculation and the lack of experimental data, we have assumed that the coupling between the internal and the external vibrational modes of motion in the crystal exists, but is either small or negligible. We have also assumed that the shape of the potential energy surfaces of the two terminal electronic states is the same, but they are only vertically displaced to one another along the totally symmetric normal mode of vibration. It is well known that the zero-order electric-dipole transition dipole moment associated with a parity forbidden excitation vanishes identically in a centrosymmetric environment, thus a vibronic coupling mechanism becomes operative. The calculation method to be developed assumes that the total electric-dipole moment may be partitioned into two contributions, as briefly discussed in the coming sections.

3.1. The vibronic crystal field contribution

In this section, we follow the symmetry-adapted approach put forward by Acevedo *et al.* [10], and introduce the vibronic crystal coupling constants $A_{v_i}^{F,\gamma}(i, \tau)$, the tensor operators $O_{\bar{\gamma}}^{\bar{F}}(T_1 \Gamma | i, \tau)$ and the general symmetry-adapted coefficients $\Pi_{(k,m)}^{[(T_1 \Gamma) \bar{F}; i, \tau]}[F_1 J_1 | F_2 J_2]$ to give a master formula to evaluate the relevant reduced matrix elements as given below:

$$\begin{aligned} & \langle \alpha_1(L_1 S J_1) \Gamma_{1j} \| O_{\bar{F}}^{\bar{F}}(T_1 \Gamma | i, \tau) \| \alpha_2(L_2 S J_2) \Gamma_2 l \rangle_m \\ &= \sum_k \Pi_{(k,m)}^{[(T_1 \Gamma) \bar{F}; i, \tau]}[F_1 J_1 | F_2 J_2] \langle \alpha_1(L_1 S) J_1 \| C^k \| \alpha_2(L_2 S) J_2 \rangle \end{aligned} \quad (1)$$

and it is straightforward to show that the reduced matrix elements on the right-hand side of the above identity, may ultimately be written in terms of the one-electron reduced matrix elements:

$$\langle 3 \| C^k \| 3 \rangle = -7 \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix}$$

With this set of identities, we may express the α th vector component of the vibronic crystal field transition dipole moment as given below:

$$\begin{aligned} \mu_{1 \rightarrow 2}^{\alpha} &= -2 \left(\frac{Ze}{\Delta E} \right) \sum_t S_{v_t} \sum_{\Gamma, \gamma, i} \sum_{\tau} A_{v_t}^{F, \gamma}(i, \tau) \sum_{\bar{F} \bar{\gamma}} \lambda(\bar{F})^{1/2} (-1)^{\bar{F} + \bar{\gamma}^+} \\ &\times V \begin{pmatrix} T_1 & \Gamma & \bar{F} \\ \alpha & \gamma & \bar{\gamma}^+ \end{pmatrix} (-1)^{F_1 + \gamma_1^+} \sum_m V_m \begin{pmatrix} F_1 & F_2 & \bar{F} \\ \gamma_1^+ & \gamma_2 & \bar{\gamma} \end{pmatrix} \\ &\times \langle \alpha_1(L_1 S J_1) \Gamma_{1j} \| O_{\bar{F}}^{\bar{F}}(T_1 \Gamma | i, \tau) \| \alpha_2(L_2 S J_2) \Gamma_2 l \rangle_m \end{aligned} \quad (2)$$

Full tabulations of the vibronic coupling constants and tensor operators involved in the calculation of $f \rightarrow f$ electronic transitions in centrosymmetric compounds are available and can be requested from R.A. (Documentation I – Appendices 1 and 2), and therefore will not be repeated here.

3.2. The vibronic ligand polarization contribution

For isotropic ligand subsystems, the α -th vector component of the ligand polarization contribution to the total transition dipole moment may be written as:

$$\mu_{1 \rightarrow 2}^{\alpha} = \sum_{k,t} S_{kt} \sum_{\Gamma, \gamma} \sum_{i, \tau} B_{k,t}^{F, \gamma}(i, \tau) \langle \alpha_1(L_1 S J_1) \Gamma_1 \gamma_1 l | M_{\gamma}^F(i, \tau) | \alpha_2(L_2 S J_2) \Gamma_2 \gamma_2 m \rangle \quad (3)$$

and the ligand polarization vibronic coupling constants $B_{k,t}^{F, \gamma}(i, \tau)$ can be obtained from R. A. (Documentation II – Appendix 3).

4. VIBRONIC INTENSITY CALCULATIONS

This section is devoted to illustrate our model calculation and its applications to the $\text{Cs}_2\text{NaSmCl}_6$ and the $\text{Cs}_2\text{NaEuCl}_6$, elpasolite systems, for which we have a database of good quality, from structural (XRD-powder) and spectroscopic techniques (linear and non-linear optics). The data available are fairly accurate so as to attempt some kind of realistic vibronic calculations, based upon a generalization of the vibronic crystal field-ligand polarization model (VCF-LP) and, the neglect of the coupling between the internal and the external normal modes of vibrations for the various ions of the crystal. This assumption should be considered with most care, since there is a coupling between the vibrational motions of the same symmetry species for the cluster LnCl_6^{3-} and that of the Na^+ and Cl^- counter ions and this neglect will have some influence on the approximate description of the normal modes of vibrations for these type systems.

4.1. The $\text{Cs}_2\text{NaSmCl}_6$ elpasolite system

As it was mentioned in Section 2, the crystallographic pattern for this elpasolite has not been reported in the International Center for Diffraction Data (J.C.P.D.S.). We have investigated the synthesis, structural characterization and the spectroscopy for the neat and the doped crystals [18]. The experimental evidence indicates that below 100 K, the site symmetry of the SmCl_6^{3-} ion undergoes a descent of symmetry following the group-subgroup chain $O_h \supset C_{4h}$ and thus the degeneracy of the $\Gamma_8(O_h)$, luminescent energy levels is lifted, the observed splitting being about 4 cm^{-1} . We have carried out an experimental study so as to enlarge the database with accurate measurements and in this way to stand on a better position to develop models to tackle the lattice dynamics for these systems as well as to formulate new models and methods to deal with some complex energy transfer processes in these crystals and related systems. Richardson *et al.* [27] have performed an accurate analysis of the database for the neat $\text{Cs}_2\text{NaSmCl}_6$. The experimental data for this system has been enlarged from the analysis of the spectrum of doped $\text{Cs}_2\text{NaYCl}_6$; SmCl_6^{3-} , and some reassignments have been done by Tanner *et al.* [8] with reference to this latter system. Additionally, Reid and co-workers [8], following pioneer works carried out by Richardson and co-workers [21,22,26–29] performed a new fitting procedure for the energy levels corresponding to the whole series of the lanthanide trivalent ions in elpasolite type systems. In particular, and with reference to the Sm^{3+} ion in the doped crystal, a basis set of 690 $\{|JM_J\rangle\}$ -states comprising 65 $\{|SLJ\rangle\}$ -multiplets was employed in the fitting procedure. In addition, experimental data for the neat $\text{Cs}_2\text{NaSmCl}_6$ is also available from Banerjee and Schwartz [30], showing a sensible and fair agreement between the observed and calculated energy levels. A rather complete and probably, most comprehensive approach is found in the research work performed by Smith [31]. In all of these energy level calculations, the computing programs written by Reid have been extensively used and a full-parameterized approach has been utilized. We have also tackled this problem, using

a rather different strategy and our philosophy is to undertake model calculations using the minimum set of adjustable parameters from the experimental data, since this latter is always rather scarce or incomplete. We also believe that these supra-parameterized models, though useful for some purposes, precludes the advance of the state-of-the-art since we believe that these formalisms obscure both the chemistry and the physics of these complex phenomena we aim to rationalize and therefore alternative approaches are most welcome in this field of research. Our model is compared with some theoretical models of the spectral intensities for this type systems, within the framework of the superposition model put forward by Newman [32], which involves a full parameterization model, which in principle, would require to fit 46-parameters from the experimental data, without mentioning, the parameters needed to modulate the intra-molecular force field so as to obtain the normal modes of vibrations for this system [9 and, references there in]. We have instead carried out an energy levels fitting, using a six-parameter model and it is shown that the energy ordering (for a selected relevant subset of allowed states) is in fair agreement with the experiment. The eigenvectors needed to perform this calculations are also tabulated along with the energy calculation and, all this information is displayed in Table 1. The greatest advantage of this work is that the parameter values, obtained using this simple but meaningful calculation have both a clear and a sound physical meaning, which is interesting and encourages us to develop new and updated model calculations,

$$\text{CF} : C_k = \frac{2e^2 \langle r^k \rangle}{R_0^{k+1} (\Delta E)}, \quad \text{LP} : a_k = \frac{\alpha_L \langle r^k \rangle}{R_0^{k+3}}, \quad \alpha_L (\text{Cl}^{-1}) = 3.0 (\text{\AA})^3$$

including the short- and the long-range interaction terms in the dynamic matrix and in this way to achieve a better picture of the coupling between the internal and the external normal modes of vibrations for the system as whole. Our calculation is based upon the experimental data, reported by Poblete and Acevedo [18], Richardson and co-workers [21] and Tanner [22], though we recognize that unit cell group analysis of the elpasolite systems needs to be carried out to gain understanding of the mixing in of internal and external vibrational modes. All of these seven atoms system calculations may be regarded as starting points for the explanation of the intensity of lattice vibrations in the electronic spectra. In our current research work, some suitable systems for experimental and theoretical studies are those for which lattice modes have anomalously high intensities in certain transitions such as the $\text{Cs}_2\text{MEuCl}_6$, where $\text{M} = \text{Li}, \text{Na}$ and for the sake of completeness, we will report our results for the Eu(III) system in the elpasolite crystal in Section 4.2. It is interesting to compare our calculated energy levels using a six-parameter model with those from both the experiment and a supra-parameterization procedure (the comparative energy level calculations is given in Table 2). We also list, in Table 3, both the relative vibronic intensity distributions and the total oscillator strengths for a number of vibronically allowed electronic excitations for this system. The results reported in Table 3 for the spectral intensities

Table 1. The Sm^{3+} ion in the $\text{Cs}_2\text{NaSmCl}_6$ elpasolite type crystal

(1)	$ E''\rangle = +0.9654 (^6H_{5/2})E''\rangle + 0.1481 (^6H_{7/2})E''\rangle + 0.1310 (^4G_{5/2}^{(1)})E''\rangle + 0.1607 (^4G_{5/2}^{(4)})E''\rangle$ $E = 0$
(2)	$ U'\rangle = +0.9623 (^6H_{5/2})U'\rangle + 0.1654 (^6H_{7/2})U'\rangle + 0.1306 (^4G_{5/2}^{(1)})U'\rangle + 0.1602 (^4G_{5/2}^{(4)})U'\rangle$ $E = 161 \text{ cm}^{-1}$
(3)	$ E'\rangle = -0.9845 (^6H_{7/2})E'\rangle - 0.1068 (^4G_{7/2}^{(1)})E'\rangle - 0.1334 (^4G_{7/2}^{(4)})E'\rangle$ $E = 1014 \text{ cm}^{-1}$
(4)	$ U'\rangle = -0.9585 (^6H_{7/2})U'\rangle + 0.1626 (^6H_{5/2})U'\rangle + 0.0556 (^6H_{9/2}^a)U'\rangle + 0.0692 (^6H_{9/2}^b)U'\rangle$ $+ 0.0741 (^6H_{11/2}^a)U'\rangle + 0.1035 (^6H_{11/2}^b)U'\rangle - 0.1040 (^4G_{7/2}^{(1)})U'\rangle - 0.1299 (^4G_{7/2}^{(2)})U'\rangle$ $E = 1207 \text{ cm}^{-1}$
(5)	$ E''\rangle = +0.9727 (^6H_{7/2})E''\rangle - 0.1468 (^6H_{5/2})E''\rangle + 0.1054 (^4G_{7/2}^{(1)})E''\rangle + 0.1316 (^4G_{7/2}^{(4)})E''\rangle$ $E = 1332 \text{ cm}^{-1}$
(6)	$ E'\rangle = +0.9910 (^6H_{9/2})E'\rangle + 0.0814 (^4G_{9/2}^{(1)})E'\rangle + 0.1018 (^4G_{9/2}^{(4)})E'\rangle$ $E = 2345 \text{ cm}^{-1}$
(7)	$ ^aU'\rangle = -0.9864 (^6H_{9/2}^a)^aU'\rangle - 0.0707 (^6H_{9/2}^b)^aU'\rangle - 0.0563 (^6H_{7/2})^aU'\rangle - 0.0810 (^4G_{9/2}^{(1)})^aU'\rangle - 0.1013 (^4G_{9/2}^{(4)})^aU'\rangle$ $E = 2432 \text{ cm}^{-1}$
(8)	$ ^bU'\rangle = -0.9854 (^6H_{9/2}^b)^bU'\rangle + 0.0750 (^6H_{9/2}^a)^bU'\rangle - 0.0639 (^6H_{7/2})^bU'\rangle - 0.0809 (^4G_{9/2}^{(1)})^bU'\rangle - 0.1012 (^4G_{9/2}^{(4)})^bU'\rangle$ $E = 2463 \text{ cm}^{-1}$
(9)	$ U'\rangle = -0.1649 (^6H_{5/2})U'\rangle - 0.1485 (^6F_{5/2})U'\rangle - 0.2514 (^4F^{(1)})U'\rangle + 0.5584 (^4F^{(3)})U'\rangle$ $+ 0.2367 (^4F^{(4)})U'\rangle + 0.3833 (^4G^{(1)})U'\rangle - 0.2672 (^4G^{(2)})U'\rangle - 0.1243 (^4G^{(3)})U'\rangle$ $E = 17\,764 \text{ cm}^{-1}$

Data: $\langle r^2 \rangle = 3.507 \times 10^{-17} \text{ cm}^2$, $\langle r^4 \rangle = 3.295 \times 10^{-33} \text{ cm}^4$, $\langle r^6 \rangle = 6.556 \times 10^{-49} \text{ cm}^6$, $\Delta E(4f \rightarrow 5d) \approx 70\,000 \text{ cm}^{-1}$.

Table 2. Comparative energy level calculations^a for the Cs₂NaSmCl₆ system

	This work ^a	Experimental data	Full parameterization
E''	0	0	0
U'	161	164	155
E'	1014	1045	1054
U'	1207	1210	1201
E''	1332	1216	1201
E'	2345	2249	2264
^a U'	2432	2369	2367
^b U'	2463	2423	2420
U'	17 764	17 742	17 755
E''	18 256	(no)	18 102

^aParameters: $E^1 = 5035\text{ cm}^{-1}$, $E^2 = 24.90\text{ cm}^{-1}$, $E^3 = 526\text{ cm}^{-1}$, $\zeta = 1168\text{ cm}^{-1}$, $(\gamma_4/\gamma_6) \approx 3.90$, $\gamma_4 = 233\text{ cm}^{-1}$, where $\gamma_k = e^2\langle r^4 \rangle / R_0^{k+1}$.

of the SmCl_6^{3-} complex ion in the $\text{Cs}_2\text{NaSmCl}_6$ system are as good as could be expected for this simple model calculation, and it is shown that the model is both suitable and adequate to deal with these highly relativistic systems. Generally speaking, the agreement between the experiment and the theoretical predictions, using such a simple model calculation is fairly good and the main sources for the

Table 3. Spectral intensities for the Cs₂NaSmCl₆ system

Electronic transition	$f_3 : f_4 : f_6$	Exp	$f \times 10^8$
$ U'\rangle \rightarrow E''\rangle$	0.02:1.00:0.54	[0.16:1.00:0.12]	2.33
$ U'\rangle \rightarrow U'\rangle$	1.00:0.83:0.81	[1.00:0.10:0.10]	0.44
$ U'\rangle \rightarrow E'\rangle$	0.10:0.04:1.00	[0.50:1.00:1.00]	1.20
$ U'\rangle \rightarrow E''\rangle$	1.00:0.05:0.10	[no] ^a	1.13
$ U'\rangle \rightarrow U'\rangle$	0.40:0.23:1.00	[1.30:1.10:1.00] ^b	68,69
$ U\rangle \rightarrow E'\rangle$	1.00:0.14:0.92	[1.00:0.60:0.60]	85.52
$ U'\rangle \rightarrow ^aU'\rangle$	1.00:0.37:1.00	[1.25:0.25:1.00]	98.54
$ U'\rangle \rightarrow ^bU'\rangle$	0.36:0.29:1.00	[0.25:0.40:1.00]	82.05

Dimensionless coefficients used in the vibronic intensity calculation.
^aFor this excitation, the experimental evidence is not clear since these vibronic transitions are almost coincident with that of the $|U'\rangle \rightarrow |U'\rangle$.
^bFor these excitations, the juxtaposition of transitions $|U'\rangle \rightarrow |E''\rangle$ and $|U'\rangle \rightarrow |U'\rangle$ is notably strong with an energy gap of about 19 cm^{-1} .

spectral intensities indicates, that the main features in the spectrum involve the odd parity vibrational modes of the SmCl_6^{3-} cluster ion. We have indicated at the bottom of the Table 3, those electronic transitions for which a substantial superposition of vibronic excitations is expected and, in these cases the results should be looked at with care and caution.

4.2. The $\text{Cs}_2\text{NaEuCl}_6$ elpasolite system

The database employed for this system by Richardson *et al.* [27] is made up from studies carried out for systems such as $\text{Cs}_2\text{NaEuCl}_6$ and $\text{Cs}_2\text{NaYCl}_6\text{:EuCl}_6^{3-}$. In a subsequent experimental study performed by Tanner and Yu-Long Liu [23], the data were updated utilizing experimental data from Raman, luminescence and absorption studies. Additionally, these data were again analyzed, including the studies by Richardson and co-workers [26] together with the two observed energy levels for the quintuplets $^5D_3$ in the neat $\text{Cs}_2\text{NaEuCl}_6$ crystal, as informed in Ref. [27]. There are also some data from studies available for the hexafluoroelpasolite crystals [8, 33–38], which is currently used to enlarge the database so as to achieve a better fitting among the observed and calculated energy levels. The magnificent computing programs library, written by Reid and known as Documentation, has been employed to evaluate matrix elements, wavefunctions, energy levels and parameters and thus to provide a sensible set of calculated energy levels, as reported by Reid and co-workers [8]. For Eu^{3+} , a total of 235 (JM_J)-states comprising 25 (SLJ) multiplets, were employed in the basis set for the crystal field energy level calculations. It must be emphasized that, in spite of all these efforts, the result of obtained fitting procedure does not enable a clear comparison of the crystal field parameters B_0^4 and B_0^6 in the $\text{Cs}_2\text{NaEuCl}_6$ and the $\text{Cs}_2\text{NaYCl}_6\text{:EuCl}_6^{3-}$ to be made. When a full parameterization calculation is carried out and 27 energy levels employed, then the calculated mean square deviation for this system is about $\sigma = 24.80 \text{ cm}^{-1}$. As far as the vibronic intensity calculations are concerned, the detailed mechanisms whereby these excitations acquire electric-dipole intensity have been discussed in detail [11, 13, 15, 16, 39].

For materials in which the rare earth ion occupies a centrosymmetric site, the intensity must be due to the vibrational motion of the surrounding ions. Thus to a first approximation, the vibronic perturbation may be regarded as due to the motions of the chloride ions relative to the rare earth ion. It is well known that, generally speaking, the $\text{Cs}_2\text{NaLnCl}_6$ crystals over a wide range of temperature are cubic and the trivalent lanthanide ions occupy a perfect octahedral site of symmetry. As for the Eu^{3+} -system, the crystal field energy levels are not well separated among themselves and in some cases the energy gaps are about $15\text{--}100 \text{ cm}^{-1}$. It is therefore to be expected that: (1) there cannot be an accurate relative energy ordering associated to the various crystal field energy levels, and (2) there is possibility of having superpositions of peaks and/or bands corresponding to different electronic transitions. A thorough analysis of the literature, indicates that several

papers have been published regarding vibronic transitions for these type of systems [3,28,40–45]. It is interesting to observe that vibronic intensity calculations for this system have been done previously by Faulkner and Richardson [3] and also by Acevedo *et al.* [46] and many questions are still open to discussion, so that new and updated calculations using generalized models (including the coupling between the internal and the external vibrations) are needed. As informed [3,8,28,46], the spectroscopic data for these emissions is resolved satisfactorily, and we observe the presence of a rich vibronic structure. Our calculation was performed using a minimum number of parameters to be fitted from the experimental data (six model parameters) and the results obtained are shown in Tables 4–6. In calculations, already in progress in our laboratory, we plan to introduce a new scheme to deal with the full lattice dynamics for these types of elpasolite systems. In a preliminary research work [46], we reported the best possible values for the parameters needed to diagonalize the energy matrix ($F_k : k = 2, 4, 6, B_l : l = 4, 6$) and the spin–orbit coupling constant ζ_{s0} . These magnitudes have been employed to work out both a consistent and sensible set of eigenvectors (Table 4) and eigenvalues (Table 5). We have then proceeded to work out intensity ratios for the three false origins of the EuCl_6^{3-} complex ion in the $\text{Cs}_2\text{NaLnCl}_6$ system, as well as the calculated total oscillator strengths for a number of selected emissions. A close examination of these tables indicates that this simple model calculation is both useful and flexible to account for the intensity of the main spectral features in the spectra of the rare earths and lanthanide complex systems. We are fully aware that the VCF-closure-LP models may be improved substantially relaxing the use of closure approximation over the central metal ion's allowed states and to actually include the most likely intermediate electronic states, using a truncated basis set of odd parity states [13–15]. This implies to have available a better and more comprehensive approach for the estimate of the vibronic intensities and to include in an explicit form in the model mechanistic factors in the intensity calculations (the most likely path for the transitions to take place). In the current work, we have tried to improve the quality of our wavefunctions, the relaxation of some approximations and have included a better set of SCF-radial functions.

5. SUMMARY

The results of our calculations indicate that it is advisable to move forward and to actually include the coupling between normal modes of the same and also to build up the dynamic matrix, taken into account both the short- and the long-range interactions in the crystal. We have shown with reference to the Cs_2UBr_6 crystal [16] that a full lattice dynamics calculation on stoichiometric elpasolite type systems, is by no means a trivial task, though it is a very challenging task to assume from both the theoretical and experimental viewpoints. We need some additional experimental data to make possible to perform accurate lattice dynamics

Table 4. Eigenvectors for the Eu^{3+} in the $\text{Cs}_2\text{NaEuCl}_6$ elapsolite type crystal**I. A_1 symmetry species**

- (1) $|A_1\rangle = +0.9644|(^7F_0)A_1\rangle + 0.1585|(^5D_0^{(1)})A_1\rangle + 0.0541|(^5D_0^{(2)})A_1\rangle - 0.2007|(^5D_0^{(3)})A_1\rangle$
 $-0.0417|(^7F_4)A_1\rangle$
- (2) $|A_1\rangle = -0.0403|(^7F_0)A_1\rangle + 0.9959|(^7F_4)A_1\rangle + 0.0489|(^5D_4^{(1)})A_1\rangle + 0.0167|(^5D_4^{(2)})A_1\rangle$
 $-0.0620|(^5D_4^{(3)})A_1\rangle$
- (3) $|A_1\rangle = -0.2616|(^7F_0)A_1\rangle + 0.5852|(^5D_0^{(1)})A_1\rangle + 0.2013|(^5D_0^{(2)})A_1\rangle - 0.7411|(^5D_0^{(3)})A_1\rangle$
- (4) $|A_1\rangle = -0.0807|(^7F_0)A_1\rangle + 0.6043|(^5D_4^{(1)})A_1\rangle + 0.2061|(^5D_4^{(2)})A_1\rangle - 0.7653|(^5D_4^{(3)})A_1\rangle$

II. A_2 symmetry species

- (5) $|A_2\rangle = +0.9906|(^7F_3)A_2\rangle + 0.0831|(^5D_3^{(1)})A_2\rangle + 0.0284|(^5D_3^{(2)})A_2\rangle - 0.1053|(^5D_3^{(3)})A_2\rangle$
- (6) $|A_2\rangle = -0.1371|(^7F_3)A_2\rangle + 0.6006|(^5D_3^{(1)})A_2\rangle + 0.2049|(^5D_3^{(2)})A_2\rangle - 0.7606|(^5D_3^{(3)})A_2\rangle$

III. E symmetry species

- (7) $|E\rangle = +0.9836|(^7F_2)E\rangle + 0.1094|(^5D_2^{(1)})E\rangle + 0.0373|(^5D_2^{(2)})E\rangle - 0.1386|(^5D_2^{(3)})E\rangle$
- (8) $|E\rangle = +0.9967|(^7F_4)E\rangle + 0.0489|(^5D_4^{(1)})E\rangle + 0.0167|(^5D_4^{(2)})E\rangle - 0.0620|(^5D_4^{(3)})E\rangle$
- (9) $|E\rangle = -0.1805|(^7F_2)E\rangle + 0.5964|(^5D_2^{(1)})E\rangle + 0.2034|(^5D_2^{(2)})E\rangle - 0.7552|(^5D_2^{(3)})E\rangle$
- (10) $|E\rangle = -0.0807|(^7F_4)E\rangle + 0.6043|(^5D_4^{(1)})E\rangle + 0.2061|(^5D_4^{(2)})E\rangle - 0.7653|(^5D_4^{(3)})E\rangle$

IV. T_1 symmetry species

- (11) $|T_1\rangle = +0.9640|(^7F_1)T_1\rangle + 0.1389|(^5D_1^{(1)})T_1\rangle + 0.0474|(^5D_1^{(2)})T_1\rangle - 0.1759|(^5D_1^{(3)})T_1\rangle$
 $+0.0877|(^7F_3)T_1\rangle + 0.0324|(^7F_4)T_1\rangle$

- (12) $|T_1\rangle = -0.0869|(^7F_1)T_1\rangle + 0.9863|(^7F_3)T_1\rangle + 0.0827|(^5D_3^{(1)})T_1\rangle + 0.0282|(^5D_3^{(2)})T_1\rangle$
 $-0.1048|(^5D_3^{(3)})T_1\rangle + 0.0261|(^7F_4)T_1\rangle$
- (13) $|T_1\rangle = -0.0268|(^7F_1)T_1\rangle - 0.0239|(^7F_3)T_1\rangle + 0.9961|(^7F_4)T_1\rangle + 0.0489|(^5D_4^{(1)})T_1\rangle$
 $+0.0167|(^5D_4^{(2)})T_1\rangle - 0.0620|(^5D_4^{(3)})T_1\rangle$
- (14) $|T_1\rangle = -0.2301|(^7F_1)T_1\rangle + 0.5901|(^5D_1^{(1)})T_1\rangle + 0.2013|(^5D_1^{(2)})T_1\rangle - 0.7472|(^5D_1^{(3)})T_1\rangle$
- (15) $|T_1\rangle = -0.1371|(^7F_3)T_1\rangle + 0.6006|(^5D_3^{(1)})T_1\rangle + 0.2049|(^5D_3^{(2)})T_1\rangle - 0.7606|(^5D_3^{(3)})T_1\rangle$
- (16) $|T_1\rangle = -0.0807|(^7F_4)T_1\rangle + 0.6043|(^5D_4^{(1)})T_1\rangle + 0.2061|(^5D_4^{(2)})T_1\rangle - 0.7653|(^5D_4^{(3)})T_1\rangle$
- V. T_2 symmetry species
- (17) $|T_2\rangle = +0.9777|(^7F_2)T_2\rangle + 0.1087|(^5D_2^{(1)})T_2\rangle + 0.0371|(^5D_2^{(2)})T_2\rangle - 0.1378|(^5D_2^{(3)})T_2\rangle$
 $+0.1088|(^7F_3)T_2\rangle$
- (18) $|T_2\rangle = -0.1088|(^7F_2)T_2\rangle + 0.9824|(^7F_3)T_2\rangle + 0.0824|(^5D_3^{(1)})T_2\rangle + 0.0282|(^5D_3^{(2)})T_2\rangle$
 $-0.1044|(^5D_3^{(3)})T_2\rangle - 0.0691|(^7F_4)T_2\rangle$
- (19) $|T_2\rangle = -0.1179|(^7F_3)T_2\rangle + 0.9889|(^7F_4)T_2\rangle + 0.0485|(^5D_4^{(1)})T_2\rangle + 0.0166|(^5D_4^{(2)})T_2\rangle$
 $-0.0615|(^5D_4^{(3)})T_2\rangle$
- (20) $|T_2\rangle = -0.1805|(^7F_2)T_2\rangle + 0.5964|(^5D_2^{(1)})T_2\rangle + 0.2034|(^5D_2^{(2)})T_2\rangle - 0.7552|(^5D_2^{(3)})T_2\rangle$
- (21) $|T_2\rangle = -0.1371|(^7F_2)T_2\rangle + 0.6006|(^5D_3^{(1)})T_2\rangle + 0.2049|(^5D_3^{(2)})T_2\rangle - 0.7606|(^5D_3^{(3)})T_2\rangle$
- (22) $|T_2\rangle = -0.0807|(^7F_4)T_2\rangle + 0.6043|(^5D_4^{(1)})T_2\rangle + 0.2061|(^5D_4^{(2)})T_2\rangle - 0.7653|(^5D_4^{(3)})T_2\rangle$
-

Table 5. Energy levels for Eu^{3+} in $\text{Cs}_2\text{NaEuCl}_6$

Major state	Species	This work ^a	Ref. [47]	Exp.
${}^7F_0$	A_1	0.000	0.000	0.000
${}^7F_1$	T_1	0.358	0.332	0.356
${}^7F_2$	E	1.051	0.821	0.872
${}^7F_2$	T_2	1.156	1.038	1.086
${}^7F_3$	A_2	1.984	1.751	1.798
${}^7F_3$	T_2	2.051	1.846	1.900
${}^7F_3$	T_1	2.082	1.901	1.964
${}^7F_4$	T_2	3.074	2.629	2.660
${}^7F_4$	E	3.197	2.915	2.976
${}^7F_4$	T_1	3.222	2.949	3.010
${}^7F_4$	A_1	3.274	2.979	3.036
${}^5D_0$	A_1	17.738	19.780	17.206
${}^5D_1$	T_1	18.555	20.545	18.961
${}^5D_2$	T_2	21.263	22.099	21.381
${}^5D_2$	E	21.276	22.194	21.495
${}^5D_3$	T_1	22.947	24.642	24.232
${}^5D_3$	T_2	22.841	24.675	24.249
${}^5D_3$	A_2	22.732	24.639	24.296
${}^5D_4$	T_1	25.545	—	—
${}^5D_4$	T_2	25.558	—	—
${}^5D_4$	E	25.567	—	—
${}^5D_4$	A_1	25.642	—	—

^aParameters: $\langle r^2 \rangle = 3.310 \times 10^{-17} \text{ cm}^{-2}$, $\langle r^4 \rangle = 3.001 \times 10^{-33} \text{ cm}^{-4}$, $\langle r^6 \rangle = 5.848 \times 10^{-49} \text{ cm}^{-6}$, $R_0 = 2.76 \times 10^{-8} \text{ cm}^{-1}$, $E^1 = 5141 \text{ cm}^{-1}$, $E^2 = 27.10 \text{ cm}^{-1}$, $E^3 = 520.23 \text{ cm}^{-1}$, $\zeta = 1320 \text{ cm}^{-1}$, $(\gamma_4/\gamma_6) \approx 3.91$, $\gamma_4 = 217.40 \text{ cm}^{-1}$, $\Delta E(4f \rightarrow 5d) \approx 70\,000 \text{ cm}^{-1}$.

calculations, based upon a minimum set of parameters and to avoid supra-parameterization schemes which may obscure both the physics and the chemistry in connection with radiative processes in these elpasolite type systems. In summary, the results of vibronic intensity calculations for these complex systems, show that the model employed is both useful and flexible and some important generalizations and improvements may be considered in more sophisticated calculations. A close looks at the results displayed in [Tables 3 and 6](#) show that for most of the vibronic transitions; $\Gamma_k \rightarrow \Gamma_l + \nu_m$, $m = 3, 4, 6$ in these two systems, the predicted ratios for the various electronic transitions are in a fair agreement with the experimental data available, as well as the total oscillator strengths are reproduced in magnitude with remarkable accuracy.

Table 6. Spectral intensities for the $\text{Cs}_2\text{NaEuCl}_6$ system ($f \times 10^9$)

(1) $ \langle {}^5D_0A_1 \rangle \rightarrow \langle {}^7F_2 \rangle \Gamma \rangle$				(6) $ \langle {}^5D_2T_2 \rangle \rightarrow \langle {}^7F_1 \rangle T_1 \rangle$			
False Origin	E	T_2		False Origin	T_1		
f_3	19.582	5.321		f_3	16.10		
f_4	0.008	9.792		f_4	2.90		
f_6	6.259	6.107		f_6	4.11		
$E : 3.20 : 0.001 : 1.00 [0.40 : 0.70 : 1.00]$				$T_1 : 3.90 : 0.70 : 1.00 [0.20 : 0.90 : 1.00]$			
$T_2 : 0.90 : 1.60 : 1.00 [0.40 : 0.60 : 1.00]$							
(2) $ \langle {}^5D_1T_1 \rangle \rightarrow \langle {}^7F_1 \rangle T_1 \rangle$				(7) $ \langle {}^5D_2T_2 \rangle \rightarrow \langle {}^7F_2 \rangle \Gamma \rangle$			
False Origin	T_1			False Origin	E	T_2	
f_3	33.62			f_3	0.63	0.01	
f_4	14.68			f_4	0.83	3.29	
f_6	34.89			f_6	0.63	2.08	
$T_1 : 0.90 : 0.40 : 1.00 [0.40 : 0.70 : 1.00]$				$E : 1.00 : 1.30 : 1.00 [1.00 : 0.50 : 1.00]$			
				$T_2 : 0.005 : 1.60 : 1.00 [0.15 : 0.80 : 1.00]$			
(3) $ \langle {}^5D_1T_1 \rangle \rightarrow \langle {}^7F_2 \rangle \Gamma \rangle$				(8) $ \langle {}^5D_2T_2 \rangle \rightarrow \langle {}^7F_3 \rangle \Gamma \rangle$			
False Origin	E	T_2		False Origin	A_2	T_1	T_2
f_3	2.55	4.44		f_3	0.002	76.64	79.31
f_4	4.64	0.51		f_4	0.118	15.58	37.51
f_6	2.89	0.95		f_6	0.054	42.69	20.39
$E : 0.90 : 1.60 : 1.00 [1.50 : 1.00 : 1.00]$				$A_2 : 0.04 : 2.20 : 1.00 [0.70 : 2.20 : 1.00]$			
$T_2 : 4.70 : 0.50 : 1.00 [0.40 : 0.50 : 1.00]$				$T_1 : 1.80 : 0.40 : 1.00 [0.60 : 0.90 : 1.00]$			
				$T_2 : 3.90 : 1.80 : 1.00 [0.30 : 1.50 : 1.00]$			
(4) $ \langle {}^5D_1T_1 \rangle \rightarrow \langle {}^7F_3 \rangle \Gamma \rangle$				(9) $ \langle {}^5D_2T_2 \rangle \rightarrow \langle {}^7F_4 \rangle \Gamma \rangle$			
False Origin	A_2	T_1	T_2	False Origin	A_1	E	T_1 T_2
f_3	3.47	0.05	1.46	f_3	0.53	0.81	2.46 0.14
f_4	5.50	3.26	2.96	f_4	1.09	0.63	3.28 8.52
f_6	2.25	7.30	0.83	f_6	0.84	0.36	0.11 5.35
$A_2 : 1.50 : 2.40 : 1.00 [1.60 : 6.40 : 1.00]$				$A_1 : 0.60 : 1.30 : 1.00 [0.90 : 0.80 : 1.00]$			
$T_1 : 0.007 : 0.40 : 1.00 [1.20 : 0.80 : 1.00]$				$E : 2.30 : 1.80 : 1.00 [0.30 : 0.60 : 1.00]$			
$T_2 : 1.80 : 3.60 : 1.00 [1.40 : 1.80 : 1.00]$				$T_1 : 22.40 : 29.80 : 1.00 [0.30 : 0.50 : 1.00]$			
				$T_2 : 0.03 : 1.60 : 1.00 [0.50 : 1.60 : 1.00]$			
(5) $ \langle {}^5D_2T_2 \rangle \rightarrow \langle {}^7F_0 \rangle A_1 \rangle$							
False Origin	A_1						
f_3	3.06						
f_4	4.18						
f_6	3.40						
$A_1 : 1.20 : 0.40 : 1.00 [0.40 : 0.80 : 1.00]$							

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REFERENCES

- [1] S. F. Mason, *Inorg. Chim. Acta*, 1984, **94**, 313.
- [2] O. L. Malta, *J. Phys. Chem. Solids*, 1995, **56** (8), 1053.
- [3] T. R. Faulkner and F. S. Richardson, *Mol. Phys.*, 1978, **35**, 1141.
- [4] B. R. Judd, *Phys. Scr.*, 1980, **21**, 543.
- [5] M. Stavola, L. Isganitis and M. G. Sceats, *J. Chem. Phys.*, 1981, **74**, 4228.
- [6] J. Dexpert-Ghys and F. Auzel, *J. Chem. Phys.*, 1984, **80**, 4003.
- [7] G. Blasse, *Int. Rev. Phys. Chem.*, 1992, **11**, 71.
- [8] P. A. Tanner, V. V. Rabi Kanth Kumar, C. K. Jayasankar and M. F. Reid, *J. Alloys Comp.*, 1994, **215**, 349.
- [9] S. M. Crooks, M. F. Reid, P. A. Tanner and Y. Y. Zhao, *J. Alloys Comp.*, 1997, **250**, 297.
- [10] R. Acevedo, C. D. Flint, T. Meruane, G. Muñoz, M. Pasman and V. Poblete, *J. Mol. Struct. (Theochem)*, 1997, **390**, 109.
- [11] P. A. Tanner, R. Acevedo, T. Meruane and O. F. Hurtado, *J. Alloys Comp.*, 2001, **323–324**, 718.
- [12] R. Acevedo, T. Meruane, P. A. Tanner and Y. Y. Zaho, *Rev. Méx. Fís.*, 2001, **47** (3), 245.
- [13] R. Acevedo, M. Passman and G. Navarro, *Acta Phys. Polonica A*, 2001, **99** (2), 215.
- [14] R. Acevedo, T. Meruane and G. Navarro, *Acta Phys. Polonica A*, 2001, **99** (2), 233.
- [15] R. Acevedo, O. F. Hurtado, C. Portillo and W. Strek, *Acta Phys. Polonica A*, 2001, **100** (6), 829.
- [16] R. Acevedo and E. Cortes, *Theor. Chem. Acc.*, 2002, **107** (4), 187.
- [17] V. Poblete, R. Acevedo and P. A. Tanner, *Rev. Méx. Fís.*, 1998, **44 S1**, 29.
- [18] V. Poblete and R. Acevedo, *Rev. Méx. Fís.*, 1998, **44 S1**, 32.
- [19] G. Navarro, V. Martín, C. Pereda, M. Escudero and R. Acevedo, *Rev. Méx. Fís.*, 2002, submitted for publication.
- [20] H. M. Rietveld, *J. Appl. Cryst.*, 1969, 265.
- [21] D. R. Foster, F. S. Richardson and R. W. Schwartz, *J. Chem. Phys.*, 1985, **2**, 618.
- [22] P. A. Tanner, *Chem. Phys. Lett.*, 1989, **155** (1), 59.
- [23] P. A. Tanner and Yu-Long Liu, *J. Alloys Comp.*, 1994, **204**, 93.
- [24] B. R. Judd, *Phys. Rev.*, 1962, **127**, 150.
- [25] G. S. Ofelt, *J. Chem. Phys.*, 1962, **37**, 511.
- [26] J. P. Morley, T. R. Faulkner, F. S. Richardson and R. W. Schwartz, *J. Chem. Phys.*, 1982, **77**, 1734.
- [27] F. S. Richardson, M. F. Reid, J. J. Dallara and R. D. Smith, *J. Chem. Phys.*, 1985, **83**, 3813.
- [28] C. D. Flint and F. L. Stewart-Darling, *Mol. Phys.*, 1981, **44** (1), 61.
- [29] M. F. Reid and F. S. Richardson, *J. Chem. Phys.*, 1985, **83**, 3831.
- [30] A. K. Banerjee and R. W. Schwartz, *J. Chem. Phys.*, 1981, **58**, 255.
- [31] R. D. Smith, BSc. Thesis, University of Virginia, Charlottesville, 1982.
- [32] D. J. Newman, *Adv. Phys.*, 1971, **20**, 197.
- [33] H. D. Amberger, *Z. Anorg. Allg. Chem.*, 1980, **467**, 231.
- [34] L. C. Thompson, S. C. Kuo and H. D. Amberger, *Eur. J. Solid State Inorg. Chem.*, 1991, **28**, 187.
- [35] B. Nissen-Sobocinsko, W. Strek, J. Hanuza, K. Hermanowicz, G. Denisenko, S. Aleksandrov and V. N. Voronov, *J. Appl. Spectrosc.*, 1991, **62**, 94.
- [36] P. A. Tanner, *Mol. Phys.*, 1984, **53**, 813.

- [37] P. Selbert, C. Linger and B. Lütti, *Z. Phys. B Cond. Matter*, 1984, **55**, 19.
- [38] B. Nissen, W. Strek and C. D. Flint., Unpublished data, private communication, 2001.
- [39] R. Acevedo, G. Navarro, T. Meruane, P. A. Tanner and Y. Y. Zaho, *Rev. Méx. Fís.*, 2001, **47** (3), 245.
- [40] R. W. Schwartz, *Mol. Phys.*, 1975, **30**, 81.
- [41] O. A. Serra and L. C. Thompson, *Inorg. Chem.*, 1976, **15**, 504.
- [42] H. D. Amberger, *Spectrochim. Acta*, 1978, **34A**, 627.
- [43] H. D. Amberger, *Z. Phys. Chem. N.F.*, 1978, **102**, 279.
- [44] C. D. Flint and P. A. Tanner, *J. Chem. Soc. Faraday Trans. II*, 1978, **74**, 2210.
- [45] C. A. Morrison, R. P. Leavitt and D. E. Wortman, *J. Chem. Phys.*, 1981, **73**, 2530.
- [46] R. Acevedo, O. F. Hurtado, T. Meruane, G. Navarro, V. Díaz and J. Pozo, *Rev. Méx. Fís.*, 1998, **44**, 41.
- [47] J. P. Morley, T. R. Faulkner and F. S. Richardson, *J. Chem. Phys.*, 1982, **77**, 1710.

Jahn–Teller Effect in Laser Crystal LiCaAlF₆: Cr³⁺

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Abstract

In this chapter we have theoretically investigated the Jahn–Teller effect in the excited $^4T_{2g}$ states of the laser crystal LiCaAlF₆:Cr³⁺. The Cr³⁺ (3d³) ion has octahedral site symmetry in the host crystal and its low-lying energy levels are obtained in a static crystal field model. The fine structure of the $^4T_{2g}$ state due to spin–orbit interaction and mixing of ^2E_g , $^4T_{2g}$ and $^2T_{1g}$ have been calculated. The dynamical Jahn–Teller effect in a moderate crystal field and intermediate vibronic coupling have been considered to calculate the Ham reduction of total splitting of the $^4T_{2g}$ term. The linear spin–orbit and the linear vibronic coupling Hamiltonians are used. The results are compared with the experimental data.

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1. INTRODUCTION

Trivalent chromium ions have been inserted into a wide variety of host materials, and play a central role in the development of tunable solid-state lasers [1–3].

There are numerous advantages of using Cr³⁺ ions, as active centers in tunable laser materials, and as sensitizer in rare-earth-doped host materials, although each ion/host combination must be judged on a case-by-case basis. The special merit of Cr³⁺ impurity includes [2]:

- (1) the stability of trivalent state against both oxidation and reduction;
- (2) the presence of broad absorption bands and therefore efficient flash-lamp pumping;
- (3) the resistance of the $^4T_2$ state to nonradiative decay;

- (4) the tendency of Cr^{3+} impurities to preferentially dissolve in octahedral sites in the presence of other types of host sites.

The spectra of many crystals containing the Cr^{3+} ion consist of a set of sharp lines and a set of broad bands extending from infrared to well into ultraviolet. The broadband transitions take place between levels with the same total spin, while those giving rise to the sharp lines involve a change in the total spin. Thus, the spectra are divided into the sharp spin-forbidden doublet-to-quartet transitions and the broad spin-allowed quartet-to-quartet transitions. It turns out that the spin-orbit coupling in the Cr^{3+} ion is so small that it contributes only in a very minor way to the energy level. However, much more important is the mixing of levels with the same symmetry, especially in the doublet and quartets through the spin-orbit coupling parameter because this modifies the transition probabilities for the spin-forbidden lines. A good laser host material for Cr^{3+} ions is LiCaAlF_6 (denoted further LiCAF), named colquirite, after the Colquiri tin mine in Bolivia where it was discovered [4]. This transition metal vibronic laser was discovered by Payne *et al.* [5]. The Cr^{3+} impurity in LiCaAlF_6 substitutes the Al^{3+} cation and as a result is surrounded by six fluorines in a nearly octahedral arrangement. The $\text{LiCaAlF}_6:\text{Cr}^{3+}$ has several advantages such as: a better transmission in a large spectral domain, a higher cross-section, an easier growth of the crystal because of lower growth temperature, and more importantly a good slope efficiency as laser material. The experimental data of absorption and emission spectra [5,6] and excited state absorption (ESA) [7] provide information concerning spectroscopic properties of $\text{LiCAF}:\text{Cr}^{3+}$ crystals. Also, the experimental fine structure of zero phonon line and side-band vibrational structure have been obtained [8]. The ground-state absorption spectrum of $\text{LiCAF}:\text{Cr}^{3+}$ consists of two broadband transitions ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$, ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}^a$ and two sharp lines ${}^4\text{A}_{2g} \rightarrow {}^2\text{E}_g$, and ${}^4\text{A}_{2g} \rightarrow {}^2\text{T}_{2g}$ [5]. The emission spectra [5] are typical of the ${}^4\text{T}_{2g} \rightarrow {}^4\text{A}_{2g}$ transitions (U-bands). In this case, as in many cases of impurity centers formed by $3d^3$ ions, there is a strong interaction between the electrons of Cr^{3+} ions and the phonons of the host material LiCAF, which significantly affects the optical properties of $\text{LiCAF}:\text{Cr}^{3+}$. This means that it is necessary to investigate the host material vibrations and the energy levels of chromium ions in this host material. The aim of this paper is to study the phonons of LiCAF in the first Brillouin zone and to calculate the low-lying energy levels structure of Cr^{3+} due to the crystal field of the host material. The influence of the spin-orbit interaction and vibronic coupling between the energy levels of chromium ion and lattice phonons are taken into account. We have neglected the trigonal component of the octahedral crystal field and used the linear Hamiltonian for both spin-orbit and vibronic interactions. Comparison with experiments is discussed.

2. SYMMETRY AND VIBRATION OF LiCAF CRYSTAL

The LiCaAlF_6 salt crystallizes in the trigonal space group P_{31c} (D_{3d}^2) with lattice constants $a = 4.996 \text{ \AA}$ and $c = 9.636 \text{ \AA}$ [9]. All the metal cations of the crystal are

surrounded by six fluorines. The Li–F, Ca–F and Al–F distances are 2.01, 2.27 and 1.80 Å, respectively [9]. The Al³⁺ site is of the greatest concern since Cr³⁺ is found to substitute for this host ion. Thus the Cr³⁺ occupies an octahedral site surrounded by six fluorine ions and the *c* axis of the crystal corresponds to the trigonal axis of the CrF₆ octahedron. If the Cr³⁺ is situated in a perfect octahedron of fluorines, all the Cr–F distances would be equal and the F–Cr–F bond angles would be either 90 or 180°. While the Cr–F separations are all 1.80 Å, the bond angles differ slightly from the perfect octahedron requirements. By considering the positions of the six neighboring fluorines with respect to a *C*₃ axis of the octahedron, we find that the triangles of three fluorines above and below the Cr³⁺ ion are rotated relative to each other. As a result the F–Cr–F bond angle changes from 90 to 90.87°. This distortion has even parity (*t*_{2g} type) and may introduce a small trigonal field splitting in the ⁴*T* states. The second symmetry-lowering operation from a hypothetical perfect CrF₆ octahedron involves the destruction of the inversion center and therefore will induce oscillator strength into the d–d transitions. These symmetry operations can be described by the *t*_{2u} representation. This *t*_{2u} distortion is responsible for the polarization dependence of the absorption bands [8]. As a result of these symmetry-lowering operations, the site symmetry for Al is reduced from *O*_h to *D*₃.

In considering the vibronic side-bands to be expected in the optical spectra when we augment the static crystal field model by including the electron–phonon interaction, we must know the frequencies and symmetries of the lattice phonons at various critical points in the phonon density of states. We shall be particularly interested in those critical points which occur at the symmetry points Γ , A and at the Δ line in the Brillouin zone. Using the method of factor group for crystals we have:

$$(a) \Gamma_{\Gamma} = 4A_{1u} + 3A_{1g} + 5A_{2g} + 6A_{2u} + 8E_g + 10E_u$$

$$(b) \Gamma_A = 7A_1 + 11A_2 + 18E$$

$$(c) \Gamma_{\Delta} = 9A_1 + 9A_2 + 18E_u$$

From these normal vibrations, three of symmetry *A*_{2u} + *E*_u at the Γ point are acoustic vibrations and the others are optical vibrations.

3. LOW-LYING ENERGY LEVELS IN STATIC CRYSTAL FIELD MODEL

The ground-state absorption spectrum of the Cr³⁺ impurity incorporated in LiCAF crystals consists of two absorption bands occurring at 15 873 and 23 255 cm^{−1} due to ⁴*A*_{2g} → ⁴*T*_{2g} and ⁴*A*_{2g} → ⁴*T*_{1g} transitions, respectively, as well as two sharp features near 15 413 and 16 408 cm^{−1} which arise from ²*E*_g and ²*T*_{1g} excited states [5]. The emission spectra are typical for the ⁴*T*_{2g} → ⁴*A*_{2g} transition, with the peak situated near 13 200 cm^{−1} and the full-width half-maximum of about 2000 cm^{−1} [5].

The splitting of zero phonon line is 60 cm^{-1} and the side-band vibrational structures are (in cm^{-1}) [8]: $a_{1g} = 561$, $e_g = 452$, $t_{1u} = 308$ and $t_{2g} = 217$.

In order to explain these results we consider at present that the CrF_6^{3-} complex has a perfect octahedral symmetry, without spin–orbit and phonon interactions. A trigonal splitting of the levels by the distorted octahedral symmetry is neglected because the low-temperature ground-state absorption spectra do not show any signs for an appreciable splitting [8].

The energy levels of Cr^{3+} in octahedral symmetry are generally understood by referring to the standard Tanabe–Sugano diagram [10] in the strong field approach, neglecting spin–orbit and phonon coupling. The Tanabe–Sugano diagram for Cr^{3+} is plotted in Fig. 1. Within the strong field description, we may consider the 3d orbitals of Cr^{3+} as being split into two subshells: three t_2 orbitals lying 4Dq below the baricenter and two e orbitals 6Dq above. The ground state arises from the occupation of the t_2 orbitals at the maximum spin multiplicity and is therefore designated by ${}^4A_2(t_2^3)$. Three additional excited state quartets are derived from the t_2^2e and t_2e^2 configurations. They are ${}^4T_{2g}(t_2^2e)$, ${}^4T_{1g}(t_2^2e)$, and ${}^4T_{1g}(t_2e^2)$ states. The ${}^2E_g$, ${}^2T_{1g}$ and ${}^2T_{2g}$ excited states are derived from the same t_2^3 configuration like the ${}^4A_2$ ground state. Two spin-allowed absorptions, due to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions are observed as broad bands, while the ${}^4T_{2g}$ excited state is found to be metastable and to emit via the ${}^4T_{2g} \rightarrow {}^4A_{2g}$ transition.

Now, since the ${}^4A_{2g}$ ground state, as well as the ${}^2E_g$ and ${}^2T_{1g}$ states, has the t_2^3 strong-field electron configuration, all of these states are expected to have a similar equilibrium configuration of the crystal lattice and therefore the ${}^4A_{2g} \rightarrow {}^2E_g$ and ${}^4A_{2g} \rightarrow {}^2T_{1g}$ transitions are observed as narrow lines. Based on this understanding, we can simplistically argue that the ${}^4T_{2g}(t_2^2e) \rightarrow {}^4T_{1g}(t_2^2e)$ ESA transition should

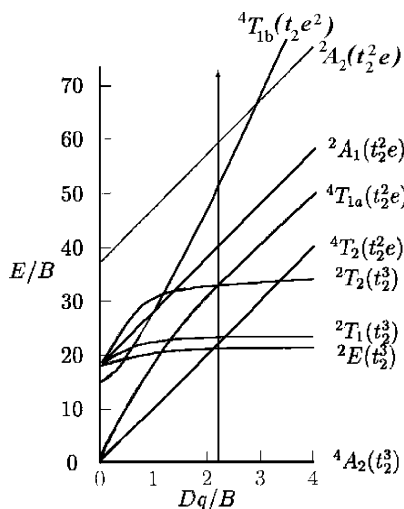


Fig. 1. Tanabe–Sugano diagram for octahedral Cr^{3+} .

be observed as a narrow line near 7600 cm⁻¹. From the Tanabe–Sugano diagram (Fig. 1) it can be found that the field parameter $Dq = 1590\text{ cm}^{-1}$, and Racah parameters $B = 740\text{ cm}^{-1}$, $C = 4.5B = 3330\text{ cm}^{-1}$ fit the experimental LiCAF:Cr³⁺ spectra. The vertical line in Fig. 1 indicates the energy levels obtained for $Dq/B = 2.15$. The low-lying energy levels of LiCAF:Cr³⁺ have been calculated using point charge model (PCM) and exchange charge model (ECM) [11]. For completion, we give that result in Table 1.

The rather good agreement with experimental data for ECM was obtained by taking into account the effect of overlap of central ion and ligand wave function, whereas the results obtained in PCM reveal the well-known weakness of this model.

Let us consider the influence of spin–orbit interaction of 3d³ electrons of Cr³⁺ ions in octahedral O_h symmetry in the CrF₆³⁻ complex, without phonon coupling and neglecting the trigonal component of the site symmetry field of Cr³⁺ ion. Matrices describing the electron–electron interaction, the crystal field interaction and the spin–orbit coupling for all the quartet and doublet states of 3d³ manifold, have been listed by Eisenstein [12]. In a cubic environment there are two single electron spin–orbit parameters, ξ and ξ' and we assume that they are equal [13]. Also, we consider the Racah parameters B and C to be isotropic. In order to obtain the level scheme for the crystal field terms of Cr³⁺ in LiCAF we have diagonalized the Eisenstein matrices with parameters $Dq = 1590\text{ cm}^{-1}$, $B = 740\text{ cm}^{-1}$, $C = 3330\text{ cm}^{-1}$ as in the previous section and $\xi = 218\text{ cm}^{-1}$ for the spin–orbit coupling parameter, which is the free-ion value [14] reduced by a factor of 0.80 as an effect of covalence. According to group theory the spin–orbit interaction splits the low-lying levels of Cr³⁺ in LiCAF as:

$$\begin{array}{lll} {}^4A_{2g} \rightarrow \Gamma_8 & {}^2E_g \rightarrow \Gamma_8 & {}^4T_{2g} \rightarrow \Gamma_6 + \Gamma_7 + \Gamma_8^a + \Gamma_8^b \\ {}^2T_{1g} \rightarrow \Gamma_6 + \Gamma_8 & {}^2T_{2g} \rightarrow \Gamma_7 + \Gamma_8 & {}^4T_{1g} \rightarrow \Gamma_6 + \Gamma_7 + \Gamma_8^a + \Gamma_8^b \end{array}$$

Concerning the ⁴T_{2g} a very important factor which affects its fine structure is the sequence of the three excited states: ²E_g, ²T_{1g} and ⁴T_{2g}. The ⁴T_{2g} quartet is lying *in between* the ²E_g doublet – first excited state – and the ²T_{1g} doublet. Since the electronic states ²E_g, ⁴T_{2g} and ²T_{1g} are close in energy, to obtain the fine structure of the ⁴T_{2g} state after the diagonalization of the Eisenstein’s matrices, we must take into account the admixture of different spinors Γ_i of these three states, following

Table 1. Low-lying energy levels of LiCAF:Cr³⁺ (cm⁻¹)

Level	PCM [11] (cm ⁻¹)	ECM [11] (cm ⁻¹)	Experimental [5] (cm ⁻¹)
⁴ T _{1g} (⁴ F)	23 095	23 129	23 255
² T _{1g} (² G)	16 541	16 483	16 408
⁴ T _{2g} (⁴ F)	15 899	15 878	15 873
² E _g (² G)	15 866	15 427	15 413
⁴ A _{2g} (⁴ F)	0	0	0

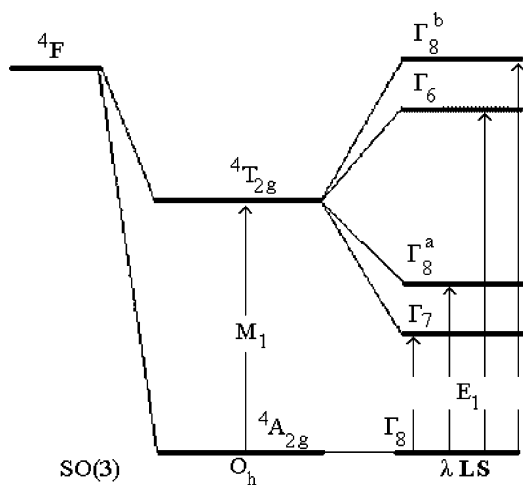


Fig. 2. Schematic fine-structure energy scheme for ${}^4T_{2g}$ state of Cr^{3+} in LiCAF. Selection rules for transitions are indicated.

Grinberg [15] and Tsukerblat *et al.* [16]. The fine structure for the crystal field term ${}^4T_{2g}$ of Cr^{3+} in LiCAF is shown schematically in Fig. 2.

The total spin–orbit splitting of the ${}^4T_{2g}$ zero phonon line has been calculated in the frame of Eisenstein’s matrices with full mixing of close-lying energy states ${}^2E_g$, ${}^4T_{2g}$ and ${}^2T_{1g}$ [17]. The obtained result, 431 cm^{-1} , is to be compared to the experimental value [8] of 60 cm^{-1} , which is indicative of quenching by the Ham effect. This effect reduces the total spin–orbit splitting of the ${}^4T_{2g}$ state. We thus drop the assumption that the lattice is rigid and consider the changes in the fine structure caused by coupling the d electrons to the lattice phonons.

4. JAHN–TELLER EFFECT IN THE ${}^4T_{2g}$ STATE

The calculation of the influence of Jahn–Teller coupling on the fine structure splitting of the ${}^4T_{2g}$ term is motivated by the fact that the measured splittings of the multiplet are larger than those predicted by the rigid lattice model. Absorption and emission spectra of the octahedrally coordinated Cr^{3+} ion in LiCAF can be illustrated by the well-known model of the adiabatic potential [16,17]. In the case of a moderate crystal field and intermediate vibronic coupling, the manifold of ${}^2E_g$ term remains lowest, closely followed in energy by the ${}^4T_{2g}$ and ${}^2T_{1g}$ manifolds and they become vibronically mixed due to the spin–orbit interaction. This means that the conditions of validity for the adiabatic approximation are broken, and we are dealing with a non-adiabatic spin-vibronic problem [16]. The Hamiltonian for Cr^{3+}

ion in the octahedral crystal field of LiCAF host material is:

$$H = H_{\text{FI}} + H_{\text{CF}} + H_{\text{S-O}} + H_{\text{JT}} \quad (1)$$

where H_{FI} represents the Hamiltonian of the free ion, H_{CF} , the Hamiltonian of the octahedral crystal field, $H_{\text{S-O}}$, the Hamiltonian of the spin–orbit and H_{JT} , the Jahn–Teller Hamiltonians.

We have followed a phenomenological approach and used the cluster model [18]. In this model the e_g -type distortion interacts more strongly with the electronic state of an octahedral coordinated Cr³⁺ ion than the distortions of t_{2g} symmetry. According to Ham [19], we assume that the continuum of vibrational modes with e_g character can be approximated by a single mode with an effective frequency ω , mass μ and coupling constant V . The collective coordinates of the e_g mode are conventionally known as Q_θ ($\sim x^2 - y^2$) and Q_ε ($\sim 3z^2 - r^2$). The linear Jahn–Teller Hamiltonian in equation (1) for the ${}^4T_{2g}$ state is [18]:

$$H_{\text{JT}} = \frac{1}{2\mu} \left[P_\theta^2 + P_\varepsilon^2 + \mu^2 \omega^2 (Q_\theta^2 + Q_\varepsilon^2) \right] - V \begin{bmatrix} -\frac{1}{2}Q_\theta + \frac{\sqrt{3}}{2}Q_\varepsilon & 0 & 0 \\ 0 & -\frac{1}{2}Q_\theta - \frac{\sqrt{3}}{2}Q_\varepsilon & 0 \\ 0 & 0 & Q_\theta \end{bmatrix} \quad (2)$$

Here P_α ($\alpha = \theta, \varepsilon$) is the momentum conjugate to Q_α . In the absence of spin–orbit interaction, the e_g vibration does not mix the orbital components of the ${}^4T_{2g}$ and we have vibrational potential energy surfaces consisting of three separate (‘disjoint’) paraboloids in the two-dimensional (2D) space of the Q_θ and Q_ε coordinates of the e_g vibration. The Jahn–Teller coupling leads only to a uniform shift ($-E_{\text{JIT}} = -V^2/2\mu\omega^2 \equiv -Sh\omega$) of all vibronic levels.

The Jahn–Teller interaction of an e_g lattice mode with the ${}^4T_{2g}$ level of chromium ion quenches the total spin–orbit splitting of this level. For the calculation of the splitting, we take the Jahn–Teller interaction parameter $\gamma = 1.920$ [20] and splitting of the ${}^4T_{2g}$ mode = 414 cm^{-1} (see Section 3). This yields 60 cm^{-1} for the total splitting of the ${}^4T_{2g}$ level, agreeing well with experimental data [8]. The adopted model will be useful to investigate the band shape of the luminescence of LiCAF and the ESA spectrum ${}^4T_{2g} \rightarrow {}^4T_{1g}$.

5. CONCLUSION

We have calculated the energy of low-lying levels of Cr³⁺ doped in LiCaAlF₆ crystal taking into account the vibrations of the complex CrF₆³⁻. The fine structure of ${}^4T_{2g}$ of Cr³⁺ ion has been obtained by diagonalization of the Eisenstein matrices and

by mixing of the ${}^2E_g$, ${}^4T_{2g}$ and ${}^2T_{1g}$ states. In the moderate crystal field and intermediate vibronic coupling between $3d^3$ electrons of chromium ion and lattice phonons, the vibronic interactions lead to quenching of the total spin–orbit splitting of the ${}^4T_{2g}$ level. This splitting is quenched by the Jahn–Teller interaction and is in good agreement with experimental data.

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REFERENCES

- [1] P. F. Multon, in *Laser Handbook* (eds M. Bass and M. L. Stich), North-Holland, Amsterdam, 1985, Vol. 5, p. 203.
- [2] J. A. Caird, in *Tunable Solid State Lasers II* (eds A. Budgon, L. Esterowitz and L. G. De Shazer), Springer, Berlin, 1986, p. 20.
- [3] N. P. Barnes, in *Tunable Lasers Handbook* (ed. F. J. Duarte), Academic Press, New York, 1995, p. 219.
- [4] M. Fleisher, G. Y. Chao and N. W. Francis, *Am. Miner.*, 1981, **66**, 878.
- [5] S. A. Payne, L. L. Chase, N. W. Newkirk, L. L. Smith and W. F. Krupke, *IEEE J. Quantum Electron.*, 1988, **24**, 2243.
- [6] S. A. Payne, S. L. Chase, L. K. Smith and B. H. T. Chai, *Opt. Quantum Electron.*, 1990, **22**, S259.
- [7] H. W. Lee, S. P. Payne and L. L. Chase, *Phys. Rev.*, 1988, **B39**, 8907.
- [8] S. A. Payne, L. L. Chase and G. D. Wilke, *J. Lumin.*, 1989, **44**, 167.
- [9] V. W. Viebahn, *Z. Anorg. Allg. Chem.*, 1971, **386**, 335.
- [10] Y. Tanabe and S. Sugano, *J. Phys. Soc. Jpn*, 1954, **9**, 766.
- [11] M. G. Brik, C. N. Avram and N. M. Avram, in OSA trends in optics and photonics (eds M. E. Fermann and L. R. Marshall), *Advanced Solid-State Lasers*, Optical Society of America, Washington, DC, 2002, Vol. 68, p. 275.
- [12] J. C. Eisenstein, *J. Chem. Phys.*, 1961, **34**, 1628.
- [13] S. Sugano, Y. Tanabe and H. Kamimura, *Transition-Metal Ions in Crystals*, Academic Press, New York, 1970.
- [14] J. S. Griffith, *The Theory of Transitional-Metal Ions*, Cambridge University Press, Cambridge, 1972.
- [15] M. Grinberg, *J. Lumin.*, 1993, **54**, 369.
- [16] B. S. Tsukerblat, A. V. Pallii, S. M. Ostrovsky, L. L. Kulyuk and S. N. Popov, *J. Phys. Condens. Matter*, 1997, **9**, 5295.
- [17] M. Yamaga, B. Henderson and K. P. O'Donnell, *Phys. Rev.*, 1992, **46**, 3273.
- [18] M. D. Sturge, in *Advanced in Solid State Physics* (eds F. Seitz, D. Turnbull and H. Ehrenreich), Academic Press, New York, 1967, p. 91.
- [19] F. S. Ham, *Phys. Rev.*, 1965, **6A**, 1727.
- [20] C. N. Avram and M. G. Brik, *J. Lumin.*, 2003, **102–103**, 81.

Electron Correlation and Jahn–Teller Effect in Alkali-Metal-Doped C₆₀

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Abstract

We investigate the role of the electron correlation and the Jahn–Teller effect in the electronic structure of alkali-metal-doped C₆₀, A_xC₆₀ where A is alkali metal. We show that the cooperation between the two effects in A₂C₆₀ and A₄C₆₀ results in the insulating ground states while the competition between the two effects in A₃C₆₀ results in the metallic ground state. We also show that the superconductivity in A₃C₆₀ is induced by the dynamic Jahn–Teller effect.

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1. INTRODUCTION

Since the discovery in 1985 [1], the C₆₀ molecule has been widely known as a molecule consisting of only carbon atoms with the shape of a soccer ball. The study on solid C₆₀ started after the establishment of a method for preparing a large quantity of the molecules [2]. Subsequently, superconductivity was observed in K₃C₆₀ with a critical temperature of 18 K [3]. So far, the critical temperature has been raised up to 33 K in RbCs₂C₆₀ [4]. In the last decade, not only the superconductivity but also

a variety of properties of alkali-metal-doped C_{60} , A_xC_{60} where A is alkali metal, have been investigated extensively [5,6].

As well as A_3C_{60} , A_2C_{60} and A_4C_{60} have been studied in detail and, as a result, it was found that A_2C_{60} and A_4C_{60} are nonmagnetic insulators. Figure 1 shows the results of the optical conductivity measurement [7]. It is clear that K_4C_{60} is an insulator because there is no Drude-like behavior, which is a characteristic feature of metals, while K_3C_{60} shows such a behavior in agreement with the fact that the material is a metal. Figure 2 shows the results of the photoemission experiment [8]. It is also clear that K_4C_{60} is an insulator because there is no Fermi edge while K_3C_{60} shows a clear one. Furthermore, the results of the μ SR study on K_4C_{60} [9] show that the minimum energy for the electronic excitation is about 0.3 eV; this gives the lower bound of the energy gap [10]. It is, however, possible that the actual energy gap of K_4C_{60} is much larger than this lower bound if the excitonic effect is significant.

The point to be noticed is that A_2C_{60} and A_4C_{60} are insulators although they are expected to be metals according to the rigid-band picture, as explained below. The lowest unoccupied molecular orbital of the C_{60} molecule is the t_{1u} orbital, which is 3-fold degenerate. As shown in Fig. 3, the t_{1u} orbitals form three conduction bands, the t_{1u} bands, in solid C_{60} . These bands can accommodate conduction electrons up to 6 per C_{60} molecule. It is thus expected that A_2C_{60} and A_4C_{60} are metals because the filling of the t_{1u} bands is incomplete in these materials. Nevertheless, the experimental results show that A_2C_{60} and A_4C_{60} are insulators. That is, it is impossible to explain the insulating nature of A_2C_{60} and A_4C_{60} by the

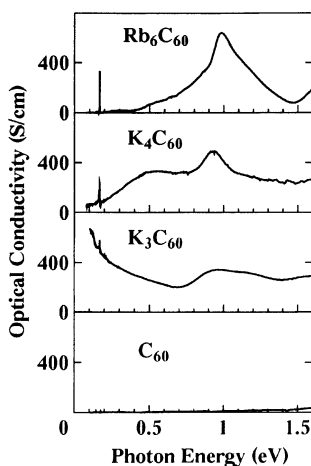


Fig. 1. Optical conductivity spectra of A_xC_{60} ($x = 0, 3, 4$, and 6) [7]. K_3C_{60} is a metal, which shows a Drude-like behavior at low energy region, while K_4C_{60} is an insulator, which does not show such a behavior.

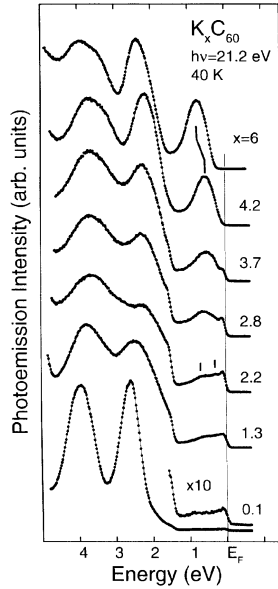


Fig. 2. Photoemission spectra of $K_x C_{60}$ [8]. $K_3 C_{60}$ ($x = 0.1, 1.3$, and 2.2) is a metal, which shows a clear Fermi edge. Also, there exists a small shoulder at 1.6 eV. On the other hand, $K_4 C_{60}$ ($x = 4.2$) is an insulator, which does not show a Fermi edge. The two phases coexist for $x = 2.8$ and 3.7 .

rigid-band picture, which is only based on the electronic transfer between the C_{60} molecules, T [11].

The following question then naturally occurs. Is $A_3 C_{60}$ a simple metal although the material is between the anomalous insulator phases, $A_2 C_{60}$ and $A_4 C_{60}$? It seems

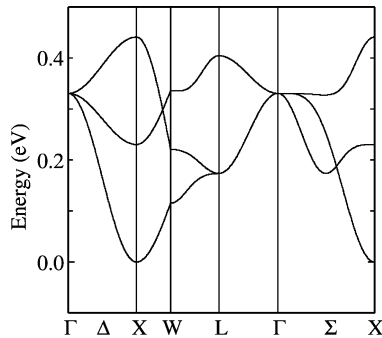


Fig. 3. t_{1u} Bands. The origin of energy is taken at the bottom of the bands. They consist of three conduction bands with a width of about 0.4 eV.

difficult to give a positive answer to this question. In fact, we can find several anomalous behaviors in A_3C_{60} as well. Although K_3C_{60} is a metal according to the photoemission spectrum shown in Fig. 2, the width of the spectrum is very broad, which is over 1 eV, in comparison to the width of the t_{1u} bands, which is about 0.4 eV. Furthermore, of great interest is a small shoulder at 1.6 eV in the spectrum. This shoulder is found only in K_3C_{60} but not in either K_4C_{60} or K_6C_{60} . It is thus important to elucidate the origin of this shoulder for obtaining useful information to understand the electronic properties of A_3C_{60} . One purpose of the present study is to give an explanation for the origin of this shoulder [12].

Recently, it has been found that a striking anomaly of A_3C_{60} is revealed by introducing the NH_3 molecule. This results in the disappearance of superconductivity and, at the same time, the material is transformed into an anti-ferromagnetic insulator. The details may be found elsewhere [13,14]. Furthermore, A_3C_{60} shows several unresolved anomalies related to the excited states. For example, although a mid-infrared absorption is observed in the optical conductivity spectrum of K_3C_{60} shown in Fig. 1, the origin of this absorption has not been elucidated yet. We thus find several anomalous behaviors not only in A_2C_{60} and A_4C_{60} but also in A_3C_{60} .

The key to understand the anomalous behaviors in A_xC_{60} is the electron–electron interaction, U , and the electron–phonon interaction, S . In A_xC_{60} , the important interaction as U is the Coulomb repulsion between the t_{1u} electrons. The importance of U has been pointed out based on the results of the photoemission experiments [15]. Also, in A_xC_{60} , the important interaction as S is the coupling of the t_{1u} electrons to the intramolecular phonons of the C_{60} molecule. The importance of S has also been pointed out based on the results of the Raman experiments [16]. Nevertheless, a complete understanding of the anomalous behaviors in A_xC_{60} has not been established yet. The reason is that the system with the orbital degree of freedom in which both U and S are important has not been known so far [17–20].

Furthermore, what is the mechanism of superconductivity in A_3C_{60} which has the orbital degree of freedom with both U and S being important? Originally, U and S were pointed out to be important in relation to the mechanism of superconductivity in A_3C_{60} . In the early 1990s, there was a point of view which claims that it is exotic superconductivity due to U [21] while there was another point of view which claims that it is usual superconductivity due to S [22]. Among such suggestions, there were two notable proposals; one is the proposal of the Moskalenko–Suhl–Kondo mechanism of the superconductivity in A_3C_{60} , which is important to multi-band superconductors [23–25], and the other is the proposal of the importance of the dynamic Jahn–Teller effect as the origin of the attractive interaction between the t_{1u} electrons [26,27]. A recent study has revealed a close relationship between the Moskalenko–Suhl–Kondo mechanism and the dynamic Jahn–Teller effect and showed that the orbital degree of freedom is indispensable to the superconductivity in A_3C_{60} [28].

The purpose of the present study is to show a unified picture for understanding the electronic properties of A_xC_{60} based on a simple model. In this model, both the electron–electron interaction U and the electron–phonon interaction S are taken

into account as well as the 3-fold t_{1u} bands described by the electronic transfer T . In particular, we discuss the dependence of the electronic properties on the valence, x , of the C₆₀ molecule. We show that the insulating nature of A₂C₆₀ and A₄C₆₀ is due to the cooperation between U and S while the metallic nature of A₃C₆₀ is due to the competition between U and S . Furthermore, it is shown that the superconductivity in A₃C₆₀ is induced by the dynamic Jahn–Teller effect when S overcomes U . Moreover, a close relationship between the dynamic Jahn–Teller mechanism and the Moskalenko–Suhl–Kondo mechanism, the stabilization mechanism of the superconductivity in multi-band superconductors, is pointed out. Finally, summary and open questions are given.

2. BASIS OF ELECTRONIC STRUCTURE

In this section, a model which gives the basis of the present study is introduced to investigate the electronic properties of A_{*x*}C₆₀ [17]. First, the one-electron part of the Hamiltonian, which describes the itinerant motion of the t_{1u} electrons in terms of the electron transfer T , is given. Next, the electron–electron interaction U and the electron–phonon interaction S are examined; U represents the Coulomb repulsion between the t_{1u} electrons and S represents the coupling of the t_{1u} electrons to the intramolecular phonons of the C₆₀ molecule. In particular, it is noteworthy that both U and S are almost the same or larger in magnitude than the width of the t_{1u} bands. Finally, the importance of the dynamical aspect of S is pointed out.

2.1. t_{1u} Bands

Most of the molecular orbitals and the intramolecular phonons of the C₆₀ molecule are highly degenerate, reflecting the high symmetry of the molecule, the icosahedral symmetry I_h . To study the electronic properties of A_{*x*}C₆₀, the 3-fold degeneracy of the t_{1u} orbital, which is the lowest unoccupied molecular orbital of the C₆₀ molecule, is important. It may be useful for visualizing the t_{1u} orbital to imagine the p atomic orbital because the basis functions of the t_{1u} orbital are transformed in the same way as those of the p atomic orbital; in the present study, three basis functions of the t_{1u} orbital are accordingly denoted by x , y , and z . Also, one of the two intramolecular phonons to which the t_{1u} electrons couple is called the H_g mode, as explained below in detail; the H_g mode is 5-fold degenerate. It may be useful for visualizing the H_g mode to imagine the molecular distortion similar to the d atomic orbital because the normal coordinates of the H_g mode are transformed in the same way as the basis functions of the d atomic orbital.

In the solid state, the C₆₀ molecules are crystallized into the fcc lattice and the conduction bands, the t_{1u} bands, are formed of the t_{1u} orbitals of the C₆₀ molecules. Saito and Oshiyama carried out the electronic structure calculations on solid C₆₀ and found that it is a semiconductor with a calculated band gap of 1.5 eV, preserving the molecular characteristics strongly [29]. Their results also show that the width of

the t_{1u} bands is about 0.4 eV and there are other unoccupied bands just above the t_{1u} bands apart by about 1 eV. Accordingly, the conduction electrons donated by alkali metal atoms occupy the t_{1u} bands and it is thus reasonable to consider only the t_{1u} bands for understanding the electronic properties of A_xC_{60} . It should, however, be stressed again that one cannot explain the reason why A_2C_{60} and A_4C_{60} are nonmagnetic insulators as long as we consider only these one-electron properties.

The Hamiltonian H_0 , which describes the itinerant motion of the t_{1u} electrons, is given by

$$H_0 = \sum_{m,n,a,b,\sigma} t_{ab}^{mn} a_{m\sigma}^\dagger b_{n\sigma} = \sum_{\alpha k \sigma} \xi_{\alpha k}^0 \alpha_{k\sigma}^\dagger \alpha_{k\sigma} \quad (1)$$

The three curves shown in Fig. 3 are the ones calculated by using this Hamiltonian. Here, t_{ab}^{mn} is the electronic transfer T between the t_{1u} orbital a of the m th C_{60} molecule and the t_{1u} orbital b of the n th C_{60} molecule, where a and b denote x , y , and z ; t_{ab}^{mn} is chosen so as to reproduce the result of the electronic structure calculations. We also use $a_{m\sigma}^\dagger$ ($a_{m\sigma}$) to denote the creation (annihilation) operator of the σ -spin electron in the t_{1u} orbital a of the m th C_{60} molecule. Furthermore, $\xi_{\alpha k}^0$ is the band energy of the t_{1u} electron of the band index α ($\alpha = 1, 2$, and 3) and the wavenumber k ; the band energies are obtained by diagonalizing the Hamiltonian H_0 and we use $\alpha_{k\sigma}^\dagger$ ($\alpha_{k\sigma}$) to denote the corresponding creation (annihilation) operators.

2.2. Electron correlation and Jahn–Teller effect

Here, we describe the electron–electron interaction U and the electron–phonon interaction S . These two interactions were pointed out to be important by many researchers soon after the discovery of the superconductivity in A_3C_{60} . The magnitude of each interaction was estimated theoretically by using the Hartree–Fock and density functional calculations and was also estimated experimentally by using the photoemission and Raman spectroscopy techniques. Although most of early studies focused on only one of the two interactions, it has been gradually revealed that both U and S are indispensable for understanding the electronic properties of A_xC_{60} as experimental results were accumulated.

We first examine U . The most important interaction as U is the Coulomb repulsion between two t_{1u} electrons on a C_{60} molecule. To estimate the order of magnitude of U , it may be useful to regard the C_{60} molecule as a sphere of a diameter D , which is about 7 Å. The lower bound of U can be obtained by considering the Coulomb repulsion between two electrons which move on the surface of the sphere always being at the opposite position to each other separated by the distance D . We then find the lower bound of U to be $e^2/\epsilon D \sim 0.4$ eV, where $\epsilon \sim 4\text{--}5$ is the dielectric constant of undoped solid C_{60} . On the other hand, the upper bound of U can be obtained by considering the Coulomb repulsion between

two electrons which move on the surface of the sphere independently. We then find the upper bound of U to be $2e^2/\epsilon D \sim 0.8$ eV. The actual U may be between these two values and it is likely to be about 0.6 eV. This value of U is larger than the width of the t_{1u} bands, which is about 0.4 eV, and thus the effect of U must be taken into account.

On the other hand, the exchange interaction, J_C , originated in the Coulomb repulsion between the t_{1u} electrons does not play an important role in understanding the electronic properties of A_xC₆₀. To show this, it is necessary to note that there are two kinds of repulsion as U to be precise; one is the intraorbital repulsion, U_{intra} , which represents the Coulomb repulsion between two t_{1u} electrons in an equal t_{1u} orbital and the other is the interorbital repulsion, U_{inter} , which represents the Coulomb repulsion between two t_{1u} electrons in different t_{1u} orbitals. It can be shown that the difference between U_{intra} and U_{inter} is one order of magnitude smaller than U_{intra} and U_{inter} themselves; the difference is about 10% of U . On the other hand, since the equation $U_{\text{intra}} = U_{\text{inter}} + 2J_C$ holds due to the symmetry of the t_{1u} orbital, J_C is found to be about 0.03 eV. Accordingly, the magnitude of Hund's coupling between the t_{1u} electrons is of this order and it is overcome by the Jahn–Teller effect due to S as shown in Section 3.

We next examine S . The most important interaction as S is the coupling of the t_{1u} electrons to the intramolecular phonons of the C₆₀ molecule. Among a number of intramolecular phonons, the modes which couple to the t_{1u} electrons are of two kinds, i.e., the A_g mode and the H_g mode. The former is the breathing mode, which is totally symmetric, and it affects only the center of energy of the t_{1u} levels. On the other hand, the latter is the Jahn–Teller mode and it can split the t_{1u} levels. The coupling constants of these modes can be estimated from the results of the calculations on the Jahn–Teller distortion of the C₆₀[−] molecule by Koga and Morokuma [30]. It is shown that the coupling constant of the A_g mode, S_{A_g} , and that of the H_g mode, S_{H_g} , are both about 0.4 eV. We thus find that the electron–phonon interaction S is almost the same in magnitude as the width of the t_{1u} bands. That is, it is also indispensable to take into account S for understanding the electronic properties of A_xC₆₀.

Furthermore, of great importance is the dynamic aspect, or the nonadiabatic effect, of S . Since the t_{1u} orbital consists of the π orbitals which are perpendicular to the surface of the C₆₀ molecule, the modes which significantly affect the distances between the carbon atoms are responsible for changing the π bonding considerably. The frequencies of such modes are, however, about 0.2 eV; this is too large to treat them by using the adiabatic approximation as usual. That is, it is appropriate to treat S in A_xC₆₀ by using the anti-adiabatic approximation instead of the adiabatic approximation. An important interaction then arises as follows; a pair of t_{1u} electrons occupying an equal t_{1u} orbital can be transferred into another t_{1u} orbital without breaking the pair. This is the pair-transfer interaction, which is largely affected by the nonadiabatic effect due to S . It is this interaction that induces the dynamic Jahn–Teller effect and, consequently, the superconductivity in A₃C₆₀ as shown in Section 4.

We give the Hamiltonian of the effective interaction between the t_{1u} electrons, which takes into account both U and S as follows:

$$H_{\text{int}} = \frac{1}{2} \sum_{\sigma, \tau} \sum_{m, a, b, c, d} V_{abcd} a_{m\sigma}^\dagger c_{m\tau}^\dagger d_{m\tau} b_{m\sigma} \quad (2)$$

Then the total Hamiltonian of the system is given by

$$H = H_0 + H_{\text{int}} \quad (3)$$

In equation (2), V_{abcd} are classified into the intraorbital repulsion V_{intra} , the interorbital repulsion V_{inter} , the exchange interaction J , and the pair-transfer interaction K as schematically shown in Fig. 4. These are defined by

$$V_{\text{intra}} \equiv U_{\text{intra}} - \frac{1}{2} S_{A_g} - \frac{1}{2} S_{H_g} \quad (4)$$

$$V_{\text{inter}} \equiv U_{\text{inter}} - \frac{1}{2} S_{A_g} + \frac{1}{4} S_{H_g} \quad (5)$$

$$J \equiv J_C - \frac{3}{8} S_{H_g} \quad (6)$$

and

$$K \equiv K_C - \frac{3}{8} S_{H_g} \quad (7)$$

In equation (7), K_C is the pair-transfer interaction originated in the Coulomb repulsion and its value is the same as J_C . Although J and K have the same value, it is noteworthy that these interactions represent different physical processes. Furthermore, it should be noted that the equation $V_{\text{intra}} = V_{\text{inter}} + 2K$ still holds due to the equation $U_{\text{intra}} = U_{\text{inter}} + 2J_C$. Consequently, the independent parameters of the effective interaction are two. In the present study, we employ V_{intra} and K as two independent parameters. It is found that V_{intra} is about 0.2 eV, V_{inter} is about 0.4 eV, and both J and K are about -0.1 eV owing to the estimation already given. Of great importance here is the

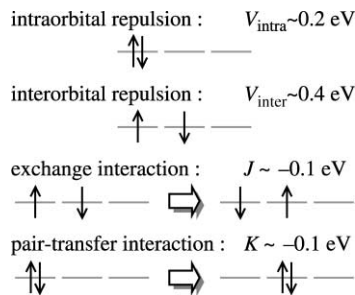


Fig. 4. Effective interaction between the t_{1u} electrons.

following two points; both V_{intra} and V_{inter} are positive due to the effect of U while both J and K are negative largely affected by the nonadiabatic effect due to S .

3. PHOTOEMISSION SPECTRUM

In this section, we study the characteristics of the ground states of A_xC_{60} by examining the photoemission spectra. In particular we focus on the reason why A_2C_{60} and A_4C_{60} are nonmagnetic insulators while A_3C_{60} is a metal. To study the photoemission spectra theoretically, we calculate the imaginary part of the one-particle Green function, or the spectral function, by using the effective interaction (2) [12] and employing the dynamical mean field theory [31]. The results given below are those for A_4C_{60} and A_4C_{60} and A_3C_{60} ; the electronic structure of A_2C_{60} can be obtained by exchanging electrons and holes in the electronic structure of A_4C_{60} .

3.1. A_4C_{60}

We show the results of the calculations on A_4C_{60} in Fig. 5. The spectral function of A_4C_{60} is shown in Fig. 5(a) and that of the isolated C_{60}^{4-} molecule is shown in Fig. 5(b); here, the latter is calculated analytically. The origin of energy is taken at the Fermi level. The spectral function of A_4C_{60} clearly shows that the material is an insulator. Furthermore, a detailed analysis has shown that the ground state of A_4C_{60} is nonmagnetic [12]. The energy gap is about 1 eV. It is reasonable to consider that the origin of this energy gap is the energy gap of about 1.5 eV which originally exists in the spectral function of the isolated C_{60}^{4-} molecule shown in Fig. 5(b) although the energy gap of A_4C_{60} is slightly smaller due to the electronic

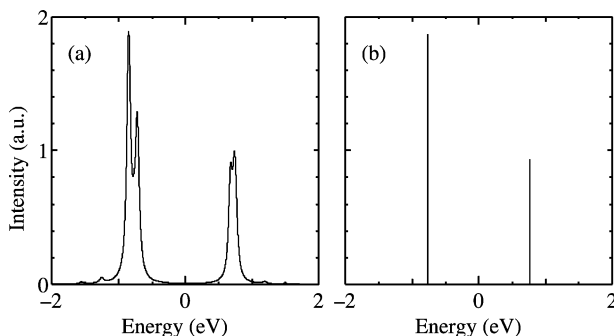


Fig. 5. Calculated spectral functions of A_4C_{60} . (a) The spectral function of A_4C_{60} and (b) that of the isolated C_{60}^{4-} molecule. The origin of energy is taken at the Fermi level. The result shows that A_4C_{60} is an insulator. The energy gap of A_4C_{60} is originated in the energy gap of the isolated C_{60}^{4-} molecule.

transfer T ; one can see the effect of T in Fig. 5(a) as the broadness of the peaks in the spectral function with a width of about 0.4 eV.

We now study the reason why A_4C_{60} is a nonmagnetic insulator. To this end, it is useful to consider the ground state of the isolated C_{60}^{4-} molecule as schematically shown in Fig. 6. We begin with the origin of the nonmagnetic nature of the ground state. In Fig. 6, 3-fold degenerate t_{1u} levels are split into 2-fold degenerate lower ones and a nondegenerate upper one; the former is occupied by four t_{1u} electrons while the latter is unoccupied. The situation illustrated in Fig. 6 is unusual in a sense that the spins of electrons in degenerate levels are usually aligned parallel to each other due to Hund's coupling. The reason why the ground state of A_4C_{60} is nonmagnetic is that the Jahn–Teller effect overcomes Hund's coupling in A_xC_{60} . In other words, the exchange interaction given by equation (6) is negative due to the coupling of the t_{1u} electrons to the H_g intramolecular phonons.

We next examine the origin of the energy gap. It should be noted that there is a large contribution to the energy gap not only of S but also of U as shown in Fig. 6; the latter contribution is exactly of the same kind as the origin of the energy gap in the Mott insulator. If we neglect the contribution of U , which is about 0.6 eV, the energy gap of A_4C_{60} is underestimated by 60% smaller than its actual value. It is thus indispensable to take into account both U and S for understanding the origin of the energy gap of A_4C_{60} . Emphasizing this aspect, A_4C_{60} is often called the Mott–Jahn–Teller insulator [18]. Consequently, by taking into account the effect due to T , the energy gap of A_4C_{60} is given by $U + S - T$.

It is also instructive to reproduce the above result from another point of view. To this end, consider two C_{60}^{4-} molecules far apart from each other as schematically shown in Fig. 7. To estimate the energy gap of A_4C_{60} , we calculate the energy necessary to transfer an electron from one molecule to the other [10]. In Fig. 7(a), which illustrates the situation before the transfer of an electron, the energy loss due to U is minimized because the charge distribution is uniform. At the same time, in this state, the energy gain due to S is maximized because there exists no unpaired electrons. On the other hand, in Fig. 7(b), which illustrates the situation after the transfer of an electron, the energy loss due to U is not minimized because the charge distribution is not uniform; the energy loss in Fig. 7(b) is larger by U than in Fig. 7(a). At the same time, in this state, the energy gain due to S is not maximized

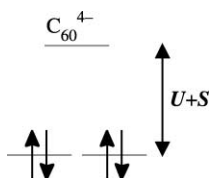


Fig. 6. Ground state of the C_{60}^{4-} molecule. The ground state is nonmagnetic because the Jahn–Teller effect overcomes Hund's coupling. There is a large contribution to the energy gap not only of S but also of U .

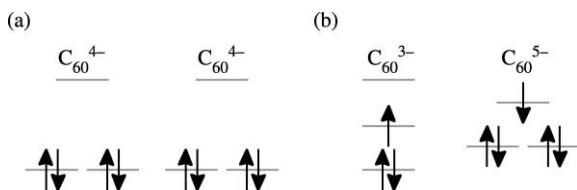


Fig. 7. Schematic diagram for (a) the uniformly charged state, $2C_{60}^{4-}$, and (b) the charge disproportionated state, $C_{60}^{3-} + C_{60}^{5-}$. The former is favorable to both U and S while the latter is not favorable to either U or S . As a result, the uniformly charged state is stabilized by the cooperation between U and S .

because there exists unpaired electrons; the energy gain in Fig. 7(b) is smaller by S than in Fig. 7(a). The energy necessary to transfer an electron from one molecule to the other is thus given by $U + S$. Taking into account the effect of T , we arrive at the same conclusion that the energy gap of A_4C_{60} is given by $U + S - T$.

We can summarize the characteristics of the ground state of A_4C_{60} as follows. The ground state is nonmagnetic because the Jahn–Teller effect overcomes Hund's coupling. The material is also an insulator because U and S cooperatively open the energy gap, which is given by $U + S - T$. Furthermore, the charge fluctuation is strongly suppressed due to the cooperation between U and S and consequently the ground state is properly described as an assembly of the C_{60}^{4-} molecules.

3.2. A_3C_{60}

We show the results of the calculations on A_3C_{60} in Fig. 8. The spectral function of A_3C_{60} is shown in Fig. 8(a) and that of the isolated C_{60}^{3-} molecule is shown in

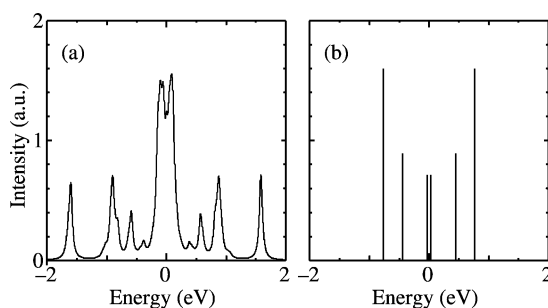


Fig. 8. Calculated spectral functions of A_3C_{60} . (a) The spectral function of A_3C_{60} and (b) that of the isolated C_{60}^{3-} molecule. The origin of energy is taken at the Fermi level. The result shows that A_3C_{60} is a metal. The continuous features spread over ± 1 eV around the Fermi level in the spectral function of A_3C_{60} are originated in the peaks shown in that of the isolated C_{60}^{3-} molecule. On the other hand, in the spectral function of the isolated C_{60}^{3-} molecule, there are no counterparts of the satellites at about ± 1.6 eV in the spectral function of A_3C_{60} .

Fig. 8(b); here, the latter is calculated analytically. The origin of energy is taken at the Fermi level. The spectral function of A_3C_{60} clearly shows that the material is a metal. The spectral function is considerably broad as shown in Fig. 8(a). Furthermore, the spectrum consists of two components; one is continuous features spread over ± 1 eV around the Fermi level and the other is the satellites at about ± 1.6 eV. Of great importance, when comparing two spectral functions given in Fig. 8(a) and (b), is the fact that there are no counterparts of the satellites in the spectral function of the isolated C_{60}^{3-} molecule although there exist original peaks corresponding to the continuous features. This is the key to understand the electronic structure of A_3C_{60} .

To find the reason why there exist the satellites in the spectral function of A_3C_{60} , it is first necessary to elucidate the reason why A_3C_{60} remains metallic despite that both U and S are significantly strong. To this end, consider two C_{60}^{3-} molecules far apart from each other as schematically shown in Fig. 9. In Fig. 9(a), which illustrates the situation before the transfer of an electron, the energy loss due to U is minimized because the charge distribution is uniform. However, in this state, the energy gain due to S is not maximized because there exists unpaired electrons. On the other hand, in Fig. 9(b), which illustrates the situation after the transfer of an electron, the energy loss due to U is not minimized because the charge distribution is not uniform; the energy loss in Fig. 9(b) is larger by U than in Fig. 9(a). However, in this state, the energy gain due to S is maximized because there are no unpaired electrons; the energy gain in Fig. 9(b) is larger by S than in Fig. 9(a). The energy necessary to transfer an electron from one molecule to the other is thus $U - S$, which is considerably small. As a result, the energy gap disappears in A_3C_{60} due to the effect of T and the material remains metallic.

Furthermore, the above consideration indicates that the charge fluctuation, $2C_{60}^{3-} \rightleftharpoons C_{60}^{2-} + C_{60}^{4-}$, occurs in A_3C_{60} . That is, these two states coexist in A_3C_{60} , resonating with each other, because the energy necessary for the transfer of an electron from the state shown in Fig. 9(a) to the state shown in Fig. 9(b) is considerably small. On the other hand, since the spectral function shown in Fig. 8(b) is that for the isolated C_{60}^{3-} molecule, the component originated in the charge disproportionate state, $C_{60}^{2-} + C_{60}^{4-}$, cannot be described only by considering a single

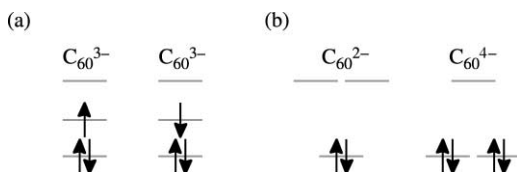


Fig. 9. Schematic diagram for (a) the uniformly charged state, $2C_{60}^{3-}$, and (b) the charge disproportionate state, $C_{60}^{2-} + C_{60}^{4-}$. The former is favorable to U while not favorable to S . On the contrary, the latter is favorable to S while not favorable to U . As a result, these two states coexist in A_3C_{60} due to the competition between U and S , resonating with each other.

isolated C₆₀^{3−} molecule. This is the reason why there are no counterparts of the satellites in Fig. 8(b). In other words, it is necessary to consider not only the uniformly charged state shown in Fig. 9(a) but also the charge disproportionate state shown in Fig. 9(b) as an initial state of the photoemission process.

We now explain that the origin of the satellites is the initial state C₆₀^{2−} + C₆₀^{4−}. The two initial states shown in Fig. 10(a) and (b) give rise to the two final states shown in Fig. 10(c) and (d). The important point is that the final state (d) can arise only from the initial state (b) although the final state (c) can arise from both the initial states (a) and (b). That is, the origin of the satellite is the process in which an electron is emitted from the C₆₀^{2−} molecule in the initial state (b) and the C₆₀[−] molecule is left in the final state (d). To understand this, we estimate the energy difference between the two final states; since the final state (c) gives rise to the emission at the Fermi level, the energy difference between (c) and (d) gives the position of the satellite relative to the Fermi level. First, the energy loss due to U in the final state (d) is larger by $2U$ than in the final state (c) because the charge imbalance is significant in the final state (d). Next, we can find by detailed calculations that the energy gain due to S in the final state (d) is smaller by S than in the final state (c). Consequently, the satellite appears at $2U + S$, which is about 1.6 eV, from the Fermi level.

The satellite obtained by our calculations most likely corresponds to the small shoulder at 1.6 eV observed in the photoemission spectrum of K₃C₆₀ shown in Fig. 2. In fact, the shoulder is observed only in K₃C₆₀ but not in either K₄C₆₀ or K₆C₆₀. Furthermore, this is also the case in the photoemission spectra of Rb_xC₆₀. These experimental results strongly suggest that the shoulder is intrinsic for A₃C₆₀. Finally, it is noteworthy that the continuous features around the Fermi level are originated in the excited states of the C₆₀^{2−} molecule in the final state (c) shown in Fig. 10; the details are found elsewhere [12].

We can summarize the characteristics of the ground state of A₃C₆₀ as follows. The reason why A₃C₆₀ remains metallic despite that both U and S are significantly strong is that the two interactions compete in this material. Furthermore, this competition

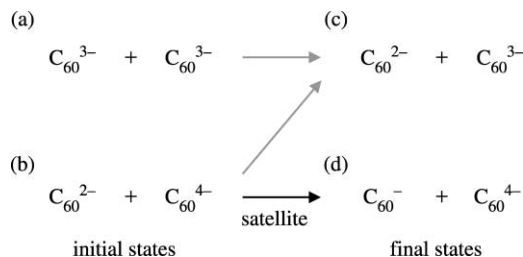


Fig. 10. Schematic diagram for the photoemission process in A₃C₆₀. The left part shows two initial states, i.e., (a) the uniformly charged state and (b) the charge disproportionate state, and the right part shows two final states, i.e., (c) the one, which results from both the initial states and (d) the one, which results only from the charge disproportionate initial state. The origin of the satellite is the process (b) → (d).

induces the charge fluctuation $2C_{60}^{3-} \rightleftharpoons C_{60}^{2-} + C_{60}^{4-}$. As a result, the charge disproportionate state $C_{60}^{2-} + C_{60}^{4-}$ gives rise to the satellite in the spectral function of A_3C_{60} . The shoulder observed in the photoemission spectrum of A_3C_{60} most likely corresponds to the satellite obtained in the present study.

4. SUPERCONDUCTIVITY

As explained in the previous section, charge fluctuation is enhanced in A_3C_{60} while suppressed in A_4C_{60} . This means that the interaction between the t_{1u} electrons can be attractive in the former while repulsive in the latter. Here, we investigate the superconductivity which occurs when the interaction between the t_{1u} electrons is attractive [28]. We first show that the attractive interaction is originated in the pair-transfer interaction which is negative due to the nonadiabatic effect of S . It is then shown that this can be interpreted as a manifestation of the dynamic Jahn–Teller effect. Next, after examining possible types of the order parameter of superconductivity, we construct the BCS theory for A_3C_{60} and study the characteristics of the superconductivity. In particular, we point out that the origin of the superconductivity is the dynamic Jahn–Teller effect when we consider it in the real space and, at the same time, the origin is the Moskaleiko–Suhi–Kondo mechanism when we consider it in the wavenumber space.

4.1. Dynamic Jahn–Teller effect

The dynamic Jahn–Teller effect describes the situation where the nuclei undergoes the tunneling motion between the equivalent distorted configurations of the molecule, resulting in the stabilization of the vibronic ground state of the coupled electron–phonon system. For the one-electron Jahn–Teller problem, the degeneracy of the vibronic ground state remains the same as that of the original electronic ground state. On the other hand, in the many-electron Jahn–Teller problem, the high degeneracy of the original electronic ground state is lifted by the dynamic Jahn–Teller effect, resulting in the multiplet terms. In particular, as shown below, a nondegenerate and totally symmetric vibronic ground state is realized for the C_{60}^{2-} and C_{60}^{4-} molecules produced by the charge fluctuation in A_3C_{60} ; this type of vibronic state may be referred to as the orbital-singlet state.

For simplicity, we examine the interaction between two t_{1u} electrons, comparing the energy difference between $2C_{60}^-$ and $C_{60} + C_{60}^{2-}$ in the vanishing T limit. First, there is no interaction energy due to H_{int} in $2C_{60}^-$ because the two t_{1u} electrons reside on different molecules apart from each other. On the other hand, there exists an interaction energy due to H_{int} in $C_{60} + C_{60}^{2-}$ because the two t_{1u} electrons reside in an equal molecule simultaneously. For example, if the two-electron state of the C_{60}^{2-} molecule is $|x \uparrow x \downarrow\rangle$, the interaction energy is

given by V_{intra} . Since this is positive, there is only repulsive interaction between the t_{1u} electrons as long as we consider such a state.

It is, however, important to notice that the state $|x \uparrow x \downarrow\rangle$ is not an eigenfunction of H_{int} . In fact, when applying H_{int} to $|x \uparrow x \downarrow\rangle$, there arise $|y \uparrow y \downarrow\rangle$ and $|z \uparrow z \downarrow\rangle$ due to the pair-transfer interaction K . The ground state of C_{60}^{2-} molecule is thus the most stable state among the linear combinations of these three states. This is given by

$$\frac{1}{\sqrt{3}}(|x \uparrow x \downarrow\rangle + |y \uparrow y \downarrow\rangle + |z \uparrow z \downarrow\rangle) \quad (8)$$

because the pair-transfer interaction K is negative. We refer to this type of state as the orbital-singlet state and this can be interpreted as a manifestation of the dynamic Jahn–Teller effect. The reason is that each of $|x \uparrow x \downarrow\rangle$, $|y \uparrow y \downarrow\rangle$, and $|z \uparrow z \downarrow\rangle$ is accompanied by the different Jahn–Teller distortion in the static case. The energy of the state (8) is given by $V_{\text{intra}} + 2K$ and this is lower than that of the state $|x \uparrow x \downarrow\rangle$ by $2|K|$. Thus, if we define

$$g \equiv -(V_{\text{intra}} + 2K) \quad (9)$$

$C_{60} + C_{60}^{2-}$ is more stable than $2C_{60}^-$ when $V_{\text{intra}} + 2K < 0$, i.e.,

$$g > 0 \quad (10)$$

This is the condition of the attractive interaction between the t_{1u} electrons originated in the dynamic Jahn–Teller effect and, for this condition to be satisfied, S must overcome U as we can see from equations (4) and (7).

Extending the above consideration to the actual superconductor A_3C_{60} , we can find the condition of the attractive interaction between the t_{1u} electrons by comparing the energy difference between $2C_{60}^{3-}$ and $C_{60}^{2-} + C_{60}^{4-}$. As a result, we obtain exactly the same condition $g > 0$ as the condition (10). In A_xC_{60} , since V_{intra} is about 0.2 eV and K is about -0.1 eV, the attractive interaction between the t_{1u} electrons can arise although it is rather subtle. Thus, in our model, the negative pair-transfer interaction K stabilizes the orbital-singlet state and, consequently, the attractive interaction between the t_{1u} electrons due to the dynamic Jahn–Teller effect arises when the pair-transfer interaction K dominates the intraorbital repulsion V_{intra} .

4.2. Order parameter

We now study the characteristics of the order parameter of the superconductivity induced by the attractive interaction between the t_{1u} electrons originated in the dynamic Jahn–Teller effect. To this end, we estimate the energy gain per C_{60} molecule due to the superconductivity by using a simple consideration of H_{int} . It is reasonable to expect that there can be three types of order parameter, i.e., those of the A_g , H_g , and T_{1g} symmetries, because $t_{1u} \times t_{1u}$ is reduced to the sum of these three representations. We examine the three possibilities below.

We first study the order parameter of the A_g symmetry. This type of order parameter, P_{A_g} , is given by

$$P_{A_g} \equiv \langle x_{\uparrow}^{\dagger} x_{\downarrow}^{\dagger} \rangle = \langle y_{\uparrow}^{\dagger} y_{\downarrow}^{\dagger} \rangle = \langle z_{\uparrow}^{\dagger} z_{\downarrow}^{\dagger} \rangle \quad (11)$$

This is of the spin-singlet type. In this case, the energy gain ΔE_{A_g} is given by

$$\Delta E_{A_g} = 3(V_{\text{intra}} + 2K)P_{A_g}^2 = -3gP_{A_g}^2 \quad (12)$$

The superconductivity of the A_g symmetry then gives rise to the energy gain when $g > 0$. This condition is exactly the same as the condition (10) and is possible to be satisfied in A_3C_{60} .

We next consider the cases of the order parameters of the H_g and T_{1g} symmetries. The order parameter of the H_g symmetry is, for example, given by

$$P_{H_g} \equiv \langle x_{\uparrow}^{\dagger} x_{\downarrow}^{\dagger} \rangle = \langle y_{\uparrow}^{\dagger} y_{\downarrow}^{\dagger} \rangle = -\frac{1}{2} \langle z_{\uparrow}^{\dagger} z_{\downarrow}^{\dagger} \rangle \quad (13)$$

This is also of the spin-singlet type as in the case of the A_g symmetry. The energy gain due to this type of superconductivity is then given by

$$\Delta E_{H_g} = 6(V_{\text{intra}} - K)P_{H_g}^2 \quad (14)$$

The superconductivity of the H_g symmetry thus can arise if $V_{\text{intra}} - K < 0$. It is, however, impossible for this condition to be satisfied in A_3C_{60} because V_{intra} is positive and K is negative. Also, the order parameter of the T_{1g} symmetry is, for example, given by

$$P_{T_{1g}} \equiv \langle x_{\uparrow}^{\dagger} y_{\uparrow}^{\dagger} \rangle \quad (15)$$

This is of the spin-triplet type. The energy gain due to this type of superconductivity is then given by

$$\Delta E_{T_{1g}} = (V_{\text{intra}} - 3K)P_{T_{1g}}^2 \quad (16)$$

The superconductivity of the T_{1g} symmetry thus can arise if $V_{\text{intra}} - 3K < 0$. It is, however, also impossible for this condition to be satisfied in A_3C_{60} .

4.3. BCS theory for A_3C_{60}

As expected from the above consideration, it is most likely that the order parameter of the superconductivity in A_3C_{60} is of the A_g symmetry and spin-singlet. We confirm this by constructing the BCS wavefunction of the A_g type, $|\Psi\rangle$, as follows:

$$|\Psi\rangle = \prod_{\alpha k} (u_{\alpha k} + v_{\alpha k} \alpha_{k\uparrow}^{\dagger} \alpha_{-k\downarrow}^{\dagger}) |0\rangle \quad (17)$$

Here, $u_{\alpha k}$ and $v_{\alpha k}$ satisfy the conditions

$$u_{\alpha Rk} = u_{\alpha k} \quad (18)$$

and

$$v_{\alpha Rk} = v_{\alpha k} \quad (19)$$

for $|\Psi\rangle$ to be of the A_g type, where R is any symmetry operation of the system. We next calculate the expectation value of H_{int} by using $|\Psi\rangle$. The expectation value consists of two parts; one is the contribution of the Hartree–Fock type and the other is the contribution of the BCS type. The Hartree–Fock contribution can be taken into account by replacing the bare one-electron energy $\xi_{\alpha k}^0$ with the Hartree–Fock one-electron energy $\xi_{\alpha k}$. The BCS contribution is given by

$$\langle \Psi | H_{\text{int}} | \Psi \rangle_{\text{BCS}} = \frac{1}{2} \sum_{\sigma} \sum_{\alpha k, \beta l} V_{\alpha\beta\alpha\beta}^{kl-k-l} \langle \Psi | \alpha_{k\sigma}^{\dagger} \alpha_{-k-\sigma}^{\dagger} | \Psi \rangle \langle \Psi | \beta_{-l-\sigma} \beta_{l\sigma} | \Psi \rangle \quad (20)$$

Here, $V_{\alpha\beta\alpha\beta}^{kl-k-l}$ is the coupling constant of the effective interaction expressed with the band index and the wave number. The results of the calculations show that the ground state energy is given by

$$\langle \Psi | H_0 + H_{\text{int}} | \Psi \rangle = 2 \sum_{\alpha k} \xi_{\alpha k} v_{\alpha k}^2 - 3NgP_{A_g}^2 \quad (21)$$

where

$$P_{A_g} = \frac{1}{3N} \sum_{\alpha k} u_{\alpha k} v_{\alpha k} \quad (22)$$

with N being the total number of the C₆₀ molecules in the system. Also, $g = -(V_{\text{intra}} + 2K)$ is exactly the same as the one defined by equation (9). By minimizing the expectation value (21), we obtain the gap equation and find that the condition of the occurrence of superconductivity is $g > 0$. This again reproduces the same result as the condition (10). The solution of the gap equation is finally given by

$$\Delta = gP_{A_g} \approx 2\hbar\omega_c \exp\left(-\frac{1}{gN_F}\right) \quad (23)$$

where $\hbar\omega_c$ is the cut-off energy and N_F is the density of states at the Fermi level per spin per orbital.

It is noteworthy that the BCS contribution (20) contains the energy gain due to the interband pair-transfer process of the Cooper pairs, which is a remarkable feature of multi-band superconductors, as well as the energy gain due to the usual intra-band pair-scattering process of the Cooper pairs. That is, the energy gain in a single-band superconductor is originated only in the pair-scattering process in the single band while the energy gain in a multi-band superconductor is originated not only in this process but also in the pair-transfer process between the different bands; this further stabilizes the superconductivity. This stabilization mechanism due to the interband pair-transfer process in multi-band superconductors is known as the Moskalenko–Suhl–Kondo mechanism [32–34].

It is thus reasonable to conclude that the mechanism of the superconductivity in A_3C_{60} is the dynamic Jahn–Teller effect when we consider it in the real space while it is the Moskaleiko–Suhl–Kondo mechanism when we consider it in the wave-number space, as schematically shown in Fig 11. That is, for A_3C_{60} the superconductivity induced by the dynamic Jahn–Teller effect is equivalent to that induced by the Moskaleiko–Suhl–Kondo mechanism. Soon after the discovery of the superconductivity in A_3C_{60} , Rice *et al.* [23], Asai and Kawaguchi [24], and Kristoffel and Örd [25] pointed out the importance of the Moskaleiko–Suhl–Kondo mechanism in the superconductivity of A_3C_{60} . This is a remarkable suggestion although, at that time, it was too early to understand a variety of behaviors of A_xC_{60} in a unified way.

Furthermore, the considerations given above indicate that the high symmetry in the vicinity of the C_{60} molecule is indispensable to the superconductivity in A_3C_{60} . Otherwise, it is most likely that the formation of the orbital-singlet state is suppressed because the pair-transfer interaction, which is the origin of the attractive interaction, cannot be used efficiently. This may be justified by considering the fact that the structure of most of superconducting A_3C_{60} is fcc and also the fact that the structure of Cs_3C_{60} , which is not a superconductor under usual conditions, is not fcc. Moreover, it is also likely that the disappearance of superconductivity and the appearance of anti-ferromagnetic state in $NH_3A_3C_{60}$ is a result of the reduction of the symmetry of the structure from fcc to a lower one.

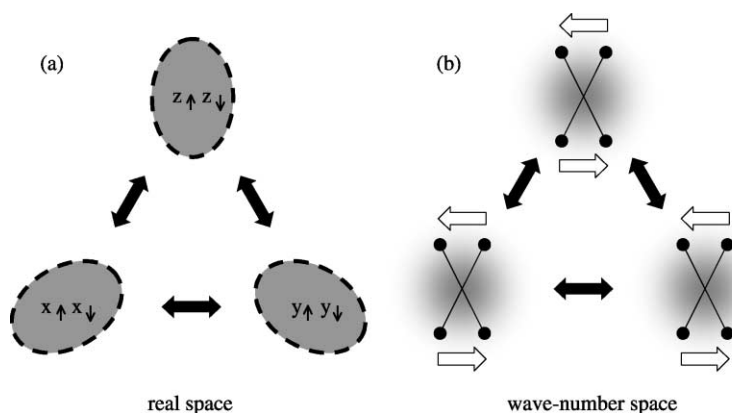


Fig. 11. Schematic diagram for (a) the dynamic Jahn–Teller effect and (b) the Moskaleiko–Suhl–Kondo mechanism. In the former, the distorted C_{60}^{2-} molecule undergoes the tunneling motion between three equivalent configurations. This results in the formation of the orbital-singlet state. In the latter, as shown by the black arrows, the Cooper pairs are transferred from one Fermi sphere to another, which is the pair-transfer process, a remarkable feature of multi-band superconductors, and stabilizes the superconductivity. Also, as shown by the white arrows, the Cooper pairs are scattered coherently within each Fermi sphere, which is the pair-scattering process in usual superconductors.

5. SUMMARY AND OPEN QUESTIONS

We have investigated the reason why A_2C_{60} and A_4C_{60} are nonmagnetic insulators while A_3C_{60} is a metal and even a superconductor. These are the behaviors revealed for the first time, which arise when both U and S are important in a system with the orbital degree of freedom. One of the important points is that the cooperation between U and S results in the insulating ground states of A_2C_{60} and A_4C_{60} while the competition between them results in the metallic ground state of A_3C_{60} although both U and S are significantly strong. Another important point is that the superconductivity in A_3C_{60} arises when S dominates U and the origin is the dynamic Jahn–Teller effect when we consider it in the real space while it is the Moskaleiko–Suhl–Kondo mechanism when we consider it in the wave-number space.

In the future study, it is necessary to resolve the following problems. First, there remains a question why A_3C_{60} is the only superconductor among A_xC_{60} [35]; that is, although there exists a fcc non-superconducting metal ABa_2C_{60} , which can be regarded as A_5C_{60} , the reason why this material is not a superconductor is not revealed yet [36]. Also, the study of $NH_3A_3C_{60}$ is important to the elucidation of the reason of the disappearance of superconductivity and the appearance of anti-ferromagnetic state in this material [13,14]. Furthermore, there remain other problems of the electronic properties of A_3C_{60} : the extremely high electrical resistivity of about $2\text{ m}\Omega\text{ cm}$ [37], which is retained even at low temperatures in the normal state, the mid-infrared absorption in the optical conductivity spectra [7], the extraordinary decrease of the nuclear relaxation time with increasing temperature [38], etc. The resolution of these problems will provide us with further understanding of the electronic properties of the materials with strong electron–electron and electron–phonon interactions.

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REFERENCES

- [1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.
- [2] W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354.
- [3] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, 1991, **350**, 600.
- [4] K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo and S. Kuroshima, *Nature*, 1991, **352**, 222.
- [5] H. Ehrenreich and F. Spaepen (eds), *Solid State Physics*, Academic Press, New York, 1994, Vol. 48.
- [6] O. Gunnarson, *Rev. Mod. Phys.*, 1997, **69**, 575.

- [7] Y. Iwasa and T. Kaneyasu, *Phys. Rev. B*, 1995, **51**, 3678.
- [8] P. J. Benning, F. Stepniak and J. H. Weaver, *Phys. Rev. B*, 1993, **48**, 9086.
- [9] R. F. Kiefl, T. L. Duty, J. W. Schneider, A. MacFarlane, K. Chow, J. W. Elzey, P. Mendels, G. D. Morris, J. H. Brewer, E. J. Ansaldo, C. Niedermayer, D. R. Noakes, C. E. Stronach, B. Hitti and J. E. Fischer, *Phys. Rev. Lett.*, 1992, **69**, 2005.
- [10] The energy gap in the photoemission spectrum is the minimum energy necessary to transfer an electron from one of two samples to the other.
- [11] It should be noted that it is also impossible to explain the insulating nature of A_4C_{60} even if one takes into account the bct structure of the material. See, for example, S. C. Erwin, in *Buckminsterfullerenes* (eds W. E. Billups and M. A. Ciufolini), VCH Publishers, New York, 1992.
- [12] T. Chida, S. Suzuki and K. Nakao, *J. Phys. Soc. Jpn*, 2002, **71**, 525.
- [13] H. Tou, Y. Maniwa, Y. Iwasa, H. Shimoda and T. Mitani, *Phys. Rev. B*, 2000, **62**, R775.
- [14] T. Takenobu, T. Muro, Y. Iwasa and T. Mitani, *Phys. Rev. Lett.*, 2000, **85**, 381.
- [15] See, for example, J. H. Weaver, *J. Phys. Chem. Solids*, 1992, **53**, 1433; R. W. Lof, M. A. van Veenendaal, B. Koopmans, H. T. Jonkman and G. A. Sawatzky, *Phys. Rev. Lett.*, 1992, **68**, 3924.
- [16] See, for example, S. J. Duclos, R. C. Haddon, S. Glarum, A. F. Hebard and K. B. Lynos, *Science*, 1991, **254**, 1625; P. Zhou, K.-A. Wang, A. M. Rao, P. C. Eklund, G. Dresselhaus and M. S. Dresselhaus, *Phys. Rev. B*, 1992, **45**, 10838.
- [17] S. Suzuki and K. Nakao, *Phys. Rev. B*, 1995, **52**, 14206.
- [18] M. Fabrizio and E. Tosatti, *Phys. Rev. B*, 1997, **55**, 13465.
- [19] L. F. Chibotaru, A. Ceulemans and S. P. Cojocaru, *Phys. Rev. B*, 1999, **59**, 12728.
- [20] J. E. Han, E. Koch and O. Gunnarsson, *Phys. Rev. Lett.*, 2000, **84**, 1276.
- [21] See, for example, S. Chakravarty, M. P. Gelfand and S. Kivelson, *Science*, 1991, **254**, 970.
- [22] See, for example, C. M. Varma, J. Zaanen and K. Raghavachari, *Science*, 1991, **254**, 989; M. Schlüter, M. Lannoo, M. Needels, G. A. Baraff and D. Tománek, *Phys. Rev. Lett.*, 1992, **68**, 526.
- [23] M. J. Rice, H. Y. Choi and Y. R. Wang, *Phys. Rev. B*, 1991, **44**, 10414.
- [24] Y. Asai and Y. Kawaguchi, *Phys. Rev. B*, 1992, **46**, 1265.
- [25] N. Kristoffel and T. Örd, *Fullerene Sci. Technol.*, 1994, **2**, 201.
- [26] K. Yabana and G. Bertsch, *Phys. Rev. B*, 1992, **46**, 14263.
- [27] A. Auerbach, N. Manini and E. Tosatti, *Phys. Rev. B*, 1994, **49**, 12998.
- [28] S. Suzuki, S. Okada and K. Nakao, *J. Phys. Soc. Jpn*, 2000, **69**, 2615.
- [29] S. Saito and A. Oshiyama, *Phys. Rev. Lett.*, 1991, **66**, 2637.
- [30] N. Koga and K. Morokuma, *Chem. Phys. Lett.*, 1992, **196**, 191.
- [31] A. Georges, G. Kotliar, W. Krauth and M. J. Rozenberg, *Rev. Mod. Phys.*, 1996, **68**, 13.
- [32] V. A. Moskalenko, *Fiz. Met. Metall.*, 1959, **8**, 503.
- [33] H. Suhl, B. T. Matthias and R. Walker, *Phys. Rev. Lett.*, 1959, **3**, 552.
- [34] J. Kondo, *Prog. Theor. Phys.*, 1963, **29**, 1.
- [35] M. Kosaka, K. Tanigaki and N. Fitch, *Phys. Rev. B*, 1999, **59**, R6628.
- [36] K.-F. Thier, C. Goze, M. Mehring, F. Rachdi, T. Yildirim and J. E. Fischer, *Phys. Rev. B*, 1999, **59**, 10536.
- [37] X.-D. Xiang, J. G. Hou, G. Briceño, W. A. Vareka, R. Mostovoy, A. Zettl, V. H. Crespi and M. L. Cohen, *Science*, 1992, **256**, 1190.
- [38] Y. Maniwa, N. Muroga, H. Tou, K. Kikuchi, S. Suzuki, Y. Achiba, M. Kosaka, K. Tanigaki, Y. Iwasa, H. Shimoda and T. Mitani, *Synth. Met.*, 1999, **103**, 2458.

Vibronic Renormalization of Superconductivity Gaps in a Two-Band Model of Cuprates

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Abstract

A two-band model of a cuprate superconductor is developed which incorporates a ‘defect’ band created by doping above the itinerant band. Interband transfer of intraband pairs leads to superconductivity. Vibronic interaction hybridizes these band components and opens a channel for phonon softening. This becomes maximal at the under/overdoped border, when band overlapping starts. One then observes a structural transition in the CuO_2 plane. Superconductivity gaps become vibronically renormalized. Consequently, at underdoping, the normal state displays two pseudogaps as recently observed. Entering the optimal doping region only a common pseudogap of vibronic origin survives.

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Already in the seminal paper of Bednorz and Müller [1], the guide to look for systems with a high superconductive transition temperature (T_c), has been the presence of strong electron–phonon interactions. Such interaction has been known to exist in a wide class of perovskite type oxides. The authors mention [1] the vibronic Jahn–Teller polaron effect [2] in this context. They also emphasize the fact that the Cu^{2+} -ion is a well-known Jahn–Teller system and this circumstance preserves significance in the physics of cuprate superconductors [3–7]. As a microscopic cause for ferroelectric ordering the interband vibronic hybridisation has been supposed [8–11] enlargening the view on perovskites as Jahn–Teller systems.

Cuprates show a rich variety of structural transformations on the bulk, the mesoscopic, and the local level [12]. Of special interest are the structural transformations in the playground of superconductivity within the CuO_2 planes. Hole doping leads to phase separation into charge-rich and charge-poor regions whereby a striped structure in the planes is formed [14–17]. The lattice responses with the transformation ($\text{LTO} \rightarrow \text{LTT}$), changing the Cu–O bond lengths [18] and tilting of the building octahedral blocks when the optimal composition border line is reached by doping [13].

Strong electronic correlations, which are also present in cuprates and operate in the phase separation process, determine the essentially nonrigid behaviour of the electron spectrum upon doping. Various investigations [19–27] lead to the conclusion that hole doping creates a new ‘defect-midgap’ distribution of states near the Fermi level above the itinerant valence band. Progressive doping leads these bands to merge. The participation of a ‘defect-polaronic’ subsystem besides the itinerant one is the essence of the cuprate superconductivity two-component scenario [3,28]. It will be tentative to ascribe the ‘defect’ band to the ‘defect’ subsystem and both electronic components correspondingly to the hole-rich and hole-poor regions formed at striped phase separation. This picture is essentially supported by the results of diverse investigations over a considerable time period leading to the acceptance [29] of the two-band behaviour of cuprate superconductors.

A nontraditional pairing mechanism must correspond to the two-component scenario. The presence of two bands near the Fermi level rises the question about the role of the interband pair-transfer interaction as the source of superconductivity. Corresponding two-band models [30,31] are known for a long time and have been applied to cuprates in quite different realizations. At the present time it becomes clear that such approaches must be built up on the electronic background evolving from doping. There are some examples of this kind [25,32–34]. So in Ref. [39], the minibands with the corresponding gaps due to the striping are used.

The approach [32] preceding the present communication has used a very simple model to account the creation and expansion of the defect band until the overlap with the itinerant band. Transfer of (intraband) pairs between these components yields the superconducting ordering with high- T_c values for plausible parameter values (for a general scheme see Ref. [35]). Regards this it is known that the optimally doped region corresponds to overlapping component bands with the chemical potential (μ) intersecting both of them. The model of Ref. [32] is able to describe some peculiarities in the behaviour of the superconductivity gaps and the natural presence of the pseudogap at underdoping. There the band components do not overlap and the pseudogap is defined as the minimal excitation energy of the itinerant band quasiparticle. Further speculations in explaining the changes in cuprate properties can be made on this basis in connection with the presence of a specific doping concentration (c_0) where the band components begin to overlap [32].

Coupling of different electronic states renormalizes the bands. The corresponding energy lowering allows the spontaneous symmetry breaking along the ‘mixing’ parameter with its complicated (restory) dynamics in finite systems. Regards the activity of lattice distortions one considers Jahn–Teller situations. Analogously, the dynamical hybridisation of the electronic components of the model [32] opens a channel for phonon softening. Hence, all superconductivity gaps became vibronically renormalized. Incorporation of this channel enlarges the ability of the model [32] in explaining the cuprate properties, especially of the pseudogap behaviour in the normal state. This will be the aim of the present communication. The analogy of the pseudogap behaviour with the vibronic gap renormalization has

been pointed out in Ref. [39] and there have been some theoretical attempts to exploit the vibronic interaction for the pseudogap formation [36,37].

Also the experimental indications on the essential role of the interband electron–phonon coupling, which follows from the investigation of phonon frequency anomalies at the onset of superconductivity must be mentioned [38].

The sole phonon softening in connection with the spectrum in Ref. [32] has been investigated in Ref. [40], see also Ref. [41]. The whole doping region has been followed up with the result that the phonon softening factor has its maximum at the critical concentration c_0 , which is smaller than the concentration corresponding to the T_c maximum. Experimentally, one observes the enhancement of the phonon softening when reaching the under/optimally doping border [42]. It is also here where the CuO_2 -plane structural transition is going on [13].

The linearized Hamiltonian describing the pairing *via* the interband scattering of intraband pairs and the vibronic interband mixing (coupling constant V) is written in the form

$$H = \sum_{\vec{k}\sigma} \varepsilon_a(\vec{k}) a_{\vec{k}\sigma}^+ a_{\vec{k}\sigma} + \sum_{\vec{k}\sigma} \varepsilon_b(\vec{k}) b_{\vec{k}\sigma}^+ b_{\vec{k}\sigma} + \Delta_a \sum_{\vec{k}} [a_{\vec{k}\uparrow} a_{-\vec{k}\downarrow} + a_{-\vec{k}\downarrow}^+ a_{\vec{k}\uparrow}^+] - \Delta_b \sum_{\vec{k}} [b_{\vec{k}\uparrow} b_{-\vec{k}\downarrow} + b_{-\vec{k}\downarrow}^+ b_{\vec{k}\uparrow}^+] + VQ \sum_{\vec{k}\sigma} [a_{\vec{k}\sigma}^+ b_{\vec{k}\sigma} + b_{\vec{k}\sigma}^+ a_{\vec{k}\sigma}] \quad (1)$$

Usual designations are used and positive gap parameters $\Delta_{a,b}$ are chosen, reading

$$\begin{aligned} \Delta_a(\vec{q}) &= 2 \sum_{\vec{k}} W(\vec{q}, \vec{k}) \langle b_{\vec{k}\uparrow} b_{-\vec{k}\downarrow} \rangle, \\ \Delta_b(\vec{q}) &= 2 \sum_{\vec{k}} W(\vec{q}, \vec{k}) \langle a_{-\vec{k}\downarrow} a_{\vec{k}\uparrow} \rangle \end{aligned} \quad (2)$$

These gaps close simultaneously at T_c . The quasiparticle energies, renormalized by the vibronic interaction corresponding to equation (1), read (the band energies $\varepsilon_{a,b}$ contain the chemical potential μ)

$$E_{\pm}^2(\vec{k}) = \frac{1}{2} \left\{ \varepsilon_{a\vec{k}}^2 + \Delta_a^2 + \varepsilon_{b\vec{k}}^2 + \Delta_b^2 + 2V^2 Q^2 \pm \sqrt{[(\varepsilon_{a\vec{k}}^2 + \Delta_a^2)^2 - (\varepsilon_{b\vec{k}}^2 + \Delta_b^2)^2] + 4V^2 Q^2 [(\varepsilon_{a\vec{k}}^2 + \varepsilon_{b\vec{k}}^2)(\Delta_a + \Delta_b)^2]} \right\} \quad (3)$$

The phonon coordinate Q describes the whole averaged active branch.

The underlying cuprate electron spectrum incorporates the itinerant valence band (b) covering energies from $-D$ to zero with the weight of $1 - c$. The doping-created band (a) distributes its width from d to $d - \alpha c$ with the weight c .

The doped hole concentration c must be scaled for a given case. Constant densities of states for the bands are $\rho_a = 1/\alpha$, $\rho_b = (1 - c)/D$. The bands start to overlap at $c_0 = d/\alpha$. For $\mu \geq 0$ it equals $d - \alpha c$ and for $\mu \leq 0$, $\mu = (d - \alpha c) \times [1 + (1 - c)\alpha D^{-1}]^{-1}$. For illustration the same parameter values as in Refs. [31,39]

with $|VQ_0| = 0.01$ eV will be used. Here Q_0 stands for the realized lattice distortion or its root-mean square fluctuation.

According to equation (3) all the superconductivity gaps become vibronically renormalized. Defining the (larger) pseudogap as the minimal excitation energy of the band b quasiparticle one has

$$\begin{aligned}\Delta_p &= \sqrt{(d - \alpha c)^2 + \tilde{\Delta}_b^2}, & \mu &\geq 0 \\ \Delta_p &= \tilde{\Delta}_b, & \mu &\leq 0\end{aligned}\quad (4)$$

with superconductivity gaps $\tilde{\Delta}_{a,b} = \Delta_{a,b}^2 + V^2 Q_0^2$. For the normal phase pseudogap

$$\begin{aligned}\Delta_p &= \sqrt{(d - \alpha c)^2 + V^2 Q_0^2}, & \mu &\geq 0 \\ \tilde{\Delta}_a &= |VQ_0|\end{aligned}\quad (5)$$

and

$$\Delta_p = \tilde{\Delta}_a = \tilde{\Delta}_b = |VQ_0|, \quad \mu \leq 0 \quad (6)$$

In this manner, the vibronic hybridisation guarantees the presence of a pseudogap in the whole doping region, as observed [21,42,44]. However, in the underdoped region there are two pseudogaps in the form of Δ_p and $|VQ_0|$. These gaps are of different nature and of different scales. The mainly electronic type Δ_p joins with $\tilde{\Delta}_a$ when entering the optimal doping region to a common pseudogap of vibronic origin. Two pseudogaps of different energy scales have been found in the tunnelling spectra of a Bi-based cuprate superconductor [45]. The behaviour of the gaps vs doping is illustrated for the superconducting state in Fig. 1 and for the normal state in Fig. 2.

In the tunnelling spectra of cuprates a characteristic peak–dip–hump complex appears [45–49]. The present model associates the peak with $\tilde{\Delta}_a$ and the hump with the Δ_p pseudogap. The hump broadens and is shifted to larger energies with diminishing underdoping. It remains persisted in the normal state at doping values where T_c becomes optimised. These effects are also in agreement with the observations.

The ratio Δ_p/kT_c is nearly constant in the optimal doping region and it increases rapidly with c diminishing from c_0 . It is possible to speculate on various further properties of cuprates on the basis of the present model. If one asks about the temperature dependence of the normal state gaps, one must incorporate the complicated calculation of $Q_0(T)$ [8] and account for the fluctuations of the superconductivity order parameter.

In summary the account of interband vibronic interactions in the doping-dependent electron spectrum of cuprates allows to explain the presence of two normal state pseudogaps at underdoping and the extent of the pseudogap behaviour to the whole doping region. Such results are far away from the basic Jahn–Teller effect framework and illustrate the brightness of the basic vibronic hybridization idea.

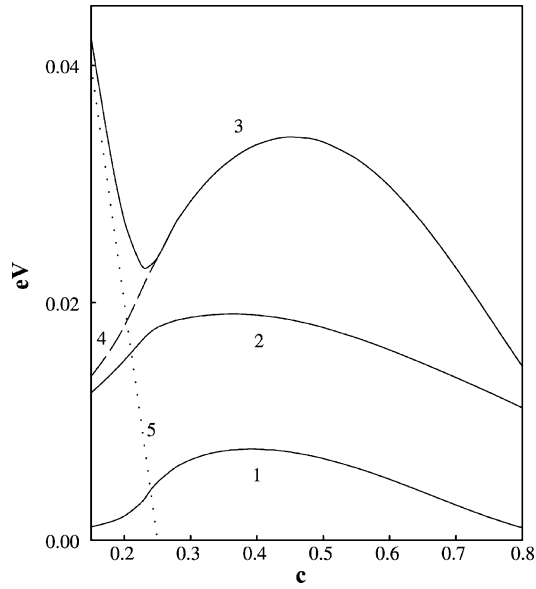


Fig. 1. The superconductivity characteristics vs. doping: 1 – T_c ; 2 – $\tilde{\Delta}_a$; 3 – Δ_p ; 4 – $\tilde{\Delta}_b$ and 5 – μ .

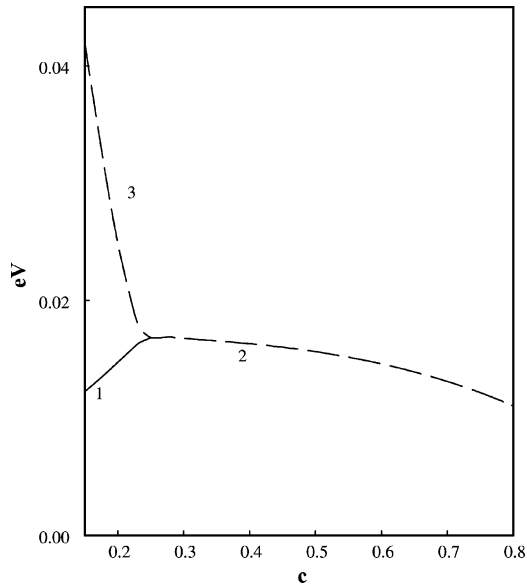


Fig. 2. Normal state pseudogaps vs. doping: (1-2) – $|VQ_0|$; 3 – $\sqrt{(d-\alpha c)^2 + V^2 Q_0^2}$.

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REFERENCES

- [1] J. G. Bednorz and K. A. Müller, *Rev. Mod. Phys.*, 1988, **60**, 585.
- [2] H. Höck, H. Nickisch and H. Thomas, *Helv. Phys. Acta*, 1983, **56**, 237.
- [3] K. A. Müller, *Physica C*, 2000, **341**, 11.
- [4] G. I. Bersuker and J. B. Goodenough, *Physica C*, 1997, **274**, 267.
- [5] A. S. Moskvina, *Physica B*, 1998, **252**, 186.
- [6] S. R. Markiewicz, *J. Phys. Chem. Sol.*, 1997, **58**, 1179.
- [7] V. V. Kabanov and D. Mihailovic, *Phys. Rev. B*, 2002, **65**, 212508.
- [8] N. Kristoffel and P. Konsin, *Phys. Stat. Sol. B*, 1988, **149**, 11.
- [9] I. B. Bersuker, *Ferroelectrics*, 1995, **164**, 75.
- [10] P. Konsin and N. Kristoffel, *Ferroelectrics*, 1999, **226**, 95.
- [11] I. B. Bersuker, *Chem. Rev.*, 2001, **101**, 1067.
- [12] Y. Bar-Yam and T. Egami, J. Mustre de Leon, A. R. Bishop (eds), *Lattice Effects in High- T_c Superconductors*, World Scientific, Singapore, 1992.
- [13] E. Kaldos, *et al.*, *Phys. Rev. Lett.*, 1997, **79**, 4899.
- [14] V. J. Emery and S. A. Kivelson, *Physica C*, 1993, **209**, 597.
- [15] A. Bianconi, *et al.*, *Phys. Rev. B*, 1996, **54**, 12018; A. Bianconi, *et al.*, *J. Phys.: Cond. Mat.*, 2000, **12**, 10655.
- [16] J. Tranquada, *J. Supercond.*, 1997, **9**, 397.
- [17] T. Egami, *J. Low. Temp. Phys.*, 1996, **105**, 791.
- [18] E. S. Bózin, *et al.*, *Phys. Rev. B*, 1999, **59**, 4445.
- [19] Y. Ando, *et al.*, *Phys. Rev. Lett.*, 2001, **87**, 017001.
- [20] A. M. Castro-Neto, *Phys. Rev. B*, 2001, **64**, 104509.
- [21] M. Moraghebi, *et al.*, *Phys. Rev. B*, 2001, **63**, 214513.
- [22] A. S. Alexandrov and P. P. Edwards, *Physica C*, 2000, **331**, 97.
- [23] M. G. Zacher, *et al.*, *Phys. Rev. B*, 2000, **85**, 2585.
- [24] P. A. Avramov and S. G. Ovchinnikov, *Fiz. Tverd. Tela*, 2000, **42**, 770.
- [25] D. DiCastro, *et al.*, *Eur. Phys. J. B*, 2000, **18**, 617.
- [26] P. Schwaller, *et al.*, *Eur. Phys. J. B*, 2000, **18**, 215.
- [27] A. Sherman and M. Schreiber, *Physica C*, 1998, **303**, 257.
- [28] A. Bianconi and N. Saini (eds), *Stripes Related Phenomena*, Kluwer Academic Publishers, New York, 2000.
- [29] A. Mourashkine, *Physica C*, 2000, **341–348**, 917.
- [30] H. Suhl, B. T. Matthias and L. R. Walker, *Phys. Rev. Lett.*, 1959, **3**, 552.
- [31] V. A. Moskalenko, *Fiz. Met. Mettaloved.*, 1959, **8**, 503.
- [32] N. Kristoffel and P. Rubin, *Physica C*, 2001, **356**, 141; N. Kristoffel and P. Rubin, *Solid State Commun.*, 2002, **122**, 265.
- [33] A. Perali, *et al.*, *Phys. Rev. B*, 2000, **62**, 9295.
- [34] A. Bussmann-Holder, *et al.*, *J. Phys. Cond. Mat.*, 2001, **13**, L169.
- [35] N. Kristoffel, P. Konsin and T. Örd, *Rivista Nuovo Cim.*, 1994, **17**, 1.
- [36] M. Sardar, *Physica C*, 1998, **298**, 254.
- [37] R. Szczesniak, M. Mierzejewski and J. Zielinski, *Physica C*, 2001, **355**, 126.
- [38] E. Ya. Sherman and C. Ambrosch-Draxl, *Phys. Rev. B*, 1993, **47**, 5390.
- [39] N. Kristoffel, *Ferroelectrics Lett.*, 1998, **24**, 33.
- [40] N. Kristoffel, *Physica C*, 2002, **377**, 264.

- [41] N. Kristoffel, *Phys. Stat. Sol. B*, 1998, **209**, 123.
- [42] C. Falter, M. Klenker and W. Ludwig, *Phys. Rev. B*, 1993, **47**, 5390.
- [43] J. Tallon and W. Loram, *Physica C*, 2001, **349**, 53.
- [44] K. Kitazawa, *Physica C*, 2000, **311**, 19.
- [45] R. M. Distasil, *et al.*, *J. Phys. Soc. Jpn*, 2002, **71**, 1535.
- [46] N. Miyakawa, *et al.*, *Phys. Rev. Lett.*, 1998, **80**, 157; N. Miyakawa, *et al.*, *Phys. Rev. Lett.*, 1999, **83**, 1018.
- [47] M. R. Norman, *et al.*, *Phys. Rev. Lett.*, 1997, **79**, 3506.
- [48] Ch. Renner, *et al.*, *Phys. Rev. Lett.*, 1998, **80**, 149.
- [49] V. M. Krasnov, *et al.*, *Phys. Rev. Lett.*, 2000, **84**, 5860.

Orbital Ordering and the Cooperative Jahn–Teller Effect in Single Crystals of the Magnetic Perovskite $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$

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Abstract

In the low-doped magnetic perovskite $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$, a strong coupling exists between crystal structure and magnetic and electronic properties. At room temperature, the material is in a paramagnetic-semiconducting state, showing a dynamic Jahn–Teller (DJT) ordering of the Mn^{3+} ions. Below $T_{\text{JT}} = 269$ K however, the crystal goes into a cooperative Jahn–Teller (CJT) state, exhibiting antiferrodistorsive orbital ordering of the MnO_6 octahedra. This leads to an increase in resistivity by a factor of 2 and to a drop of the paramagnetic susceptibility by about 20% [Physica B 155 (1989) 362; Phys. Rev. Lett. 71 (1993) 2331]. Around $T_{\text{C}} = 188$ K, a ferromagnetic transition occurs while the CJT effect becomes gradually weaker. Below T_{C} the sample is metallic-like and shows a considerable colossal negative magnetoresistance (CMR) effect. Finally, the material goes into a charge-ordered, insulating state below $T_{\text{CO}} = 147$ K where the CJT effect completely vanishes.

When crossing the phase boundary from the DJT to the CJT state, the resistivity shows a jump-like increase by a factor of roughly 2.15. This results from a frustration of the charge transport at the onset of orbital ordering. By assuming that each Mn^{4+} ion is surrounded only by Mn^{3+} nearest-neighbors and by taking into account only charge transport along the principal axes, the square-diagonals and the cube-diagonals, we are able to calculate a jump ratio of 2.26, corresponding well to the experimental value. The CJT transition also causes a sudden decrease in the magnetic moment, which has been studied by performing field-dependent SQUID measurements around T_{JT} . Since the crystal is in a paramagnetic state around T_{JT} , the magnetization M scales with the Brillouin function $\beta(J)$, where J is the spin of small ferromagnetic clusters. Fitting the magnetization data with the Brillouin function results in a CJT-induced shrinking of magnetic clusters from roughly four Mn ions to three Mn ions. These cluster sizes can also be understood in terms of the orbital structure of the material in both phases.

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1. INTRODUCTION

Since the discovery of colossal negative magnetoresistance (CMR) in manganese perovskites of the type $R_{1-x}D_x\text{MnO}_3$, with R a trivalent rare earth and D a divalent ion, interest in these materials has grown considerably [1]. The partial substitution of the rare earth by the divalent element introduces a mixing of Mn^{3+} and Mn^{4+} ions, responsible for the observed electronic and magnetic properties. The close relationship between ferromagnetic spin alignment and enhanced charge carrier mobility between neighboring Mn^{3+} and Mn^{4+} ions has been described in terms of the double-exchange model [2] and its recent extensions, taking into account the role of electron–phonon coupling [3]. A correct description of the CMR effect in the paramagnetic state of manganites is also given by a Mott-type hopping model, in which the effective barrier depends on the mutual spin orientation at the Mn hopping sites [4,5].

To fully understand all properties of manganites, the Jahn–Teller (JT) distortion of the $\text{Mn}^{3+}\text{O}_6^{2-}$ octahedra has to be taken into account. The JT-effect causes local deformations of the crystal structure in which some of the Mn–O bonds become longer while others become shorter. This breaks the local cubic symmetry and splits the degeneracy of the 3d- e_g levels of Mn^{3+} . The e_g electrons will then occupy the orbitals with the lowest energy. In LaMnO_3 , the JT-effect leads to a structural phase transition at $T_{JT} \approx 790$ K from a high-temperature cubic phase to a low-temperature orthorhombic phase [3]. This is the result from a static ordering of JT deformed MnO_6 octahedra below the so-called JT ordering temperature T_{JT} , which lowers the elastic energy of the material on a macroscopic length scale. This JT-ordered state is characterized by a coherent orientation of the elongated axes of the distorted octahedral throughout the whole material, and by a preferential occupation of the $d_{3z^2-r^2}$ orbitals with respect to the $d_{x^2-y^2}$ states [6]. This coherent, static JT distortion therefore leads to orbital ordering and is generally called cooperative JT (CJT) distortion [7]. In particular LaMnO_3 exhibits antiferrodistorsive orbital ordering which is shown schematically in Fig. 1 and has been verified experimentally by resonant X-ray scattering [6]. This type of orbital structure causes ferromagnetic correlations within the a_0b_0 -plane and antiferromagnetic superexchange along the c_0 -axis [8]. In LaMnO_3 , these interactions are weak and lead to A-type

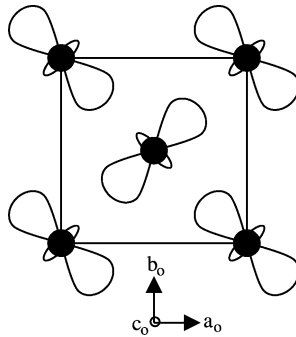


Fig. 1. Schematic view of the antiferrodistorsive orbital ordering of the $3z^2 - r^2$ orbitals in the a_0b_0 -plane of LaMnO_3 , taken from Ref. [6]. The orbital ordering along the c_0 -axis repeats the same pattern. The index ‘o’ of the lattice parameters refers to the orthorhombic unit cell of LaMnO_3 . The orbitals in this figure and in the subsequent figures of this article are not drawn on scale with respect to the lattice parameters.

antiferromagnetism below $T_N = 140$ K. Above the JT-transition temperature, the orbital ordering disappears due to the onset of a dynamic, mixed occupation of the e_g orbitals which become oriented randomly along the main crystalline axes. The JT distortion at these high temperatures is therefore called dynamic JT (DJT) distortion.

On doping LaMnO_3 by a small amount of Sr, JT-inactive Mn^{4+} ions are introduced into the material. This creates a ferromagnetic double exchange interaction and leads to a lowering of T_{JT} . However, the antiferrodistorsive orbital ordering of the e_g levels is preserved in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for $x \leq 0.15$ [3]. The investigated compound $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ (LSMO) in particular has a CJT transition temperature of $T_{JT} = 269$ K, and is a ferromagnetic insulator at low temperatures [9]. Because of its commensurate carrier concentration $x = 1/8$, LSMO also shows charge ordering (CO) at temperatures below $T_{CO} \approx 150$ K, which is confirmed by high-energy X-ray diffraction [10]. At T_{CO} a second structural phase transition to a pseudocubic low-temperature phase takes place. These structural transitions and the fact that the JT transition temperature is reduced to a value below 300 K make LSMO an ideal material to study the strong coupling in manganites between crystal structure, electronic transport, and magnetism.

The main objective of this article is to investigate the relationship between the transport properties of a $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ single crystal ($x = 1/8$) and its orbital configuration around the JT transition temperature. The difference between a random configuration and an ordered arrangement of the electron orbitals should have a significant impact on the charge transfer and the magnetic interactions on a macroscopic scale.

2. EXPERIMENTAL

Single crystals of $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ were prepared from sintered, polycrystalline rods by the floating zone method, with the growth direction approximately along the b -axis [11]. A structural characterization of the sample has revealed that some microtwinning exists in the crystal [12]. The crystal is cut into a rectangular shape with dimensions $1 \times 2 \times 3 \text{ mm}^3$. Resistivity measurements on the crystal are carried out in a conventional four-point geometry, achieved by evaporating four gold contacts onto the $2 \times 3 \text{ mm}^2$ top side and annealing them in air during 60 min at 600°C . The measuring current was flowing in the Lorentz-force free configuration parallel to the applied magnetic field. Due to the pseudocubic structure of the material, the orientation of magnetic fields during the resistivity measurements is of no consequence. The magnetoresistivity measurements were performed in a temperature range between 1.5 and 300 K in a cryostat equipped with a superconducting magnet coil generating fields up to 12 T while the magnetization was measured in a quantum design SQUID magnetometer in fields up to 5 T.

3. STRUCTURE AND TRANSPORT PROPERTIES OF LSMO

To illustrate the correlation between the structure and the resistive/magnetic properties of the LSMO crystal, the temperature dependence of the lattice constants¹ in zero-field (Fig. 2(a)) is shown together with the zero-field resistivity (Fig. 2(b)) and the magnetic moment of the sample in a field of 10 mT (Fig. 2(c)). The structural data of the crystal are measured by means of X-ray diffraction by Niemöller *et al.* [12], and correspond to the data obtained for powder samples by neutron diffraction [9]. At room temperature the structure is pseudocubic with a slight orthorhombic distortion, which means that the CJT effect is absent on a macroscopic scale. Below $T_{\text{JT}} = 269 \text{ K}$ however, the orthorhombic distortion becomes much stronger, indicating a transition to a CJT state. The a_o and b_o axes are hereby expanded while the c_o -axis is compressed. The expansion of a_o is much less pronounced than that of b_o which is somewhat uncommon. This might be related to additional lattice distortions induced by the Sr-doping. Simultaneously with the structural transition, an upward jump in the zero-field resistivity and a sudden decrease in the magnetic moment are also observed.

From the magnetic moment measurements shown in Fig. 2(c), a Curie temperature of $T_C = 188 \text{ K}$ can be derived by linear extrapolation of the inverse magnetic moment to zero. At temperatures slightly below T_C , the magnetic moment stays constant at about 3/4 of its low-temperature value, and the resistivity becomes metallic-like. Moreover, the CJT effect starts to decrease around T_C . As expected for this compound CO sets in at temperatures below $T_{\text{CO}} = 147 \text{ K}$. This leads to

¹ The slight orthorhombic distortion of LSMO which is present even above T_{JT} , leads to an orthorhombic unit cell with expanded lattice parameters $a_o = \sqrt{2}a$, $b_o = \sqrt{2}b$, and $c_o = 2c$. Here a , b , and c denote the lattice constants of the (pseudo) cubic unit cell.

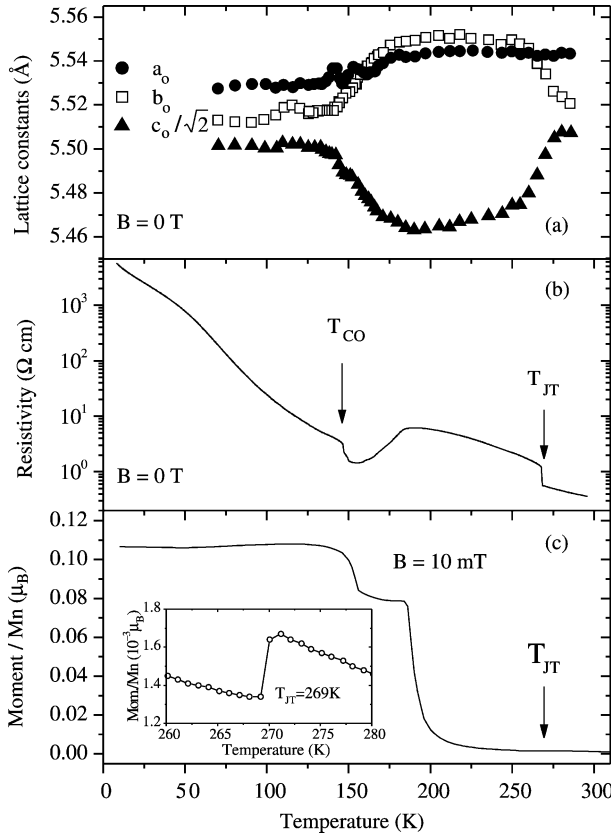


Fig. 2. Temperature dependence of (a) the lattice constants of a $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ single crystal (figure taken from Ref. [10]), (b) the resistivity, and (c) the low-field magnetic moment. The cooperative JT transition at $T_{\text{JT}} = 269$ K results in a doubling of the resistivity and a sharp drop of the magnetic moment (see inset in (c)). Below the temperature $T_{\text{CO}} = 147$ K the crystal goes into a charge-ordered state and the CJT effect vanishes.

a second structural transition and to a reentrant behavior of the lattice parameters, which at low temperature obtain back their room temperature values. Simultaneously with this structural transition, the resistivity becomes insulating while the magnetic moment shows a sudden increase to a constant low-temperature value. The two structural transitions together with the magnetic transition allow us to distinguish four distinct temperature regimes in LSMO. These different regimes will be discussed in more detail below.

(i) At room temperature the system is in a paramagnetic, semiconducting state. The JT distortion cannot be observed in the structural data and is therefore of the disordered or dynamic type (DJT). This is schematically illustrated in Fig. 3, where

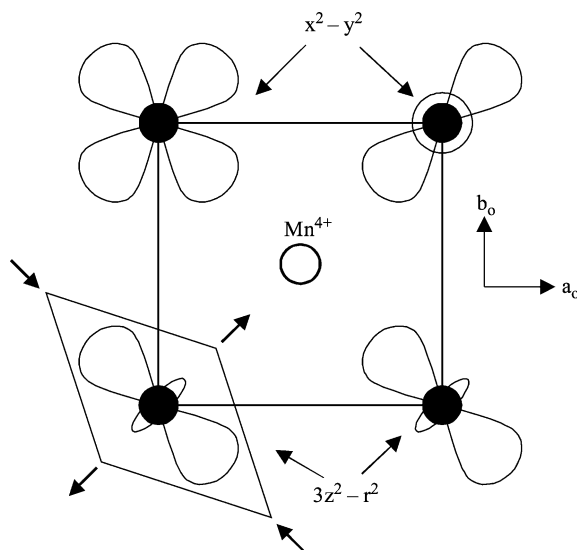


Fig. 3. Schematic view of a possible momentary orbital configuration in the dynamic Jahn–Teller state. The $x^2 - y^2$ and the $3z^2 - r^2$ orbitals are randomly occupied and a phonon mode exists, indicated by the arrows at the left $3z^2 - r^2$ orbital, which causes an oscillation between the two orbital types.

the e_g electrons of Mn^{3+} occupy the $x^2 - y^2$ as well as the $3z^2 - r^2$ orbitals, oriented along random axes.² Furthermore, there is a breathing-type phonon mode which allows for an oscillation between these two orbitals at a given Mn^{3+} site.

(ii) At $T_{JT} = 269$ K, the crystal goes into a CJT state, exhibiting antiferrodistorsive orbital ordering as experimentally verified by neutron diffraction [9]. This means that the e_g electrons will predominantly occupy the $3z^2 - r^2$ orbitals, which become ordered in the same way as shown in Fig. 1. Although Mn^{4+} ions do not have occupied e_g levels, their presence in LSMO does not disrupt the antiferrodistorsive orbital structure. The orbital ordering at T_{JT} is a first-order phase transition, as indicated by specific heat measurements [10], which will be confirmed later on by our field-dependent resistivity and magnetic moment measurements. The transition is accompanied by a sudden increase of the resistivity by roughly a factor of 2, and by an instantaneous drop of the paramagnetic susceptibility by 20%. These two interrelated effects will be discussed on grounds of the orbital structure in the following sections. Similar effects (enhancement of the resistivity and drop of the magnetic moment due to a structural transition) have also been observed in the paramagnetic phase of

² The (x, y, z) coordinates which are used in this chapter actually form a different local coordinate system for each Mn site, in such a way that the occupied orbitals can always be expressed as either $x^2 - y^2$ or $3z^2 - r^2$ instead of, for instance, $3x^2 - r^2$.

$\text{La}_{0.83}\text{Sr}_{0.17}\text{MnO}_3$ [13] and in the ferromagnetic phase of $\text{La}_{0.825}\text{Sr}_{0.175}\text{Mn}_{0.94}\text{Mg}_{0.06}\text{O}_3$ [14].

(iii) Below T_{JT} the resistivity stays semiconducting down to around 185 K. At this temperature, the magnetic moment increases rapidly and the sample enters a metallic-like state ($d\rho/dB > 0$) due to the double exchange interaction. From the extrapolation of the inverse magnetic moment to zero, we find a ferromagnetic Curie temperature $T_{\text{C}} = 188$ K. Around T_{C} the colossal negative magnetoresistivity $(\rho(0) - \rho(B))/\rho(0)$ reaches a maximum value of about 94% in a field of 12 T. The CJT effect and presumably also the antiferrodistorsive orbital ordering start to gradually become weaker below T_{C} and disappear around 150 K. This is reflected in the lattice constants, which obtain their original room temperature values. We note that the magnetic moment of the single crystal deviates from that of an ideal ferromagnet because the absolute value between 150 and 188 K stabilizes at 3/4 of the low-temperature value, even in high magnetic fields. This possibly reflects the presence of a competition between ferromagnetism induced by the small amount of Mn^{4+} , and the antiferrodistorsive ordering favoring antiferromagnetism. This competition might result in a phase separation of both ferromagnetic and antiferromagnetic areas, a phenomenon observed in a wide variety of manganite compounds [15].

(iv) At $T_{\text{CO}} = 147$ K, a first-order transition to a charge-ordered state or so-called Wigner-crystal appears. The presence of charge-order is indicated by the insulating character of the resistivity at temperatures below 150 K (see also the sudden jump-like increase in the resistivity at T_{CO} in Fig. 2(b) and the simultaneous occurrence of superstructure reflections in high-energy X-ray diffraction measurements [12]. The positions of these reflections in reciprocal space point to a charge-ordered state consisting of alternated hole-free layers and layers in which 25% of the Mn sites contain a hole [16]. The transition is accompanied by a sudden jump in the magnetic moment to the saturation value and by the vanishing of the macroscopically observed CJT distortion. In contrast to the negative CMR effect observed close to T_{C} , a *positive* magnetoresistance is observed in the temperature regime just above T_{CO} [10]. This is caused by the fact that below T_{CO} the resistivity becomes insulating, and because the transition itself shifts to higher temperatures with increasing field. At very low temperatures and at high magnetic fields in the order of 5 T, a magnetic moment per Mn ion of $3.75\mu_{\text{B}}$ is observed, which is very close to the spin-only value of $3.88\mu_{\text{B}}$. This small difference is in agreement with neutron diffraction measurements which indicate a small spin canting in LSMO [9]. The observed Wigner state however is not perfectly insulating and the finite conductivity for $T \rightarrow 0$ indicates that the Wigner crystal exhibits imperfections in the form of non-localized electrons, which might result from slight deviations from the exact 1/8 doping ratio.

The fact that LSMO is ferromagnetic in the charge-ordered, insulating state is remarkable, since it indicates that the ferromagnetic interaction at low temperatures cannot arise from the double exchange mechanism. We note here that other

manganites like $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ [17] and $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ [18] show similar FM insulating ground states at a chemical doping of $x = 1/8$. This means that orbital order plays an important role in establishing the magnetic properties in the charge-ordered state of manganites. In Ref. [19] it is even suggested that a hybridization of the $3z^2 - r^2$ and $x^2 - y^2$ orbitals takes place in the ground state of the $x = 1/8$ manganites. Since the low-temperature properties of LSMO have already been studied in detail elsewhere [10], we will focus in the next sections of this article on the JT-transition at 269 K.

4. INFLUENCE OF THE CJT TRANSITION ON THE RESISTIVITY

The resistivity as a function of magnetic field is shown in Fig. 4 for several temperatures below T_{JT} . Besides the usual CMR behavior, there is a sharp negative magnetoresistance effect upon crossing the boundary of the antiferrodistorsive phase, which is stable in low magnetic fields, and entering the disordered DJT phase in higher magnetic fields. The strong hysteresis effect (being especially pronounced at 268 K) is a further confirmation of the first-order nature of the CJT transition. Upon lowering the temperature, the transition shifts to higher fields and the hysteresis width shrinks. However, the relative height of the resistive jump is almost temperature-independent as shown in Fig. 4. The closed dots correspond to the magnetoresistance measurements, while the open dots are obtained from $\rho(T)$

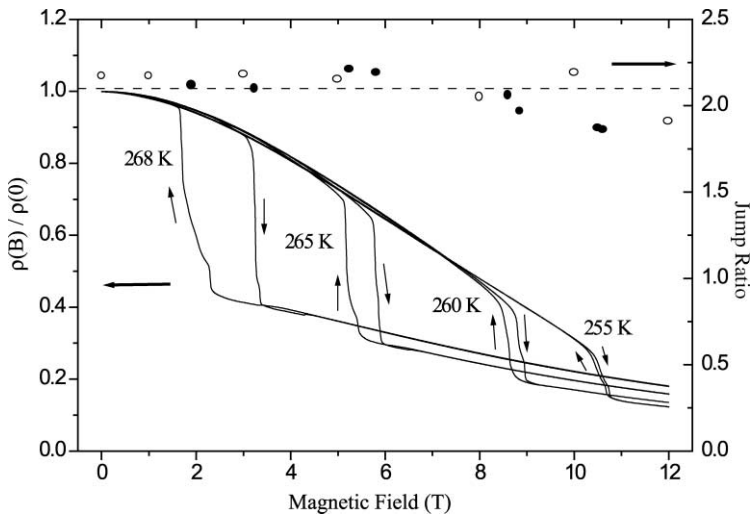


Fig. 4. Normalized magnetoresistance (left axis) at several temperatures below T_{JT} . The relative height of the resistive jump from the ordered to the disordered state is shown on the right axis. Solid dots refer to the magnetoresistance measurements, while open dots refer to temperature sweeps at fixed magnetic fields. The dotted line is a guide to the eye.

measurements at constant magnetic fields. On average the relative height of the resistive jump is 2.15 ± 0.10 .

The discontinuous jump of the resistivity at the JT-transition cannot simply be explained by a change in the double-exchange overlap integral as suggested in Ref. [14]. These authors claim that due to the CJT distortion and the exclusive occupation of the $3z^2 - r^2$ orbitals, the DE overlap integral might be lowered along the elongated axis while the overlap integrals with neighbors along the perpendicular axes might become negligible altogether. They further claim that the change in the lattice constants around T_{JT} might influence the bond angles between the Mn and O ions, which would also affect the absolute resistivity values. This is however doubtful since JT distortions, although fluctuating and in random directions, are already present above T_{JT} . Moreover, neutron diffraction on undoped LaMnO_3 has shown only an increase with decreasing temperature of the tilt angle of the MnO_6 octahedra (responsible for the buckling of the Mn–O–Mn bonds), but no sign at all of a discontinuous change of this angle around T_{JT} [20]. It seems therefore unlikely that the discontinuous jump in the resistivity can arise from the structural change of the material alone.

The doubling of the resistivity at T_{JT} may however be understood in terms of a frustration of the charge transport by the onset of orbital ordering, leading to a change in the allowed hopping paths. We postulate that charge transport between Mn^{3+} and Mn^{4+} can only occur in configurations with orbital overlap, and we consider only transport between nearest-neighbors. This means that an e_g electron in a $x^2 - y^2$ orbital can only be transferred to nearest-neighbor Mn^{4+} ions which are located in the plane of this orbital, but not in the perpendicular direction. Similarly, an e_g electron in a $3z^2 - r^2$ orbital can only be transferred to nearest-neighbor Mn^{4+} ions located along the axis of this orbital, but not in the equatorial directions. We assign to both processes an equal, dimensionless conductivity $\sigma = 1$. A possible magnetic impediment of the charge transfer due to spin misalignment will in a first approximation be ignored since it will have the same effect for temperatures just above and just below T_{JT} .

In the disordered state (see Fig. 3), the hole associated with Mn^{4+} can move to all nearest Mn^{3+} neighbors (due to the low doping we assume that all nearest-neighbors are Mn^{3+}) which provide orbital overlap and is therefore in principle mobile in three dimensions. The actual probability for orbital overlap is given by a factor 1/2: 50% of the e_g -electrons occupy $3z^2 - r^2$ orbitals, which point with a 1/3 probability into the direction of a given nearest-neighbor site. The other 50% of e_g electrons occupy $x^2 - y^2$ orbitals with a respective statistical weight of 2/3. This probability is independent of the breathing mode and arises solely from the disordered nature of the orbital arrangement.

In the CJT state below 269 K, the sample shows antiferrodistorsive order (see Fig. 1) in which all e_g electrons occupy $3z^2 - r^2$ orbitals. This confines the charge carriers within the ab -plane, since movement perpendicular to this plane is impossible due to a lack of suitable orbitals. In this state, transport is therefore mainly two-dimensional. The probability for orbital overlap within the plane is

again $1/2$ because charge transfer can occur only to two out of the four nearest neighbors.

Since the sample is a multidomain crystal exhibiting microtwinning, the current which is sent through the sample during resistivity measurements might probe equal portions of differently oriented domains. To account for this, we calculate the relative conductivity averaged along arbitrary directions of a three-dimensional cubic network, assuming that domains with various orientations contribute to the total conductivity like resistors connected in parallel. We approximate the average conductivity by considering only the three main directions of the cubic network as shown in Fig. 5: (i) the principal axes of the crystal (a , b , and c); (ii) the square-diagonals (ab , ac , and bc); (iii) the cube-diagonals. Other ways of going from point A to point B in Fig. 5 include more hops and have therefore a smaller probability.

In the three-dimensional DJT state the conductivity of a Mn^{4+} hole along the principal axes is $\sigma_p^{3d} = 1/2$, i.e., the elemental conductivity $\sigma = 1$ (one unit cell distance is spanned by one hopping event) is weighted with the probability for a suitable orbital geometry. The elemental conductivity along square-diagonals is $1/\sqrt{2}$ (two hops are required for a distance of $\sqrt{2}$ unit cells), and we take into account that there are two possible hopping paths with a respective probability for orbital overlap of $(1/2)^2$. The square-diagonal conductivity is therefore $\sigma_{sd}^{3d} = 1/\sqrt{2} \times 2 \times (1/2)^2 \approx 0.354$. Correspondingly, we obtain for cube-diagonals $\sigma = 1/\sqrt{3}$ (three hops for a distance of $\sqrt{3}$ unit cells), and there are now six possible paths with a probability factor of $(1/2)^3$. The cube-diagonal conductivity is then $\sigma_{cd}^{3d} = 1/\sqrt{3} \times 6 \times (1/2)^3 \approx 0.433$. The arithmetic mean of σ_p^{3d} , σ_{sd}^{3d} , and σ_{cd}^{3d} approximates the averaged conductivity along all possible directions and has a numerical value of $\bar{\sigma}^{3d} \approx 0.429$.

The major difference in the ordered CJT phase is the suppression of conductivity along the c -direction. Due to the antiferrodistorsive order, two steps are required on average to span a distance of one unit cell along the two remaining principal axes,

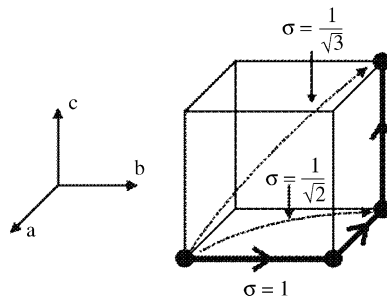


Fig. 5. Illustration of nearest-neighbor hopping on a cubic network with different conductivities for the principal axes, the square-diagonals, and the cube-diagonals. The elemental conductivities have to be weighted by the number of possible paths and by the probability for a suitable orbital-overlap configuration.

Table 1. Tabulated values of the elemental conductivity σ and the averaged conductivity for the three main directions in both the DJT and the CJT states

	DJT state	CJT state
Principal axes	$\sigma = 1, \sigma_p^{3d} = 1/2$	$\sigma = 1/2, \sigma_p^{2d} = 1/3$
Square-diagonals	$\sigma = 1/\sqrt{2}, \sigma_{sd}^{3d} \approx 0.354$	$\sigma = 1/\sqrt{2}, \sigma_{sd}^{2d} \approx 0.236$
Cube-diagonals	$\sigma = 1/\sqrt{3}, \sigma_{cd}^{3d} \approx 0.433$	$\sigma = 0, \sigma_{cd}^{2d} = 0$

i.e., the elemental conductivity σ along the principal axes is reduced by a factor of 2. The corresponding average conductivity is then $\sigma_p^{2d} = 1/3 \times (0 + 1/2 + 1/2) = 1/3$, since probability factors for orbital overlap do not have to be considered due to the static orbital arrangement. The number of steps for charge transport along the square ab -diagonal is not altered by the orbital ordering, but only one hopping path can be followed. The conductivity along the other two square-diagonal directions becomes zero. The average square-diagonal conductivity is therefore $\sigma_{sd}^{2d} = 1/3 \times (1/\sqrt{2} + 0 + 0) \approx 0.236$. It is evident that the cube-diagonal conductivity σ_{cd}^{2d} is zero and therefore the total average of all directions results in $\sigma^{2d} \approx 0.190$.

The results of these calculations are tabulated in [Table 1](#). The relative resistive jump height at the CJT transition is given by the ratio $\sigma^{3d}/\sigma^{2d} \approx 2.26$, which is in a very close agreement with the experimental jump ratios between 1.9 and 2.2 (see [Fig. 4](#)). We note that magnetoresistive measurements in untwinned single crystals, with the current path along well-defined crystallographic axes, should bring about jump ratios different from 2. However, these jump ratios will still be caused by a change of the available hopping paths due to orbital ordering.

5. INFLUENCE OF THE CJT TRANSITION ON THE MAGNETIZATION

As shown in the inset of [Fig. 2\(c\)](#), a sudden drop in the magnetic moment appears at the transition temperature T_{JT} . To study the effect of the CJT transition on the magnetic moment in more detail, we have performed field-dependent SQUID measurements at temperatures around T_{JT} and in fields up to 5 T. The results are shown in [Fig. 6](#). At temperatures slightly below T_{JT} , a sudden hysteretic upturn of the magnetic moment is observed upon leaving the CJT state which gets unstable in sufficiently high magnetic fields. With decreasing temperature, the field required to destroy the CJT distortion becomes rapidly larger. For a better comparison, [Fig. 6](#) also includes a magnetic moment curve at 272 K (i.e., above the JT-ordering temperature) and a magnetic moment curve at 265 K (i.e., entirely inside the ordered phase for fields below 5 T). These results correspond nicely with the resistivity measurements shown in [Fig. 4](#).

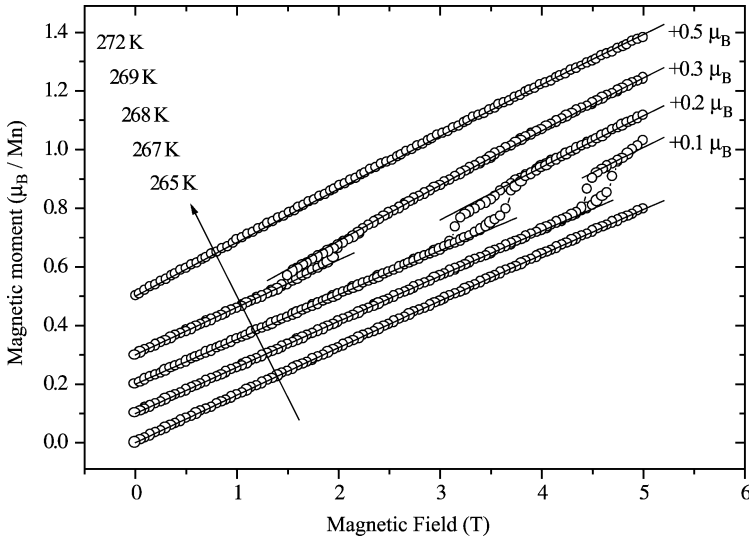


Fig. 6. Field dependence of SQUID magnetic moment measurements around the CJT transition. The solid lines are fits of the data according to equation (1). The absolute values of the magnetization curves at different temperatures are shifted by the indicated offset values for clarity.

To understand the influence of the CJT transition on the magnetic properties, we should analyze the paramagnetic magnetization data not only in the framework of a simple model with independent magnetic ions, but also take into account the existence of spin polarons. The ‘spin polaron’ denotes hereby an ensemble of neighboring unit cells with parallel (on a local scale ferromagnetic) spin alignment, which leads to a superparamagnetic behavior. The existence of these clusters in CMR manganites was postulated in Ref. [21], and found an experimental support in Refs. [4,5,22,23]. In compounds with negligible orbital order, i.e., with higher doping concentration, the charge transport is governed by the relative spin-misorientation between neighboring spin polarons, while the carriers are delocalized within their respective spin cluster [4].

For the size determination of spin polarons from the field-dependent magnetization data (SQUID results in Fig. 6) we first employed a fitting based on the Brillouin function $\beta(J)$, which is justified since the respective temperatures around T_{JT} are sufficiently above the ferromagnetic transition. The paramagnetic magnetization as a function of field is given by

$$M = g\mu_B \bar{J}/V_{\text{cell}} \beta\left(\frac{g\mu_B J B}{k_B(T - T_C)}\right) \quad (1)$$

Hereby $g = 2$ is the gyromagnetic ratio, μ_B the Bohr magneton, $\bar{J} = 1.94$ the average spin per Mn ion, V_{cell} the volume of the unit cell of LSMO, and J the spin of

the magnetic clusters responsible for the (super)paramagnetic behavior. The solid lines in Fig. 6 are fits of the magnetic moment data with equation (1). We note here that the spin size J is the only fitting parameter. The quality of the fits is very good from room temperature down to 225 K. Below this temperature the low-field magnetic moment starts to increase very fast, causing a breakdown of equation (1).

Figure 7 shows the temperature dependence of the spin-moment J . The magnetic moment measurements crossing the CJT phase boundary give two corresponding data points (solid squares and circles), while the other measurements give only one data point (open circles). The results suggest a CJT-induced shrinking of magnetic clusters from $J = 8$ in the disordered state (corresponding to about four Mn ions) to $J = 6$ in the antiferrodistorsive state (corresponding to roughly three Mn ions). Besides this shrinking there is a slight tendency towards an increasing cluster size with decreasing temperature.

To interpret the obtained cluster size, we will focus on the ferromagnetic coupling between the diluted Mn^{4+} ions to the neighboring Mn^{3+} sites. This restriction is justified since the coupling between two Mn^{3+} ions in the DJT state with random oriented e_g orbitals is only weakly ferromagnetic [8], while the antiferrodistorsive structure in the CJT state promotes A-type antiferromagnetism only at very low temperatures (e.g. $T_N = 140$ K for pure LaMnO_3). In the case of the ordered structure, a Mn^{4+} ion ($J = 3/2$) can undergo spin alignment in the sense of double exchange with only two out of six Mn^{3+} ($J = 2$) neighbors. The total J -moment of

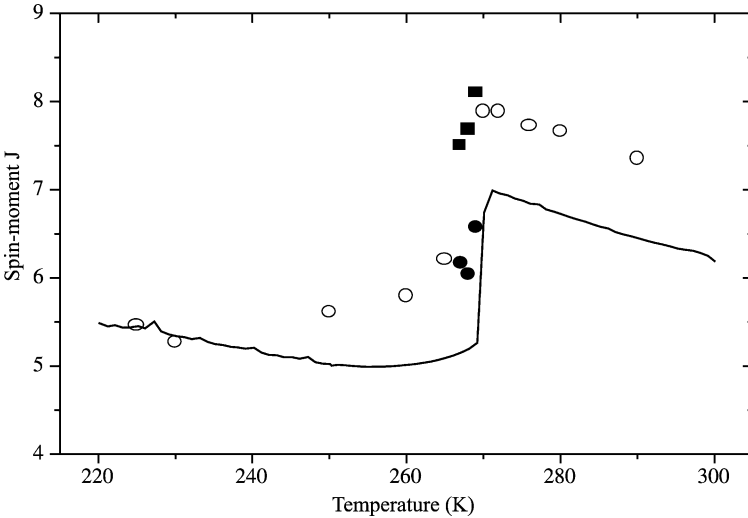


Fig. 7. Temperature dependence of the spin-moment J around the CJT transition, as derived from the fits of the magnetic moment data with equation (1). The magnetic moment measurements crossing the CJT phase boundary give two corresponding data points, indicated by the solid symbols. The solid line is calculated on the basis of the low-field magnetic moment according to equation (2).

this entity corresponds to 5.5. For the DJT-state (Fig. 3) three out of six Mn^{3+} neighbors are on average in the $x^2 - y^2$ configuration, each having a probability of $2/3$ that one of their orbital lobes is pointing towards the Mn^{4+} ion. The other three orbitals are in the $3z^2 - r^2$ state, with an overlap probability of $1/3$. The average total moment of ferromagnetic nearest-neighbor entities in the DJT state is therefore 7.5. These figures correspond closely to the experimentally observed J -values.

As an alternative method for the determination of the cluster size, we analyzed the low-field magnetic moment data from Fig. 2(c) by means of the modified susceptibility formula [24], derived from equation (1) in the low-field limit $g\mu_B B \ll k_B(T - T_C)$:

$$\chi = \frac{(g\mu_B)^2}{3} \frac{\bar{J}(J+1)}{k_B T} \quad (2)$$

The resulting J values are plotted as a solid line in Fig. 7, and are only slightly lower than the aforementioned data. This suggests that the size of the magnetic clusters is rather insensitive to the influence of external fields. We can therefore conclude that each hole-type charge carrier associated with an Mn^{4+} ion is embedded into a locally ferromagnetic environment extending to the nearest-neighbor sites. The size and shape of these magnetic clusters depend on the orbital configuration between Mn^{4+} and its nearest neighbors, illustrating once more the importance of the orbital structure on the physical properties of LSMO.

Finally, we will discuss the field dependence of the JT transition temperature T_{JT} . From the X-ray data around T_C in Fig. 2, it is clear that an enhancement of the charge carrier mobility due to magnetic ordering competes with the collective JT-distortions. In the DJT state the charge transfer is impeded by spin disorder. This spin disorder persists in the CJT state where the orbital structure however causes additional carrier localization. In both states an external magnetic field leads to an increase in carrier mobility in the framework of the double exchange mechanism. This delocalizes the carriers and hence results in a lowering of the kinetic energy in the sense of the uncertainty principle [2]. However, the gain in free energy is less pronounced in the CJT state where the application of a magnetic field tends to destroy the CJT effect and hence leads to an increase in elastic energy. This explains why with increasing magnetic field the DJT state becomes stable in a wider temperature range and the JT-transition temperature decreases.

6. SUMMARY

We investigated the resistive and magnetic behavior of a rare-earth manganite in the low-doping regime, $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$, where the high Mn^{3+} content results in a CJT effect. The phase transition from the orbitally disordered state to a phase with antiferrodistorsive orbital order has a substantial influence on the resistive as well as on the magnetic properties. The orbital ordering impedes charge transfer along certain directions, resulting in a doubling of the resistivity irrespective of external

magnetic fields and the corresponding spin-alignment and CMR effects. The magnitude of this resistive jump was calculated and found to be quantitatively correct on the basis of a simple model, and crossing the phase boundary from the orbitally ordered to the disordered state corresponds to a strong, negative magnetoresistance effect, which is independent of the CMR effect as such. The lower resistivity of the disordered state goes along with an increase of the paramagnetic susceptibility, which is especially remarkable, since it can only be explained on grounds of superparamagnetic behavior controlled by ferromagnetic spin clusters or spin polarons. The typical cluster moment was evaluated by two independent fitting procedures and corresponds to the total moments of Mn^{4+} ions and the surrounding Mn^{3+} sites, to which the Mn^{4+} has an orbital overlap. The shift of the orbital ordering transition to lower temperatures under the influence of magnetic fields was explained by a stabilization of the disordered phase through an enhancement of the carrier mobility.

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REFERENCES

- [1] R. M. Kusters, J. Singleton, D. A. Keen, R. McGreevy and W. Hayes, *Physica B*, 1989, **155**, 362; R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz and K. Samwer, *Phys. Rev. Lett.*, 1993, **71**, 2331.
- [2] P. G. de Gennes, *Phys. Rev.*, 1960, **118**, 141, and references therein.
- [3] A. J. Millis, *Phys. Rev. B*, 1996, **53**, 8434; A. J. Millis, *Nature*, 1998, **392**, 147.
- [4] P. Wagner, I. Gordon, L. Trappeniers, J. Vanacken, F. Herlach, V. V. Moshchalkov and Y. Bruynseraede, *Phys. Rev. Lett.*, 1998, **81**, 3980.
- [5] P. Wagner, I. Gordon, V. V. Moshchalkov, Y. Bruynseraede, M. Apostu, R. Suryanarayanan and A. Revcolevschi, *Europhys. Lett.*, 2002, **58**, 285.
- [6] Y. Murakami, J. P. Hill, D. Gibbs, M. Blume, I. Koyama, M. Tanaka, H. Kawata, T. Arima, Y. Tokura, K. Hirota and Y. Endoh, *Phys. Rev. Lett.*, 1998, **81**, 582.
- [7] G. A. Gehring and K. A. Gehring, *Rep. Prog. Phys.*, 1975, **38**, 1.
- [8] J. B. Goodenough and J. M. Longo, in *Crystallographic and Magnetic Properties of Perovskite and Perovskite-Related Materials* (ed. K.-H. Hellwege), Springer, Berlin, 1970.
- [9] L. Pinsard, J. Rodriguez-Carvajal, A. H. Moudden, A. Anane, A. Revcolevschi and C. Dupas, *Physica B*, 1997, **234–236**, 856.
- [10] S. Uhlenbruck, R. Teipen, R. Klingeler, B. Büchner, O. Friedt, M. Hückler, H. Kierspel, T. Niemöller, L. Pinsard, A. Revcolevschi and R. Gross, *Phys. Rev. Lett.*, 1999, **82**, 185.
- [11] A. Anane, C. Dupas, K. Le Dang, J. P. Renard, P. Veillet, A. M. de Léon-Guevara, F. Millot, L. Pinsard and A. Revcolevschi, *J. Phys.: Condens. Matter*, 1995, **7**, 7015, and references therein.
- [12] T. Niemöller, M. von Zimmermann, S. Uhlenbruck, O. Friedt, B. Büchner, T. Frello, N. H. Andersen, P. Berthet, L. Pinsard, A. M. De Léon-Guevara, A. Revcolevschi and J. R. Schneider, *Eur. Phys. J. B*, 1999, **8**, 5.

- [13] J. J. Neumeier, K. Andres and K. J. McClellan, *Phys. Rev. B*, 1999, **59**, 1701.
- [14] A. Anane, C. Dupas, K. Le Dang, J. P. Renard, P. Veillet, L. Pinsard and A. Revcolevschi, *Appl. Phys. Lett.*, 1996, **69**, 1160.
- [15] E. Dagotto, T. Hotta and A. Moreo, *Phys. Rep.*, 2001, **344**, 1.
- [16] Y. Yamada, O. Hino, S. Nohdo and R. Kanao, *Phys. Rev. Lett.*, 1996, **77**, 904.
- [17] S.-W. Cheong and H. Y. Hwang, in *Colossal Magnetoresistive Oxides* (ed. Y. Tokura), Gordon & Breach Science Publishers, Amsterdam, 2000.
- [18] R. Maezono, S. Ishihara and N. Nagaosa, *Phys. Rev. B*, 1998, **57**, R13993.
- [19] Y. Endoh, K. Hirota, S. Ishihara, S. Okamoto, Y. Murakami, A. Nishizawa, T. Fukuda, H. Kimura, H. Nojiri, K. Kaneko and S. Maekawa, *Phys. Rev. Lett.*, 1999, **82**, 4328.
- [20] J. Rodriguez-Carvajal, M. Hennion, F. Moussa, L. Pinsard and A. Revcolevschi, *Physica B*, 1997, **234–236**, 848.
- [21] J. M. D. Coey, M. Viret, L. Ranno and K. Ounadjela, *Phys. Rev. Lett.*, 1995, **75**, 3910.
- [22] J. M. De Teresa, M. R. Ibarra, P. A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. Garcia, A. Delmoral and Z. Arnold, *Nature*, 1997, **386**, 256.
- [23] O. Chauvet, G. Goglio, P. Molinie, B. Corraze and L. Brohan, *Phys. Rev. Lett.*, 1998, **81**, 1102.
- [24] N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Saunders College, Philadelphia, 1976.

Low-Temperature Phase Transition and Structure of Ordered Phase in $\text{K}_3\text{H}(\text{SO}_4)_2$ (TKHS)-Family Materials

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Abstract

Suitability of quantum chemistry to describe the structural phase transitions on the semi-quantitative level in H-bonded ferroelectrics and related materials has been demonstrated. The low-temperature H/D-ordering transitions have been treated for the TKHS-like materials in the scope of the static and dynamic Ising models. Parameters of the Ising-type Hamiltonians are evaluated on the Hartree–Fock/second-order perturbation theory level using the available diffraction data. The type of D-ordering in the low-temperature phase of $\text{M}_3\text{D}(\text{AO}_4)_2$ specimens, which is debated so far, is proposed in the limits of the static model. As shown this ordering points out the antiferroelectric-type structure with the b -doubling of paraelectric $A2/a$ cell and admits the c -doubling of this cell. Estimations of T_c in the fully deuterated specimens are obtained by the Bethe cluster approximation using the dynamic model. An absence of such transition for $\text{M}_3\text{H}(\text{AO}_4)_2$ has been explained by both the proton quantum fluctuations (tunneling effect) and the differences in geometries of H- and D-bonds (geometric isotope effect).

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1. INTRODUCTION

Theoretical treatment of order–disorder structural phase transitions in hydrogen-bonded ferroelectrics implies, in principle, the determination of the transition critical temperature T_c and accompanying crystal structure transformations.

These important, but not completely understood, problems are considered here by using the novel, quantum chemical, approach to the microscopical theory of ferroelectrics and related materials [1]. The isomorphous H-bonded crystals $M_3(H/D)(AO_4)_2$ ($M = K, Rb$; $A = S, Se$) are taken as examples. There are two reasons of such choice. This family is investigated actively at present. Moreover, it is a suitable subject of theoretical examination because of simple chemical constitution of the TKHS-like compounds (zero-dimensional H-bond network).

The present work continues our theoretical investigations [1] of this TKHS family. In contrast to [1] the Ising model is employed here to examine the possible types of deuteron ordering in the low-temperature phase (below ≈ 100 K) as well as to study the thermodynamic behavior of these materials on semi-quantitative level in the limits of the Bethe cluster approximation.

The Jahn–Teller theory terminology is not applied explicitly in this paper. However, the strong low-barrier H-bonds in considered systems demonstrate some of the inherent properties of the typical pseudo-Jahn–Teller centers.

2. MODEL HAMILTONIAN

The Ising-type Hamiltonian is usually employed for H-bonded ferroelectrics. In the more general quantum–mechanical approach (dynamic Ising model [2,3]) it has a form:

$$H = -\Omega \sum_{i=1}^N \sigma_i^x - \left(\frac{1}{2}\right) \sum_{i,j=1}^N J_{ij} \sigma_i^z \sigma_j^z \quad (1)$$

Here σ_i^x , and σ_i^z are the Pauli matrices, that act on the proton (deuteron) wavefunctions $\psi_{L,i}$ and $\psi_{R,i}$ localized in the left and right potential wells of the proton (deuteron) potential energy profile of the i th H-bond (in accordance with the available diffraction data the short H-bonds $O-H \cdots O$ with two off-center sites of a proton are considered). The parameters of Hamiltonian (1), i.e., the tunneling parameter Ω and the Ising parameters J_{ij} , describe the motion of a proton (deuteron) along H-bond and the effective pair interactions of these particles, respectively. When Ω is substantially smaller than J_{ij} the static approximation ($\Omega = 0$) becomes valid. Instead of equation (1) one has in this case

$$E = -\left(\frac{1}{2}\right) \sum_{i,j=1}^N J_{ij} \sigma_i^z \sigma_j^z \quad (2)$$

In equation (2) E is the (potential) energy of the proton (deuteron) subsystem and σ_i^z are considered as classical dihotomic variables $\sigma_i^z = \pm 1$. These values correspond to particles localized in one of two possible equilibrium positions on each H-bond.

3. PARAMETERS Ω AND J_{ij}

The parameters of Hamiltonians (1) and (2) are determined in our approach by pure theoretical way using different quantum chemical models and calculations unlike the traditional fitting the experimental thermodynamic and dielectric data. Our method of the many-pseudospin clusters [1,4] seems to be the most reliable way of J_{ij} determination. The latter are obtained in this case within the static approximation from the system of equations for a typical crystal fragment (cluster) for all possible proton distributions on H-bonds. The left-hand side of any equation expresses the cluster total energy in terms of J_{ij} , while the right-hand side is determined by means of the quantum chemical calculation of this energy.

Table 1 presents the J_{12} , J_{13} , J_{14} values (describing the couplings of a given pseudospin with the first, second, and third nearest neighboring pseudospins, respectively) calculated by such manner using the 8-spin cluster $\{1, 2, 3, 4, 1', 2', 3', 4'\}$ in the TKHS-like crystals (Fig. 1). The calculation of the total energy of this cluster was performed *ab initio*, using the pseudopotential approximation for inner electronic shells. These calculations were carried out by the use of more accurate diffraction data (see Ref. [5] for details). The signs of J_{ij} correspond to the choice of the positive directions of pseudospins depicted in Fig. 1. The values of the molecular field parameter $J_0 = \sum_j J_{ij}$ are also shown in Table 1; here $J_0 = 2J_{12} + 2J_{14} + 4J_{13}$.

These values of the major J_{ij} parameters are rather close to those obtained using the 2- and 4-spin clusters [4,5] and trend towards simultaneous decrease in each parameter on several percents with the increase in the cluster size so that the inequality $J_{12} > |J_{14}| \geq J_{13}$ is satisfied in any case.

The most reliable values of the calculated tunneling parameters Ω_{H} and Ω_{D} are presented in Table 2. These values were obtained with the help of the calculated *ab initio* potential energy profiles, corrected in according with the diffraction data for proton (deuteron) positions [5].

Table 1. Averaged values of the major Ising J_{12} , J_{14} , J_{13} , and molecular field J_0 parameters (K) for $\text{M}_3(\text{H/D})(\text{AO}_4)_2$, $\text{M} = \text{K, Rb}$; $\text{A} = \text{S, Se}$

Specimen/model	$\text{M}_3\text{H}(\text{AO}_4)_2$				$\text{M}_3\text{D}(\text{AO}_4)_2$			
	J_{12}	J_{14}	J_{13}	J_0	J_{12}	J_{14}	J_{13}	J_0
4-Spin cluster ^a	85	− 31	24	204	140	− 51	39	334
8-Spin cluster	81	− 29	21	188	129	− 47	34	300

The calculations were carried out by the pseudopotential method with SBK basis set (GAMESS codes [19,20]); see Refs. [4,5] for the details of calculations.

^aThe data for the 4-spin cluster [5] are shown for comparison.

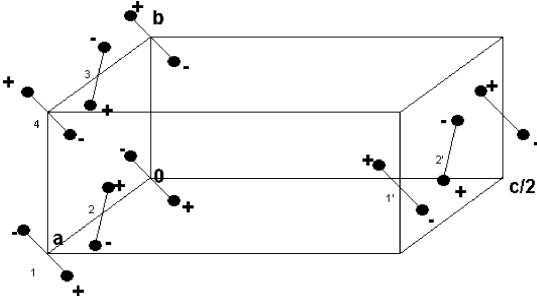


Fig. 1. H-bonds in the crystal cell of TKHS-like crystal; the sign (+) relates to covalently bonded oxygen and (−) to hydrogen-bonded one. The positive signs of all pseudospins chosen to correspond the dipole directions of H-bonds.

4. GROUND STATE OF LOCALIZED DEUTERONS

While the crystalline structures of the TKHS-like materials were studied by diffraction methods for two decades, some important structural aspects are open to question. The use of the static Ising model along with the data of Table 1 permits to make an attempt to provide insight into urgent problem of ferroelectrics crystal chemistry concerning the actual deuteron arrangement in the low-temperature phase of $M_3D(AO_4)_2$ compounds. The crystal structure of the paraelectric phase of the TKHS-like materials is commonly described by space group $A2/a$ [6] (although there appears an evidence speaking for space group $A2$ [7,8]) and the corresponding H-bond positions in crystal cell are shown in Fig. 1. It is seen that this zero-dimensional H-bond network can be considered as consisting of separate layers parallel to ab plane.

The internal geometry of all layers is identical but they can be divided into two types – L_0 and $L_{1/2}$ in respect of their position in lattice. As from Fig. 1: (1) the layers of different types are alternated, (2) the nearest-neighboring layers L_0 (as well as $L_{1/2}$) are matched by the $\pm c$ -translations, and (3) each L_0 layer is matched with its two $L_{1/2}$ neighbors by the simultaneous shifts by $b/2$ and $\pm c/2$.

Table 2. Averaged values of $\Omega_{H/D}$ for $M_3(H/D)(AO_4)_2$

$\Omega_{H/D}$, K	$M_3H(AO_4)_2$	$M_3H(AO_4)_2$
Uncorrected	570 ± 70	180 ± 40
Correction 1	430 ± 50	120 ± 20
Correction 2	420 ± 80	90 ± 15

See Ref. [5] for the details of calculations.

In the scope of the static Ising model the pseudospin (deuteron) distribution corresponding to the lowest energy of localized deuteron system (ground state) can be found for any layer. To do it in practice, our analysis has been restricted by comparison of rather simple periodic pseudospin distributions because the correct mathematical procedure is unknown in the case of arbitrary pseudospin distributions, in particular, involving nonperiodic ones. When the most strong pseudospin interactions are taken account of (describing by J_{12} , J_{14} , J_{13} ; Table 1) then the ground state in point corresponds to the pseudospin configuration $L_0(+)$ which is schematically shown on ab plane (Fig. 1). The same energy has the $L_0(-)$ configuration where all pseudospins are reversed simultaneously (as well as the similar configurations $L_{1/2}(+)$ and $L_{1/2}(-)$). The estimations of coupling parameters J_{ij} for neighboring layer pseudospins exhibit a rather weak interconnection of their pseudospin structures, so that the energy of whole lattice can be approximately presented as the sum of separate layer energies. The ground state in this case can be ascribed by the following scheme:

$$\cdots L_{1/2}(\pm)L_0(\pm)L_{1/2}(\pm)L_0(\pm)\cdots \quad (3)$$

where the signs $(+)$ and $(-)$ do not correlated in different layers.

All of structures (3) relate to antiferroelectric phase that is in an agreement with the available measurements evidencing just the same character of low-temperature phase in the $M_3D(AO_4)_2$ crystals [6]. It is also evident that the doubling of b -parameter of the paraelectric $A2/a$ cell under transition to the low-temperature D-ordered phase directly follows from proposed scheme (3). Recently, such b -doubling is observed experimentally in [7]. This scheme is also consistent with the doubling of c -parameter of $A2/a$ cell found in the cited paper. In particular, such b -doubling takes place when the layer sequence (3) takes the form:

$$\begin{aligned} \{L_0(+)L_{1/2}(\pm)L_0(-)L_{1/2}(\pm)L_0(+)\}_\infty \quad \text{or} \\ \{L_0(-)L_{1/2}(\pm)L_0(+)L_{1/2}(\pm)L_0(-)\}_\infty \end{aligned} \quad (4)$$

It should be noted, however, that we do not discuss many different structural changes in crystals accompanying the low-temperature D-ordering transition (displacements of metal cations, rotations of the AO_4 -terahedra, etc.). Therefore, our analysis is limited by specific changes in H-bond network only and does not claim on the exhaustive treatment of all crystallographic problems.

5. THERMODYNAMICS OF THE TKHS FAMILY

Our quantum chemical approach has been applied to explain the thermodynamics of the TKHS-like materials on the level of simple mean (molecular) field approximation [1,4] which, however, is not well adapted to provide for quantitative estimations of the critical temperature of phase transitions. To examine the

thermodynamic behavior of the crystals at hand at low temperatures in the range of 100 K the (Bethe) clusters approximations [3,9,10] has been applied. The latter is a natural generalization of the molecular field approximation because it allows us to have regard for proton–proton correlation effect, at least in part, and therefore it is believed to be more reliable for the quantitative treatment. In Refs. [9,10], the cluster approximation has been developed in the scope of the dynamic model (1) using KH_2PO_4 (KDP) as an example. Here the numerical version [10] of this approximation is employed.

The four-particle Hamiltonian for the $\{1, 2, 3, 4\}$ cluster

$$H_4 = -\Omega \sum_{i=1}^4 \sigma_i^x - \left(\frac{1}{2}\right) \sum_{i,j=1}^4 J_{ij} \sigma_i^z \sigma_j^z - \nu \varphi \sum_{i=1}^4 \sigma_i^z \quad (5)$$

as well as the single-particle Hamiltonian

$$H_1 = -\Omega \sigma_1^x - \varphi \sigma_1^z \quad (6)$$

are considered with this end in view. Here φ is the (variational) parameter of the mean field acting on the pseudospins 1–4 in equation (5) and on the pseudospin 1 in equation (6) from remaining pseudospins of crystal. This mean field in Hamiltonian (5) is reduced by the factor

$$\nu = 1 - \frac{J_{12} + J_{14} + J_{13}}{J_0} \approx 5/8$$

because the interactions of a given pseudospin with three nearest-neighboring pseudospins inside the cluster have already taken into account in the second term of equation (5). Then, the use of the coincidence condition for the thermal expectation value(s) $\langle \sigma_i^z \rangle$ obtained with Hamiltonians (5) and (6) results in the following consistency equation

$$\langle \sigma_i^z \rangle = \frac{\varphi}{\sqrt{\Omega^2 + \varphi^2}} \text{th} \frac{\sqrt{\Omega^2 + \varphi^2}}{k_B T} = \frac{f}{\sum_{i=1}^{16} \exp(-\lambda_i/k_B T)} \quad (7)$$

Here

$$f = \frac{1}{4} \sum_{i=1}^{16} \left\langle \Phi_i \left| \sum_{j=1}^4 \sigma_j^z \right| \Phi_i \right\rangle \exp(-\lambda_i/k_B T)$$

and

$$\Phi_i = \sum_{j=1}^{16} C_{ji} \Theta_j$$

where Θ_i and Φ_i are the basis sets, that diagonalize the matrix of the operator (5) in the cases $\Omega = 0$ and $\Omega \neq 0$, respectively, and λ_i are the eigenvalues of Hamiltonian (5) at $\Omega \neq 0$.

Table 3. Estimations of T_c for $\text{M}_3(\text{H/D})(\text{AO}_4)_2$

T_c , K	$\text{M}_3\text{H}(\text{AO}_4)_2$	$\text{M}_3\text{D}(\text{AO}_4)_2$
Uncorrected	–	–
Correction 1	–	≤ 115
Correction 2	–	$95 \div 135$
Experiment	(20^a)	$70 \div 115$

J_{ij} obtained from 8-spin cluster (Table 1) and Ω_D (Table 2) are used.

^aAccording to Ref. [13].

The critical temperature T_c of the transition from paraelectric phase to ordered phase is obtained by means of the numerical solution of (7). Table 3 gathers the T_c -values calculated for the TKHS-like crystals with the help of the data from Tables 1 and 2. One can see the reasonable agreement with the available experimental data [11,12] for the deuterated compounds. Meanwhile, equation (7) does not lead to some sort T_c for the $\text{M}_3\text{H}(\text{AO}_4)_2$ specimens, that agrees with the tendency to an absence of the low-temperature H-ordering phase transition for such materials up to helium temperatures [6,13]. The reason of such a noticeable isotope effect may be easily clarified. It can be seen that the T_c estimate goes to zero with the growth of Ω for given J_{ij} values. On the contrary, the T_c value grows together with J_{ij} , for a given Ω . Hence, an absence of the low-temperature transition to the proton-ordered phase can be explained by the quantum paraelectric behavior of these systems, i.e., the proton ordering suppression due to proton quantum fluctuations in lattice.

There are two alternative viewpoints to account for the large isotope effect on the critical temperature in H-bonded ferroelectrics. The first is the H/D tunneling effect [14,15] and the second is the ‘geometric isotope effect’ [16–18], which is based on a correlation between T_c and the differences in geometry of $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{D}\cdots\text{O}$ bonds. Our treatment of the TKHS family, in which these structural changes are explicitly incorporated at the very beginning, demonstrates that both tunneling and H-bond geometry play an essential role in the description of the origin of the H/D-ordering transitions, in particular, the quantum paraelectricity nature.

It should be marked in conclusion that the explanation of some delicate peculiarities of the TKHS-like materials (even on the semi-quantitative level), such as the x – T phase diagrams for the mixed $\text{M}_3\text{H}_x\text{D}_{1-x}(\text{AO}_4)_2$ compounds, possible transition in $\text{K}_3\text{H}(\text{SeO}_4)_2$, etc., requires, of course, more detail examinations, involving at least some of proton isotopes–lattice coupling.

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REFERENCES

- [1] S. P. Dolin, A. A. Levin, T. Yu. Mikhailova and M. V. Solin, in *Vibronic Interaction: Jahn–Teller Effect in Crystals and Molecules* (eds M. D. Kaplan and G. O. Zimmerman), Kluwer Academic Publishers, Dordrecht, 2000, p. 263.
- [2] M. E. Lines and A. M. Glass, *Glass, Principles and Application of Ferroelectrics and Related Materials*, Clarendon Press, Oxford, 1977.
- [3] V. G. Vaks, *Introduction to Microscopical Theory of Ferroelectrics*, Nauka, Moscow, 1973, in Russian.
- [4] S. P. Dolin, A. A. Levin, T. Yu. Mikhailova, M. V. Solin and L. I. Trakhtenberg, *Int. J. Quantum Chem.*, 2002, **88** (4), 463.
- [5] S. P. Dolin, A. A. Levin, T. Yu. Mikhailova, M. V. Solin and N. S. Strokach, *Int. J. Quantum Chem.*, in press.
- [6] M. Ichikawa, T. Gustafsson and I. Olovsson, *Ferroelectrics*, 1994, **159**, 73.
- [7] I. Tamura and Y. Noda, *Ferroelectrics*, 1998, **219**, 135.
- [8] T. Gustafsson, M. Ichikawa and I. Olovsson, *Solid State Commun.*, 2000, **115**, 473.
- [9] V. G. Vaks and V. I. Zinenko, *JETP*, 1973, **64**, 650, in Russian.
- [10] R. Blinc and S. Svetina, *Phys. Rev.*, 1966, **147** (2), 430.
- [11] T. Matsuo, A. Inaba, O. Yamamuro and N. Onoda-Yamamuro, *J. Phys. Condens. Matter.*, 2000, **12**, 8595.
- [12] N. Onoda-Yamamuro, O. Yamamura, T. Matsuo, M. Ichikawa, R. M. Ibberson and W. I. F. David, *J. Phys. Condens. Matter.*, 2000, **12**, 8559.
- [13] M. Endo, T. Kaneko, Y. Osaka and Y. Makita, *J. Phys. Soc. Jpn.*, 1983, **52**, 3829.
- [14] R. Blinc, *J. Phys. Chem. Solids*, 1960, **13**, 204.
- [15] R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics*, North-Holland, Amsterdam, 1974.
- [16] M. Ichikawa, *Chem. Phys. Lett.*, 1971, **27**, 103.
- [17] M. Ichikawa, *Phys. Rev.*, 1981, **B36**, 874.
- [18] M. Ichikawa, *Ferroelectrics*, 1995, **168**, 177.
- [19] M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
- [20] A. A. Granovsky, URL <http://clasiic.chem.msu.su/gran/games/index.html>

Cooperative Dynamical Effect in Rhombohedral LaMnO_3

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Abstract

The possibility of cooperative dynamical Jahn–Teller (JT) in rhombohedral LaMnO_3 is considered. For the verification of such an assumption, lattice structure and dynamic calculation are performed. The calculation is performed in the framework of pair interionic potentials and shell model explicitly allowing for the JT term in crystal energy and dynamical matrix. Using such an assumption, the structural phase transition from monoclinic to rhombohedral phase is considered. The appearance of a broad high frequency line near 640 cm^{-1} in Raman scattering spectra of rhombohedral LaMnO_3 is explained. The appearance of ferromagnetism in the rhombohedral phase, which is only due to superexchange interaction is shown.

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1. INTRODUCTION

Because of the colossal magnetoresistance (CMR) effect, manganites are of great interest [3]. The peculiarity of these compounds is the presence of the Jahn–Teller effect on the Mn^{3+} ions. This gives rise to strong coupling of vibrational orbital and magnetic degrees of freedom.

The manganites with general formula $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ have structures of distorted perovskite. Depending on the types of distortions, the structure could be called orthorhombic O' with space group $Pnma$, orthorhombic O^* with space group $Pnma$ and rhombohedral phase with the space group $R\bar{3}c$. The first structure

has static Jahn–Teller (JT) distortions. The second and third groups do not have any JT active distortions. Moreover, the $R\bar{3}c$ group does not allow for the presence of static JT active distortions.

The manganites in rhombohedral phase (in the region where $x \approx 0.3$) exhibit interesting features including CMR itself. The possibility of dynamical JT effect in rhombohedral manganites is widely discussed [4]. As was mentioned above the presence of static JT distortions is restricted by the space group symmetry. However, this symmetry could be retained only on average. It means if the crystal does have dynamical JT distortions, the observable averaged structure will be without them. The cooperative dynamical JT effect could be of two types in crystal: JT liquid, when the dynamic JT distortions around different JT ions do not correlate between each other (the model of Iliev and coworkers is close to such a type of effect [2]) and cooperative JT effect, where only some JT active mode of whole crystals are active in dynamical effect. It means that distortions around each JT active ion correlate strongly between each other, but the mean position of each ion in coordination of the JT ion corresponds to the structure with no static JT distortions. We suppose rhombohedral manganites to have the second type of JT effect because each $[\text{MnO}_6]$ octahedra shares one corner with its neighbor, which gives rise to the strong correlation in motion of JT Mn^{3+} ion coordination.

The rhombohedral manganites with $x \approx 0.3$ level of doping have a complex ground state. This is mainly because of charge carriers presence. However, there are low doped or deficient LaMnO_3 , which is observed in monoclinic and rhombohedral phases [5]. The level of structural disorder and the amount of charge carriers are significantly low comparing with the optimal doped manganites. That is why the investigation of rhombohedral LaMnO_3 could reveal the structural aspects of rhombohedral manganites. Moreover, the results of structure and lattice dynamics could be compared with the Raman scattering (RS) experiments performed by Iliev and coworkers [1,2]. The most suitable tool for the JT dielectrics structure and dynamics investigation is a pair interionic potentials approximation explicitly allowing for the JT term both in energy and in the dynamic matrix of the crystal [6,7].

In this work we perform an investigation of cooperative static in the monoclinic phase and dynamic in rhombohedral JT effect of pure LaMnO_3 using pair interionic potentials in shell model approximation with the direct inclusion of the JT term in crystal energy and dynamic matrix of a crystal. The magnetic and RS properties of the rhombohedral LaMnO_3 are simulated in the framework of the cooperative dynamical effect approximation.

2. LATTICE ENERGY CALCULATION MODEL

In lattice structure calculation the crystal lattice parameters are obtained by the optimization of crystal energy with respect to displacements of ions that do not change crystal lattice symmetry. The crystal energy is calculated in the framework

of the ionic pair potential shell model explicitly allowing for the JT term, which is simulated as the sum of lower brunches of adiabatic potentials of single [MnO₆] complexes [6,7]

$$E = E_{\text{Lat}} + E_{\text{JT}} \tag{1}$$

In the pairwise-potential approximation and the shell model, the lattice energy can be written as

$$E_{\text{Lat}} = E_{\text{Coul}} + \frac{1}{2} \sum_i \sum_{k \neq i} V_{ik} + \frac{1}{2} \sum_i k_i \bar{\delta}_i^2 \tag{2}$$

where E_{Coul} describes Coulomb interaction in crystal and the index i specifies ions in the primitive cell and the index k enumerates all ions of the crystal. The term $k_i \bar{\delta}_i^2$ describes the interaction energy between the core of the i th ion and its shell shifted relative to the core by an amount of $\bar{\delta}_i$. Short-range potential is represented by the Born-Mayer, screening and van der Waals terms

$$V_{ik} = C_{ik} \exp(-D_{ik}|\vec{r}_{ik} - \vec{\delta}_i + \vec{\delta}_k|) - \frac{A_{ik}}{r_{ik}} \exp(-B_{ik}r_{ik}) - \frac{\lambda_{ik}}{r_{ik}^6} \tag{3}$$

The screening term describes the screening of Coulomb potential due to the overlap of electronic densities of ions. Parameters of the pair potential model are listed in Table 1. The many-particle JT contribution to the crystal energy is approximated by the sum of expressions for the lower brunches of adiabatic potentials of the [MnO₆] clusters

$$E_{\text{JT}} = -|V_e| \sum_n \sqrt{Q_\theta^2(n) + Q_\epsilon^2(n)} \tag{4}$$

where V_e is the linear JT interaction constant ($|V_e| = 1.29 \text{ eV \AA}^{-1}$ [7]), and $Q_\theta(n)$, $Q_\epsilon(n)$ are projections of displacements of oxygen ions onto *local JT distortions*.

Table 1. The pair potential model parameters (all in atom units)

	La ³⁺ –O ^{2–}	Mn ³⁺ –O ^{2–}	O ^{2–} –O ^{2–}
<i>A</i>	85.623	32.689	44.862
<i>B</i>	1.276	1.671	1.0592
<i>C</i>	250.0	43.56	21.729
<i>D</i>	1.650	1.575	1.320
λ	0	0	4.513
	La ³⁺	Mn ³⁺	O ^{2–}
<i>X</i>	9	8.265	4.245
<i>Y</i>	–6	–6	–6
<i>k</i>	40.0	50.76	3.99

To calculate the phonon frequencies, one should diagonalize the dynamic matrix of the crystal for the center of the Brillouin zone (BZ)

$$D = M(F^{\text{CC}} - F^{\text{CS}}[F^{\text{SS}}]^{-1}F^{\text{SC}} + F^{\text{JT}})_0 \quad (5)$$

where $M_{k\alpha,n\beta} = \delta_{\alpha\beta}[m_k m_n]^{-1/2}$; F^{CC} and F^{SS} are the matrices of the second derivatives of the crystal energy (without the JT contribution) with respect to the displacements of the cores and shells of ions, respectively; F^{CS} and F^{SC} are the matrices of the mixed derivatives of the crystal energy (without the JT contribution) with respect to the displacements of the cores and shells of ions; and F^{JT} is the matrix of the second derivatives of the JT contribution in equation (4) with respect to the ion core displacements.

The intensities of RS lines could be estimated in the framework of the shell model because the shells simulate the electronic polarizability. The estimation is based on such an approximation:

$$I_q \propto \left(\frac{\partial \alpha_\infty}{\partial q} \right)^2 \quad (6)$$

where I_q is the intensity of mode q , and α_∞ is the high frequency polarizability. The derivative is taken with respect to the amplitude of vibration q . In the shell model approximation, the derivative could be calculated as follows:

$$\begin{aligned} \frac{\partial \alpha_{\infty\alpha\beta}}{\partial q_i} &= \frac{1}{\Omega} Y_k [U' [F^{\text{SS}}]^{-1} F^{\text{SCS}} [F^{\text{SS}}]^{-1}]_{k\alpha, i, m\beta} Y_m \\ U'_{i, n\gamma} &= \frac{1}{\sqrt{m_n}} U_{i, n\gamma} \end{aligned} \quad (7)$$

where Ω is the volume of primitive cell, U is the matrix that diagonalizes the dynamical matrix of the crystal [equation (5)], i indexes the vibrational modes, α and β index the Cartesian coordinates, k and m index the ions in the primitive cell, Y_k is the charge of the shell with number k , and m_k is the mass of the ion with number k . F^{SCS} is the matrix of third derivatives taken with respect to the shell (S) and core (C) displacements.

3. RESULTS AND DISCUSSION

Besides orthorhombic O' and O^* phases, the defected LaMnO_3 is observed in monoclinic and rhombohedral phases [5]. The monoclinic one is observed at low temperatures and with an increase of temperature it transforms to rhombohedral structure.

The orthorhombic $Pnma$ and rhombohedral $R\bar{3}c$ both contain the monoclinic $P2_1/b$ space group, i.e. both these structures could be achieved by the transformation of monoclinic structure, which keeps the space symmetry fixed.

However, the monoclinic phase differs strongly in the distortions of oxygen $[\text{MnO}_6]$ octahedra with respect to ideal perovskite structure. The observed monoclinic phase is much closer to the rhombohedral phase, which could be achieved by the R point BZ rotation of the $[\text{MnO}_6]$ octahedra around $(1\ 1\ 1)$ direction.

The rhombohedral structure, obtained *via* the optimization of crystal energy [equation (1)] without the JT term inclusion or setting $|V_e| = 0$, is stable with respect to deformations of the crystal. The experimental and calculated structure parameters are listed in Table 2. As the temperature decreases down to about 400 K [5,8] the crystal symmetry changes to monoclinic phase. The major difference between the monoclinic and rhombohedral phases is the presence of JT distortions and a doubled primitive cell. The local values of JT distortions on different Mn^{3+} ions could be obtained *via* the projection of oxygen ions coordinates onto the normal local E_g modes of each $[\text{MnO}_6]$ octahedra (the numbering of Mn^{3+} is carried out according to Fig. 1).

$$\begin{aligned}
 Q_{\varepsilon 1} &= -\sqrt{2} \left[a \left(x_{OII} - \frac{1}{4} \right) + c \left(z_{OII} - \frac{1}{4} \right) \right] \\
 Q_{\varepsilon 2} &= -\sqrt{2} \left[a \left(x_{OIII} - \frac{1}{4} \right) + c \left(z_{OIII} - \frac{1}{4} \right) \right] \\
 Q_{\varepsilon 3} &= +\sqrt{2} \left[a \left(x_{OII} - \frac{1}{4} \right) + c \left(z_{OII} - \frac{1}{4} \right) \right] \\
 Q_{\varepsilon 4} &= +\sqrt{2} \left[a \left(x_{OIII} - \frac{1}{4} \right) + c \left(z_{OIII} - \frac{1}{4} \right) \right] \\
 Q_{\theta 1} &= +\frac{2}{\sqrt{3}} \left[by_{OI} - ax_{OI} \cos(\gamma) - \frac{c + a \sin(\gamma)}{4\sqrt{2}} \right] \\
 Q_{\theta 2} &= +\frac{2}{\sqrt{3}} \left[b \left(\frac{1}{2} - y_{OI} \right) + ax_{OI} \cos(\gamma) - \frac{c + a \sin(\gamma)}{4\sqrt{2}} \right] \\
 Q_{\theta 3} &= Q_{\theta 1} \\
 Q_{\theta 4} &= Q_{\theta 2}
 \end{aligned} \tag{8}$$

Table 2. The parameters of crystal structure of rhombohedral LaMnO_3

	a	c	O^{2-}			$r_{\text{Mn-O}}$	$\varphi_{\text{Mn-O-Mn}}$	φ_R
			x	y	z			
Calculation	5.809	13.894	0.455	0	1/4	2.054	165.6	6.2
Averaged calc.	5.837	13.911	0.451	0	1/4	2.067	163.8	6.7
Exp. [5]	5.529	13.335	0.447	0	1/4	1.967	162.7	7.3

Here we use hexagonal axes description of the $R\bar{3}c$ space group. The transformation to monoclinic and rhombohedral axes can be found in Ref. [5].

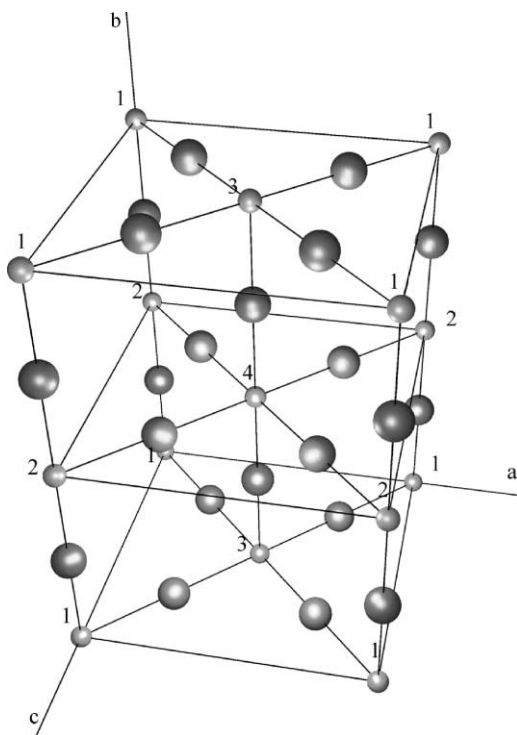


Fig. 1. The positions of different Mn^{3+} ions (small spheres) in a monoclinic phase primitive cell.

Analyzing the experimental data from Ref. [5] the following orbital structure for monoclinic phase is seen:

$$\Phi_1 \approx \pi + \Phi_2 \approx \Phi_3 \approx \pi + \Phi_4 \approx \Phi \quad (9)$$

It means that monoclinic structure is the result of freezing of E_g vibrational mode in rhombohedral structure Γ point (this mode corresponds exactly to the R_{12} mode of ideal perovskite).

The rhombohedral phase E_g vibrational mode has two components, which we denote as q_θ and q_ϵ (Fig. 2). They correspond to the local Q_θ and Q_ϵ distortions. The symmetry group of the new phase depends on the ratio of q_θ to q_ϵ . This ratio is convenient for describing by a $\tilde{\Phi}$ angle, defined as $q_\theta = \tilde{\rho} \cos \tilde{\Phi}$ and $q_\epsilon = \tilde{\rho} \sin \tilde{\Phi}$. If

$$\tilde{\Phi} = \frac{\pi}{2}; \quad \frac{\pi}{2} \pm \frac{2\pi}{3}$$

the structure will have $P2_1/b$ space symmetry, or otherwise the symmetry will be triclinic.

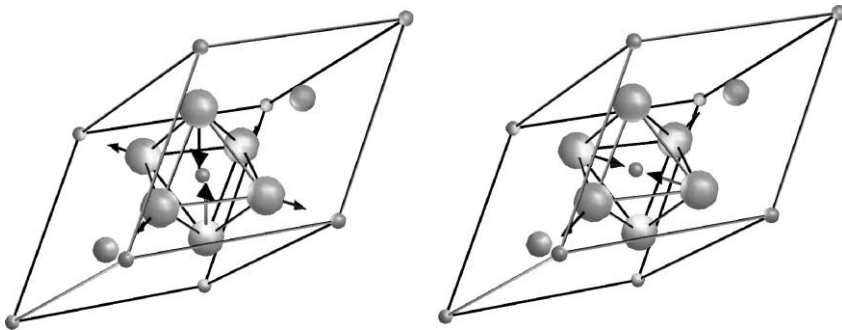


Fig. 2. The components of E_g vibrational mode (left – q_θ , right – q_ϵ).

According to the monoclinic structure analysis, the transition to monoclinic phase is the transition to static JT effect. However, the temperature of transition is small enough for this transition because the splitting of ${}^5\text{E}$ ground state of Mn^{3+} due to its effect is much greater $\Delta_{\text{JT}} = 2|V_e|\sqrt{Q_\theta^2 + Q_\epsilon^2} \approx 0.46 \text{ eV } \text{\AA}^{-1}$. That is why we suppose that, in rhombohedral phase, the JT effect is a cooperative dynamical one. For investigation of these possibilities, we calculated the ‘adiabatic potential’ for the soft E_g vibrational mode. This is the dependence of crystal energy per primitive cell on the values of q_θ and q_ϵ components. For each fixed value of q_θ and q_ϵ , the optimization of structure with respect to all possible distortions of the lowest symmetry (meaning that only inversion was retained) was performed (Table 3). However, the lattice constants were kept like those in the $R\bar{3}c$ group, i.e., only the volume and elongation in (1 1 1) direction were allowed in the optimization (such constraints do not allow for the uniform JT distortion).

The calculated dependence can be described well with the following relationship (energy per primitive cell)

$$E = \frac{k}{2}(q_\theta^2 + q_\epsilon^2) - 2|V_e|\sqrt{q_\theta^2 + q_\epsilon^2} + N(3q_\theta^2q_\epsilon - q_\epsilon^3) \quad (10)$$

where $k = 12 \text{ eV } \text{\AA}^{-2}$, $|V_e| = 1.29 \text{ eV } \text{\AA}^{-1}$ and $N = 0.0046 \text{ eV } \text{\AA}^{-3}$. Because of the small value of N , the system will perform ‘slow rotation’ at the bottom of adiabatic potential. The trajectory of motion will be approximately described by the equation $\sqrt{(q_\theta^2 + q_\epsilon^2)} = \tilde{\rho} = 2|V_e|/k$. The value of $\tilde{\rho}$ is much greater than the oxygen ions vibrational motions amplitude. We suppose that the frequency of motion at the bottom of adiabatic potential is slower than frequencies of optical phonons. Hence, an observable value that characterizes a fast process like phonons and RS must be averaged after the diagonalization of the Hamiltonian that describes them, i.e., the observable value must be calculated for each fixed value of $\tilde{\Phi}$ and averaged on the resulting dependence. On the other hand, observable values slow processes of must be obtained *via* the diagonalization of an averaged Hamiltonian, i.e., first the matrix elements of the Hamiltonian must be averaged on all values of $\tilde{\Phi}$ and after this the Hamiltonian will be diagonalized.

Table 3. The structure of monoclinic LaMnO_3 (the center of the space group is chosen as a manganese ion. The coordinates of manganese ions are $\text{MnI}(0, 0, 0)$ and $\text{MnII}(0, 1/2, 0)$)

	$T = 10 \text{ K}$ [5]	$T = 300$ [5]	$V_e = 1.29 \text{ eV \AA}^{-1}$	$V_e = 0 \text{ eV \AA}^{-1}$
a	5.462	5.469	5.751	5.718
b	7.751	7.773	8.134	8.151
c	5.522	5.525	5.851	5.809
γ	90.97	90.86	91.53	91.29
La				
x	0.503	0.504	0.5	0.5
y	0.267	0.255	0.25	0.25
z	−0.013	0.005	0.002	0
OI				
x	−0.009	−0.009	0	0
y	0.246	0.253	0.25	0.25
z	0.055	0.059	0.05	0.044
OII				
x	0.284	0.273	0.294	0.272
y	−0.033	−0.030	−0.020	−0.022
z	0.239	0.234	0.231	0.227
OIII				
x	0.224	0.231	0.206	0.227
y	0.537	0.528	0.520	0.522
z	0.257	0.276	0.269	0.272
$Q_{\varepsilon 1}$	0.176	−0.052	0.211	0
$Q_{\varepsilon 2}$	−0.146	−0.056	−0.211	0
$Q_{\theta 1}$	−0.041	0.026	−0.026	0
$Q_{\theta 2}$	0.032	−0.026	−0.026	0
ρ_1	0.180	0.058	0.212	0
ρ_2	0.149	0.061	0.212	0
Φ_1	103.1	−	97.1	−
Φ_2	−77.6	−	−82.9	−

3.1. Raman scattering in rhombohedral LaMnO_3

As mentioned by Iliev and coworkers [1,2], the Raman spectra of rhombohedral LaMnO_3 differs strongly from RS of non-JT LaAlO_3 , which has a similar structure to that of the $R\bar{3}c$ space group.

From the symmetry analysis we know that in the $R\bar{3}c$ space group only five modes are active in RS ($A_{1g} + 4E_g$). The experiment on LaAlO_3 [1] clearly shows four Raman active modes and one that has a very low frequency of 33 cm^{-1} was also observed [9]. Comparing the RS of rhombohedral LaMnO_3 one should note the strong distinction to RS of LaAlO_3 . The main difference is the appearance of a new

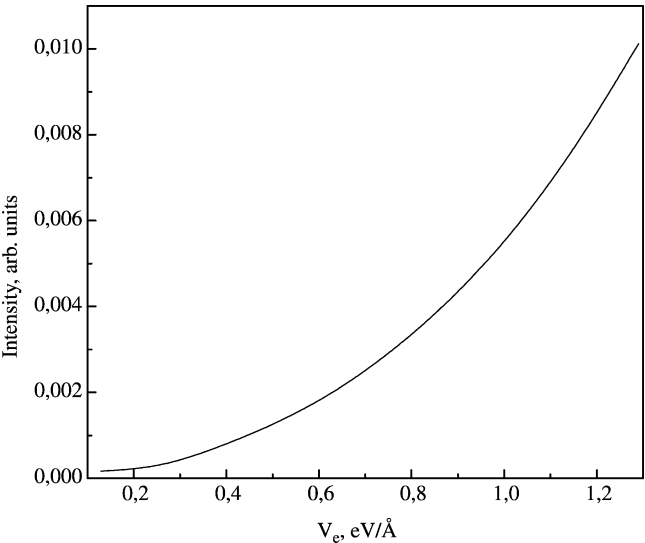


Fig. 3. The dependence of intensity of highest A_{2g} (in rhombohedral phase notation) mode on the value of $|V_e|$. The frequency and intensity were averaged on $\tilde{\Phi}$ for the value of $\tilde{\rho}$, which corresponds to the energy minimum. For each value of $\tilde{\Phi}$ the ions were ‘relaxed’ according to the scheme described in the text.

Table 4. RS lines frequencies

Mode	LaAlO ₃ ^a	LaMnO ₃ ^b	LaMnO ₃ ^a	LaMnO ₃ ^c	LaMnO ₃ ^d
E_g	33	39	—	—	61 74
A_{2g}	—	144	—	—	142
E_g	180	172	179	—	168 177
A_{1g}	123	223	236	217	235
A_{2g}	—	261	—	—	261
E_g	152	312	329	323	314 322
E_g	487	468	515	427 497	— ^e 478
A_{2g}	—	580	640	618	584

^aThe experimental values are taken from Ref. [1]. An assignment is carried out according to our intensities calculations.

^bThe calculated frequencies without the JT term in crystal energy and dynamical matrix ($R\bar{3}c$ space group).

^cThe experimental values are taken from Ref. [2].

^dAn average of the AP bottom RS frequencies.

^eThis mode corresponds to the motion along the bottom of adiabatical potential and obtaining the frequency of it will require separate consideration.

intensive high-frequency line near 640 cm^{-1} and relative increase of intensities of high frequency lines. The appearance of a new RS line is clear evidence for lowering symmetry, i.e., that the real space symmetry of rhombohedral LaMnO_3 is lower than $R\bar{3}c$. The symmetry lowering could be due to the cooperative JT effect.

For verification of such an assumption, we calculated the dependence of intensity of the highest A_{2g} (the symmetry in $R\bar{3}c$ structure) vibration on the value of $|V_e|$ we calculated the $\bar{\rho}$ that corresponds to the energy minimum (the bottom of adiabatic potential). For this value of $\bar{\rho}$ the phonon frequencies and RS lines intensity were averaged over all values of $\tilde{\Phi}$ (Fig. 3).

Because of the low symmetry at each point of trajectory after averaging the phonon frequencies of E_g , symmetry are split (Table 4). However, the value of gap is rather small to see distinct lines. That is why such splitting could give rise to the broadening of the Raman line, which was observed in experimental work [1,2].

3.2. Magnetic interactions in rhombohedral LaMnO_3

The rhombohedral manganites are known to be ferromagnetic (FM). The main origin of FM interactions is the double exchange mechanism, which is due to the presence of charge carriers [10]. However, the amount of charge carriers is relatively small in pure and slightly defected LaMnO_3 . That is why we suppose that not just double exchange could contribute to the FM interactions in rhombohedral LaMnO_3 . For the investigation of superexchange mechanism in the case of dynamical cooperative JT effect, we use the slow process averaging scheme. The description of orbital dependence of superexchange is used from the approximation in Refs. [11,12].

Let us consider a fixed value of $\tilde{\Phi}$ parameter. Hence, the values of local orbital angles are well defined. In this case the superexchange interaction for the pair of JT ions can be written as follows [12]:

$$\begin{aligned}
 J^{z_p}(n, k) &= J_0^{nk} [1 + \alpha(\cos \Phi_n + \cos \Phi_k) + \beta \cos \Phi_n \cos \Phi_k] \\
 J^{x_p(y_p)}(n, m) &= J_0^{nm} \left[1 - \frac{1}{2} \alpha((\cos \Phi_n \pm \sqrt{3} \sin \Phi_n) + (\cos \Phi_m \pm \sqrt{3} \sin \Phi_m)) \right. \\
 &\quad \left. + \frac{1}{4} \beta(\cos \Phi_n \pm \sqrt{3} \sin \Phi_n)(\cos \Phi_m \pm \sqrt{3} \sin \Phi_m) \right] \quad (11)
 \end{aligned}$$

where n, m and k index the ions, and z_p, x_p and y_p denote the pseudoperovskite axes. The orbital independent part J_0 can be written as:

$$J_0^{nk} = \frac{J_0 \cos^2 \varphi_{nk}}{r_{nk}^{10}} \quad (12)$$

where φ_{nk} is the $\text{Mn}_n^{3+}-\text{O}^{2-}-\text{Mn}_k^{3+}$ angle, and r_{nk} is the distance between Mn^{3+} ions with numbers n and k . For the frozen R_{12} mode the exchange parameters are:

$$\begin{aligned} J^z_p(\tilde{\Phi}) &= J_0[1 - \beta \cos^2 \tilde{\Phi}] \\ J^{x_p(y_p)}(\tilde{\Phi}) &= J_0 \left[1 - \frac{1}{4} \beta (\cos \tilde{\Phi} \pm \sqrt{3} \sin \tilde{\Phi})^2 \right] \end{aligned} \quad (13)$$

After averaging all the values of $\tilde{\Phi}$ we get:

$$J^z_p = J_0 \left[1 - \frac{1}{2} \beta \right] \quad J^{x_p(y_p)} = J_0 \left[1 - \frac{1}{2} \beta \right] \quad (14)$$

Using $\beta \approx 4.9$ [11], we get the negative sign of exchange parameters in all cubic directions, which means the FM interaction in rhombohedral LaMnO₃.

4. CONCLUSION

The assumption of cooperative dynamical JT effect in rhombohedral LaMnO₃ can be illustrated as follows:

- The transition from rhombohedral to monoclinic phase is, in fact, the freezing of Γ BZ point E_g vibrational mode of $R\bar{3}c$ space group or R BZ point R_{12} ideal perovskite mode. This vibration is double degenerate and the relation between components in transition corresponds to $\tilde{\Phi} \approx \pi/2$.
- The simulation of monoclinic phase shows that only the JT interaction could give rise to this phase. In the case when $|V_e| = 0$ the monoclinic phase transforms to rhombohedral.
- The temperature of transition is small relative to the value of splitting of the $\text{Mn}^{3+} {}^5E$ ground state. That is why we suppose that the transition from monoclinic to rhombohedral phase is a transition from static to dynamic JT effect. Because of the strong correlation in motion of different $[\text{MnO}_6]$ octahedra we suppose that there is a cooperative dynamical effect.
- In the framework of approximation of cooperative dynamical effect, the appearance of a new high frequency RS line in rhombohedral LaMnO₃ can be explained.
- As a result of averaging of orbital structure angle due to cooperative dynamical effect, the FM interactions just due to superexchange can appear in rhombohedral manganites.

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REFERENCES

- [1] M. V. Abrashev, A. P. Litvinchuk, M. N. Iliev, R. L. Meng, V. N. Popov, V. G. Ivanov, R. A. Chakalov and C. Thomsen, *Phys. Rev.*, 1999, **B59**, 4146.
- [2] M. N. Iliev and M. V. Abrashev, *J. Raman Spectrosc.*, 2001, **32**, 805.
- [3] A. Urushibara, Y. Morimoto, T. Arima, A. Asamitsu, G. Kido and Y. Tokura, *Phys. Rev.*, 1995, **B51**, 14103.
- [4] A. J. Millis, P. B. Littlewood and B. I. Shraiman, *Phys. Rev. Lett.*, 1995, **74**, 5144; J. B. Goodenough, A. Wold, R. J. Arnett and N. Menyuk, *Phys. Rev.*, 1961, **124**, 373.
- [5] Q. Huang, A. Santoro, J. W. Lynn, R. W. Erwin, J. A. Borchers, J. L. Peng and R. L. Greene, *Phys. Rev.*, 1997, **B55**, 14987.
- [6] A. E. Nikiforov and S. Y. Shashkin, *Phys. Solid State*, 1997, **38**, 3446.
- [7] A. E. Nikiforov and S. E. Popov, *Phys. Solid State*, 2001, **43**, 1132.
- [8] J. F. Mitchell, D. N. Argyriou, C. D. Potter, D. G. Hinks, J. D. Jorgensen and S. D. Bader, *Phys. Rev.*, 1996, **54**, 6172.
- [9] J. F. Scott, *Phys. Rev.*, 1969, **183**, 823.
- [10] C. Zener, *Phys. Rev.*, 1951, **82**, 403.
- [11] L. E. Gonchar and A. E. Nikiforov, *Solid State Phys.*, 2000, **42**, 1070.
- [12] L. E. Gontchar, A. E. Nikiforov and S. E. Popov, *JMMM*, 2001, **223**, 175.

First-order Phase Transition in UO_2 : The Interplay of the $5f^2-5f^2$ Superexchange Interaction and Jahn–Teller Effect

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Abstract

The competition of the superexchange interaction and the cooperative Jahn–Teller (JT) effect in the first-order magnetic and structural phase transition in UO_2 is analyzed. The effective spin Hamiltonian of the superexchange interaction between the neighboring U^{4+} ions in the cubic crystal lattice of UO_2 is calculated for the first time in terms of a specially adapted kinetic exchange model. The $5f^2-5f^2$ superexchange interaction is shown to be essentially non-Heisenberg: the effective spin Hamiltonian is anisotropic and contains large biquadratic terms, which formally correspond to a quadrupole–quadrupole interaction. The strength of the JT effect in UO_2 is estimated from the calculations of the linear vibronic coupling constants between the local e_g , $t_{2g}(1)$ and $t_{2g}(2)$ JT modes and the Γ_5 ground state of U^{4+} performed in terms of a semiempirical crystal field model for 5f electrons. Despite the $\Gamma_5 \otimes e_g$ and $\Gamma_5 \otimes t_{2g}(2)$ parameters are found to be much larger than $\Gamma_5 \otimes t_{2g}(1)$, the actual lattice distortion in UO_2 is of a pure $t_{2g}(1)$ character. Our results indicate that the superexchange interaction is the major driving force of the phase transition in UO_2 , which causes the magnetic and orbital ordering and suppresses the cooperative JT effect.

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1. INTRODUCTION

Being important as a nuclear fuel, uranium dioxide is one of the most frequently studied actinide compounds, which was thoroughly characterized using various experimental techniques [1–12]. UO_2 is an insulator or ionically bonded semiconductor crystallizing in the fcc fluorite structure with lattice constant $a_0 = 5.470 \text{ \AA}$ at room temperature. This is a stoichiometric compound involving tetravalent uranium ions with the $5f^2$ levels lying in a 6 eV band gap. Each U^{4+} ion is surrounded by eight oxygen atoms forming a cubic cage (Fig. 1). In such a surrounding, the ground state of U^{4+} ions is the Γ_5 triplet which, apart from being correspondent to the effective spin $S = 1$, is also a Jahn–Teller active state. The UO_2 crystal represents therefore a magnetic insulator and cooperative Jahn–Teller system, which has a rich collection of unusual electronic and magnetic properties at low temperature.

Uranium dioxide undergoes first-order phase transitions at $T_N = 30.8 \text{ K}$ [1]. Despite extensive studies for more than thirty years, many details of the basic mechanism of this phenomenon are still unclear. Below T_N a magnetic ordering and lattice distortions simultaneously appear. Earlier studies suggested a usual collinear single- $\mathbf{k}$ antiferromagnetic ordering [1–3], but more recent studies showed that the magnetic structure of UO_2 is much more complicated [4–6]. It was finally established from the analysis of numerous neutron diffraction experiments [5,6] and ^{235}U NMR data [12] that the magnetic ordering is best described by so-called triple- $\mathbf{k}$ structure, which is determined by the sum of the Fourier components corresponding to the three wave vectors $(1,0,0)$, $(0,1,0)$, and $(0,0,1)$ [6–8]

$$\begin{aligned} M_x &= M_0 \exp\left(i \frac{2\pi}{a} y\right), & M_y &= M_0 \exp\left(i \frac{2\pi}{a} z\right), \\ M_z &= M_0 \exp\left(i \frac{2\pi}{a} x\right) \end{aligned} \quad (1)$$

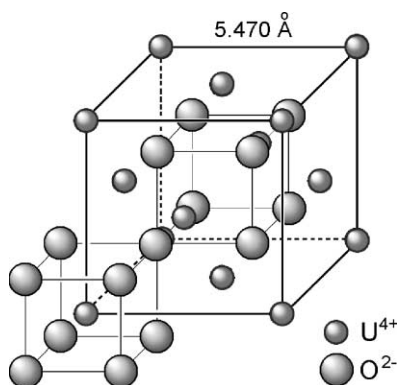


Fig. 1. The fcc fluorite structure of UO_2 .

where M_x , M_y , and M_z are the components of the localized magnetic moment on the uranium center with (x, y, z) coordinates. The corresponding $3\text{-}\mathbf{k}$ spin structure is non-collinear (Fig. 2). The magnetic moments of U^{4+} ions are directed along one of the space diagonals $\langle 111 \rangle$ so that the total magnetic moment of the cubic unit cell is zero.

It is important that the ordered moment at low temperature is considerably smaller ($1.74 \mu_B/\text{U}$) than the effective paramagnetic moment, $\sim 3 \mu_B/\text{U}$.

The magnetic ordering is accompanied by a lattice distortion, which also has a triple- $\mathbf{k}$ character

$$\begin{aligned} \delta_x &= b_0 \exp\left(i \frac{2\pi}{a} y\right), & \delta_y &= b_0 \exp\left(i \frac{2\pi}{a} z\right), & \delta_z &= b_0 \exp\left(i \frac{2\pi}{a} x\right), \\ b_0 &= \frac{\delta}{\sqrt{3}} \end{aligned} \quad (2)$$

Oxygen atoms shift by $\delta = 0.014 \text{ \AA}$ from the equilibrium positions towards the uranium ions, which remain fixed. In each UO_8 cubic cage, the central U^{4+} ion attracts two oxygen atoms lying in the $\langle 111 \rangle$ space diagonal along which the magnetic moment of U^{4+} is directed (Fig. 3). As a result, the lattice symmetry remains cubic and the unit cell volume does not change in the ordered phase.

Since the components of the Γ_5 triplet have different spatial charge density distributions, the magnetic ordering in UO_2 is followed by some orbital ordering and lattice distortions. The latter are usually associated with the cooperative Jahn–Teller effect and/or quadrupole–quadrupole (Q – Q) interaction [7,8]. It is important to note that in systems with a strong spin–orbit coupling the JT cooperative effect and exchange interactions are antagonists since the JT effect tends to stabilize a state

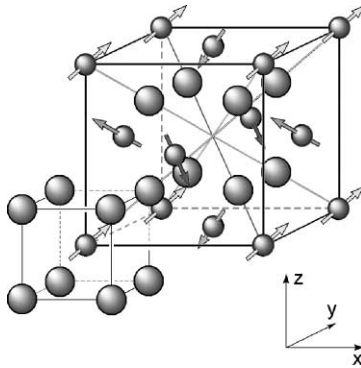


Fig. 2. The $3\text{-}\mathbf{k}$ magnetic ordering in UO_2 below $T_N = 30.8 \text{ K}$. The magnetic moments of U^{4+} are directed along one of the space diagonals $\langle 111 \rangle$ of the cubic unit cell, as described by equation (1).

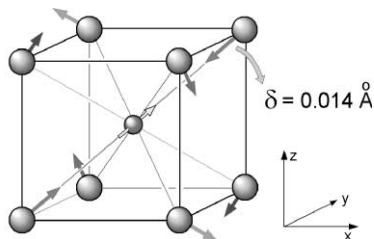


Fig. 3. The 3-**k** structure of the distortion of the UO_8 cubic cage below T_N . The central uranium ion attracts those two oxygen atom of the given cubic cage, to which its magnetic moment points. The amplitude of the displacements is as small as 0.014 Å (about 0.5% of the U–O distance). The other six oxygen atoms are attracted by uranium ions from neighboring cages.

with the quenched orbital momentum on each metal ion while the exchange interactions acts in a just opposite direction, i.e., it tends to stabilize a state with the maximum orbital momentum (which is strongly coupled with the spin *via* the spin–orbit interaction). Another feature is a very strong spin-lattice coupling in UO_2 observed experimentally in inelastic neutron scattering spectra [4–6]. The case of UO_2 is therefore quite different from the case of orbitally degenerate 3d systems (such as RMnO_3 manganites), in which magnetic ordering and orbital ordering can act independently because the orbital momentum and spin are weakly coupled to each other. The magnetic structure and lattice distortions in the low-temperature phase of UO_2 are therefore determined by a complicated interplay of the magnetic coupling between U^{4+} ions and the cooperative JT effect.

The question therefore arises as to which of these interactions dominate in UO_2 . It is important to note that, despite extensive studies for more than thirty years, there is still very little known about the actual mechanism of the U^{4+} – U^{4+} exchange interaction and the strength of the vibronic coupling in UO_2 . No satisfactory theoretical explanation of the origin of the 3-**k** magnetic and lattice distortion structure below T_N is available. It is recognized that the 3-**k** magnetic structure, lattice distortions, and magnon spectra in UO_2 cannot be accounted for in terms of the conventional isotropic exchange model [5,6]. On the other hand, since the spin on the U^{4+} ion is strongly coupled with its orbital momentum, the spin is not a good quantum number and thus the U^{4+} – U^{4+} spin coupling is expected to be essentially non-Heisenberg.

The aim of this work is to elucidate these problems. To this end, we calculate the effective spin Hamiltonian of the $5f^2$ – $5f^2$ superexchange interaction between the neighboring U^{4+} ions in the cubic crystal lattice of UO_2 and we calculate $\Gamma_5 \otimes e_g$, $\Gamma_5 \otimes t_{2g}(1)$ and $\Gamma_5 \otimes t_{2g}(2)$ linear vibronic coupling constants. These data are then used to draw a more definite conclusion about the driving force of the phase transition and especially about the actual mechanism of the spin and orbital ordering in UO_2 .

2. SUPEREXCHANGE INTERACTION BETWEEN U^{4+} IONS IN UO_2

2.1. Crystal field effect and the ground state of U^{4+} ions in UO_2

Since the Γ_5 ground electronic state of U^{4+} ions plays a very important role in the magnetic ordering and lattice distortions in UO_2 , we give here necessary details concerning the origin of this state. The U^{4+} ion is characterized by a strong spin–orbit interaction with the spin–orbit coupling constant of $\zeta_{5f} \approx 1800 \text{ cm}^{-1}$. The lowest ^3H term of the free U^{4+} ion ($5f^2$ configuration) is split by the spin–orbit interaction into the ground $^3\text{H}_4$ multiplet and excited $^3\text{H}_5$ and $^3\text{H}_6$ multiplets (Fig. 4). The total spin–orbit splitting of the lowest ^3H term is about $10\,000 \text{ cm}^{-1}$; this means that the spin and orbital momentum of U^{4+} are strongly coupled to each other.

In the cubic crystalline surrounding, the ground $^3\text{H}_4$ multiplet is split into four individual CF levels, the ground Γ_5 triplet, excited Γ_3 doublet, Γ_4 triplet, and the upper Γ_1 singlet; their energies are shown in Fig. 5 [6]. The ground state is separated by a large gap from the first excited CF state. Note that the total CF splitting of the $^3\text{H}_4$ multiplet is much smaller than the spin–orbit splitting of the lowest ^3H term of the $5f^2$ configuration, 1400 and $10\,000 \text{ cm}^{-1}$, respectively. Detailed CF calculations show that the wave functions of the Γ_5 triplet are of almost pure $^3\text{H}_4$ character. They can be written as

$$|\Gamma_5, -1\rangle = \sqrt{\frac{7}{8}} |^3\text{H}_4, -3\rangle - \sqrt{\frac{1}{8}} |^3\text{H}_4, +1\rangle \quad (3a)$$

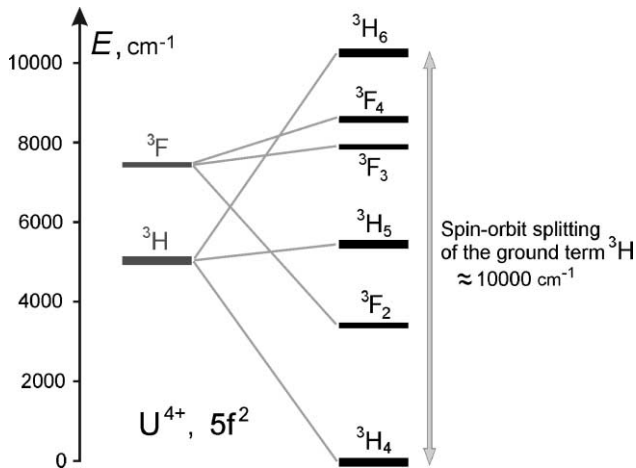


Fig. 4. The scheme of low-lying multiplets of the free U^{4+} ion. The total spin–orbit splitting of the lowest ^3H is about $10\,000 \text{ cm}^{-1}$. The energy levels are given in the actual energy scale.

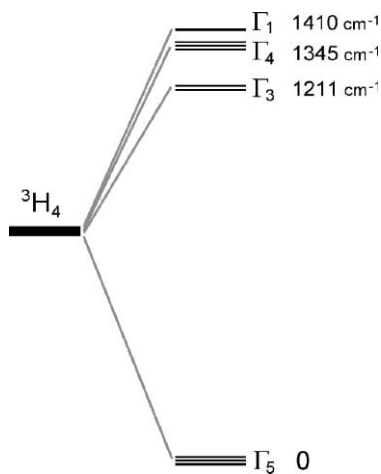


Fig. 5. Crystal field splitting of the ground $^3H_4$ multiplet of the U^{4+} ion in UO_2 . The ground CF state of U^{4+} is a well-isolated Γ_5 triplet.

$$|\Gamma_5, 0\rangle = \sqrt{\frac{1}{2}} |^3H_4, +2\rangle - \sqrt{\frac{1}{2}} |^3H_4, -2\rangle \quad (3b)$$

$$|\Gamma_5, +1\rangle = \sqrt{\frac{7}{8}} |^3H_4, +3\rangle - \sqrt{\frac{1}{8}} |^3H_4, -1\rangle \quad (3c)$$

This means that the total spin of the U^{4+} ion is not a good quantum number since it is antiparallely coupled with the orbital momentum. The Γ_5 triplet represents therefore an effective spin $S = 1$. In addition, this is a JT active state (the T term case) since its components $|\Gamma_5, m\rangle$ (1a)–(1c) have different charge density distributions.

2.2. The mechanism of the $5f^2$ – $5f^2$ superexchange interaction

The exchange interaction between the neighboring U^{4+} ions in the cubic lattice of UO_2 (Fig. 6) is analyzed in the frame of the Anderson kinetic exchange theory [13]. However, since this theory in its conventional form cannot directly be applied to the analysis of non-Heisenberg exchange interactions between the U^{4+} ions with the Γ_5 ground state, we use a modified kinetic exchange theory. In our approach, the $U^{4+}(A) \rightarrow U^{4+}(B)$ metal-to-metal electron transfers through the bridging oxygen atoms are analyzed in terms of individual many-electron states of the $5f^2$ – $5f^2$ basic configuration and $5f^1$ – $5f^3$ charge-transfer (CT) configuration of a separate $U^{4+}(A)$ – $U^{4+}(B)$ pair, rather than in terms of one-electron states. The wave functions $|m_1, m_2\rangle$ of the ground $\Gamma_5(A)$ – $\Gamma_5(B)$ level of the $U^{4+}(A)$ – $U^{4+}(B)$ pair (which is 9-fold

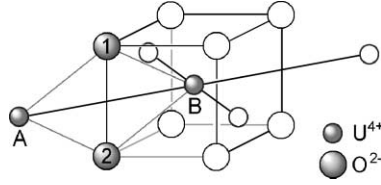


Fig. 6. The geometry of the exchange-coupled pair for two the neighboring U^{4+} ions in the crystal lattice of UO_2 . The local symmetry of the neighboring $\text{U}^{4+}(\text{A})-\text{U}^{4+}(\text{B})$ exchange pair is D_{2h} .

degenerate in the absence of exchange interactions) are written as direct antisymmetrized products of the corresponding many-electron wave functions of the $\text{U}^{4+}(\text{A})$ and $\text{U}^{4+}(\text{B})$ ions

$$|m_1, m_2\rangle = |\Gamma_5(\text{A}), m_1\rangle \otimes |\Gamma_5(\text{B}), m_2\rangle \quad (4)$$

where m_1 and m_2 are the projections of the effective spin $S = 1 (m_{1,2} = 0, \pm 1)$ of the ions $\text{U}^{4+}(\text{A})$ and $\text{U}^{4+}(\text{B})$. Similarly, the wave functions Ψ_n^{CT} of CT many-electron states are written as products of single-ion wave functions of the U(A) and U(B) centers with one missing or extra electron

$$\Psi_n^{\text{CT}}(\text{A} \rightarrow \text{B}) = \Xi_i^{\text{U}(\text{A})}(5f^1) \otimes \Xi_j^{\text{U}(\text{B})}(5f^3) \quad (5)$$

$$\Psi_n^{\text{CT}}(\text{A} \leftarrow \text{B}) = \Xi_i^{\text{U}(\text{A})}(5f^3) \otimes \Xi_j^{\text{U}(\text{B})}(5f^1) \quad (6)$$

In this representation, electron transfers between metal centers are described as $|m_1, m_2\rangle \rightarrow \Psi_n^{\text{CT}} \rightarrow |m'_1, m'_2\rangle$ transitions between the ground and CT many-electron states. Their amplitude is described by the $\langle m_1, m_2 | V_{\text{AB}} | \Psi_n^{\text{CT}} \rangle$ matrix elements of the effective one-electron operator V_{AB} , which is specified by one-electron matrix elements t_{ij} , i.e., transfer integrals connecting $5f_i(\text{A})$ and $5f_j(\text{B})$ orbitals. The $\langle m_1, m_2 | V_{\text{AB}} | \Psi_n^{\text{CT}} \rangle$ matrix elements can directly be expressed *via* the t_{ij} transfer parameters. For this, wave functions of the basic $5f^2$ configurations and $5f^1$ and $5f^3$ CT configurations of uranium ions are expanded over Slater determinants. Details of these calculations are given in Ref. [16]. The effective exchange Hamiltonian H_{eff} is obtained by the projection of CT states onto the space of the $|m_1, m_2\rangle$ wave functions of the ground level. It is completely specified by the set of the $\langle m_1, m_2 | H_{\text{eff}} | m'_1, m'_2 \rangle$ matrix elements, which are obtained from the second-order perturbation equation

$$\langle m_1, m_2 | H_{\text{eff}} | m'_1, m'_2 \rangle = - \sum_{\Psi_n^{\text{CT}}} \frac{\langle m_1, m_2 | V_{\text{AB}} | \Psi_n^{\text{CT}} \rangle \langle \Psi_n^{\text{CT}} | V_{\text{AB}} | m'_1, m'_2 \rangle}{E(\Psi_n^{\text{CT}})} \quad (7)$$

where the sum runs over all Ψ_n^{CT} states of the $\text{U}^{4+}(\text{A})-\text{U}^{4+}(\text{B})$ pair resulting from the $\text{U}(\text{A}) \rightarrow \text{U}(\text{B})$ and $\text{U}(\text{A}) \leftarrow \text{U}(\text{B})$ electron transfers, and $E(\Psi_n^{\text{CT}})$ is the corresponding CT energy. As shown below, the H_{eff} operator can easily be transformed

to the conventional spin Hamiltonian. The CT energies can be written as

$$E(\Psi_n^{\text{CT}}) = U_0 + E_p(5f^1) + E_q(5f^3) \quad (8)$$

where U_0 is the CT energy gap that separates the ground $\Gamma_5-\Gamma_5$ state of the basic $5f^2-5f^2$ configuration from the lowest state of the excited $5f^1-5f^3$ CT configuration of the $U^{4+}(\text{A})-U^{4+}(\text{B})$ pair (Fig. 7) (which is set to $U_0 = 10$ eV in our calculations), and $E_p(5f^1)$ and $E_q(5f^3)$ are the energies of individual states of the $5f^1$ and $5f^3$ configurations of uranium ions with one missed and one extra

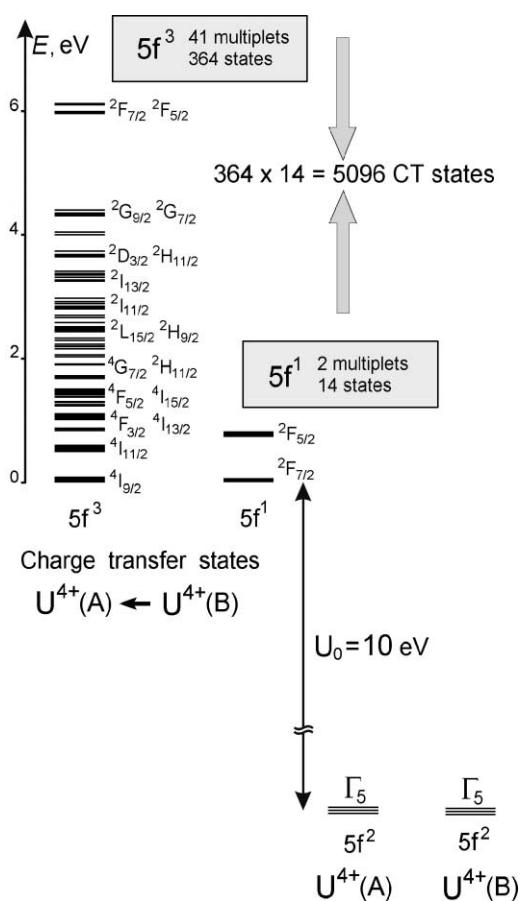


Fig. 7. The energy spectrum of CT states of the $U^{4+}(\text{A})-U^{4+}(\text{B})$ pair. The ground $\Gamma_5-\Gamma_5$ state of the basic $5f^2-5f^2$ configuration is separated from the lowest state of the excited $5f^1-5f^3$ CT configuration of the $U^{4+}(\text{A})-U^{4+}(\text{B})$ pair by a gap of U_0 , which is set to 10 eV.

electron, respectively. The total number of the CT states is given by the product of the numbers of states of the $5f^2$ (14) and $5f^3$ (364), i.e., a total of 5096 (Fig. 7).

It is important to take into account the actual energy spectrum of CT states of the $\text{U}^{4+}(\text{A})-\text{U}^{4+}(\text{B})$ pair since the total energy spacing of the $5f^1-5f^3$ CT configuration (about 7 eV) is comparable with the CT gap, $U_0 = 10$ eV (Fig. 7).

Because analytical calculations using equation (7) are impossible, a special routine for numerical calculations of the spin Hamiltonian exchange parameters was designed (see Ref. [16] for details). In these calculations, the one-centers Hamiltonians of the $5f^1$, $5f^2$, and $5f^3$ configurations of uranium ions were explicitly diagonalized using the actual free-ion parameters ($F^2 = 43\,100$, $F^4 = 41\,000$, $F^6 = 23\,800$, and $\zeta_{5f} = 1780\text{ cm}^{-1}$) and cubic crystal-field parameters [6].

Transfer integrals $t_{ij} = \langle 5f_i(\text{A}) | V_{\text{AB}} | 5f_j(\text{B}) \rangle$ describing the virtual transfers of an electron between the $\text{U}^{4+}(\text{A})$ and $\text{U}^{4+}(\text{B})$ ions *via* the bridging oxygen atoms were calculated using the conventional second-order perturbation expression corresponding to the case of weak metal–ligand covalence

$$t_{ij} = - \sum_n \sum_{\chi_k(n)} \frac{\langle 5f_i(\text{A}) | h | \chi_k(n) \rangle \langle \chi_k(n) | h | 5f_j(\text{B}) \rangle}{E(\chi_k(n)) - E(5f)} \quad (9)$$

where the first sum runs over the two bridging oxygen atoms $\text{O}(n)$ ($n = 1, 2$) and the second sum runs over the $2p$ and $2s$ orbitals $\chi_k(n)$ of these atoms. Matrix elements of the Fock operator h are resonance integrals connecting $5f_i$ orbitals of the uranium ions and $\chi_k(n)$ orbitals of the bridging oxygen atoms. The energy denominator is a ligand-to-metal promotion energy, which is given by the difference of the corresponding orbital energies. In the D_{2h} geometry of the $\text{U}^{4+}(\text{A})-\text{U}^{4+}(\text{B})$ pair (Fig. 6), the resonance integrals entering equation (9) can be expressed analytically *via* three parameters, $\sigma(\text{fp})$, $\pi(\text{fp})$, and $\sigma(\text{fs})$, corresponding to the resonance integrals defined with respect to a local U–O bond: $\sigma(\text{fp}) = \langle 5f_0 | h | 2p_0 \rangle$, $\pi(\text{fp}) = \langle 5f_{\pm 1} | h | 2p_{\pm 1} \rangle$, and $\sigma(\text{fs}) = \langle 5f_0 | h | 2s \rangle$, where $5f_k$ are uranium and $2p_k$, $2s$ are oxygen orbitals with the projection k of the orbital momentum on the metal–ligand axis ($k = 0, \pm 1$ for $2p$ and $k = 0$ for $2s$). For each of the two $\text{U}(\text{A})-\text{O}(n)-\text{U}(\text{B})$ bridges, the products $\langle 5f_i(\text{A}) | h | 2p_k \rangle \langle 2p_k | h | 5f_j(\text{B}) \rangle$ in the nominator of equation (8) can be written as some linear combinations of binary products of the $\sigma(\text{fp})$ and $\pi(\text{fp})$ parameters (Fig. 8). The coefficients in these combinations correspond to the expansion of atomic orbitals defined in the local coordinate frame of a given metal–ligand pair over orbitals defined with respect to a common coordination frame; they can be written *via* the Wigner D -functions, as described in Ref. [16].

The $\sigma(\text{fp})$, $\pi(\text{fp})$, and $\sigma(\text{fs})$ quantities can be calculated using the Wolfsberg–Helmholz formula [17]

$$\sigma(\text{fp}) = \langle 5f_0 | h | 2p_0 \rangle = [E(5f) + E(2p)]S_{\sigma}(5f, 2p) \quad (10a)$$

$$\pi(\text{fp}) = \langle 4f_{\pm 1} | h | 4p_{\pm 1} \rangle = [E(5f) + E(2p)]S_{\pi}(5f, 2p) \quad (10b)$$

$$\sigma(\text{fs}) = \langle 5f_0 | h | 2s \rangle = [E(5f) + E(2s)]S_{\sigma}(5f, 2s) \quad (10c)$$

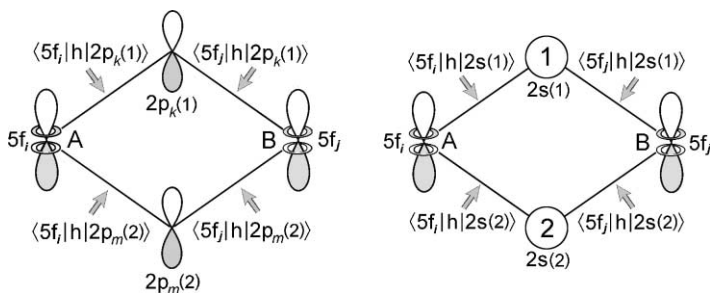


Fig. 8. Indirect interactions of $5f_i(A)$ and $5f_j(B)$ orbitals *via* the 2p and 2s orbitals of two bridging oxygen atoms.

where $S_\sigma(5f, 2p)$, $S_\pi(5f, 2p)$, and $S_\sigma(5f, 2s)$ are σ and π overlap integrals between the respective metal and ligand orbitals. These overlap integrals are calculated using the U 5f and O 2p and 2s radial wave functions reported in Ref. [18] and Ref. [19], respectively. Using the U 5f and O 2p, 2s orbital energies [18,19], we calculated the set of the t_{ij} transfer integrals.

With these data, we calculated numerically the $\langle m_1, m_2 | H_{\text{eff}} | m'_1, m'_2 \rangle$ matrix elements of the effective exchange Hamiltonian, which are presented in Table 1. Each group of matrix elements can be associated with a definite equivalent spin operator, which has the same matrix elements in the $|m_1, m_2\rangle$ basis set as those obtained from equation (7). The symmetry of these spin operators corresponds to the local symmetry of the $U^{4+}(A)-U^{4+}(B)$ exchange pair (D_{2h} , Fig. 6). Collecting all the spin operators listed in Table 1, we arrive at the total effective spin Hamiltonian, in which the spin terms are divided into several groups:

$$H = A_0 + H_1 + H_2 + H_3 + H_4 \quad (11)$$

Here A_0 is the spin-independent part, $A_0 = -56.4 \text{ cm}^{-1}$. H_1 represents the one-center spin terms, which may be called exchange-induced zero-field splitting of the Γ_5 state

$$H_1 = D[(S_A^z)^2 + (S_B^z)^2] + E[(S_A^x)^2 - (S_A^y)^2 + (S_B^x)^2 - (S_B^z)^2] \quad (12)$$

where $D = -4.6 \text{ cm}^{-1}$ and $E = 5.2 \text{ cm}^{-1}$. H_2 is the bilinear part of the spin Hamiltonian

$$H_2 = J_x S_A^x S_B^x + J_y S_A^y S_B^y + J_z S_A^z S_B^z \quad (13)$$

with the exchange parameters $J_x = 14.7$, $J_y = 22.1$, and $J_z = 18.8 \text{ cm}^{-1}$. The orientations of the local spin quantization axes x , y , and z of the $U^{4+}(A)-U^{4+}(B)$ pair is shown in Fig. 9. The bilinear part of the $5f^2-5f^2$ superexchange interaction has therefore a pronounced exchange anisotropy and corresponds to an

Table 1. Non-zero $\langle m_1, m_2 | H_{\text{eff}} | m_3, m_4 \rangle$ matrix elements of the effective exchange Hamiltonian and the equivalent spin operators (all parameters are in cm^{-1})

$\langle m_1, m_2 H_{\text{eff}} m'_1, m'_2 \rangle$					Equivalent spin operator
m_1	m_2	m'_1	m'_2		
-1	-1	-1	-1	-47.29	$C + c_1[(S_A^z)^2 + (S_B^z)^2]$ $+ c_2 S_A^z S_B^z + c_3 (S_A^z)^2 (S_B^z)^2$
1	1	1	1	-47.29	
-1	0	-1	0	-62.13	$C = -56.39$ $c_1 = -5.74$ $c_2 = 18.81$ $c_3 = 1.77$
0	-1	0	-1	-62.13	
0	1	0	1	-62.13	
1	0	1	0	-62.13	
0	0	0	0	-56.39	
-1	1	-1	1	-84.92	
-1	1	-1	1	-84.92	
-1	-1	-1	1	+5.17	$[(S_A^+)^2 + (S_A^-)^2][a_1 + b_1 (S_B^z)^2]$ $+ [(S_B^+)^2 + (S_B^-)^2][a_1 + b_1 (S_A^z)^2]$
-1	-1	1	-1	+5.17	
-1	1	-1	-1	+5.17	$a_1 = 2.69$ $b_1 = 0.11$
1	1	1	1	+5.17	
1	-1	-1	-1	+5.17	
1	-1	1	1	+5.17	
1	1	-1	1	+5.17	
-1	1	1	-1	+5.38	
0	0	1	0	+5.38	
0	-1	0	1	+5.38	
1	1	0	-1	+5.38	
0	0	-1	0	+5.38	
-1	0	0	-1	+18.40	$(S_A^+ S_B^- + S_A^- S_B^+)[a_2 + b_2 (S_A^z + S_B^z)^2]$
0	-1	-1	0	+18.40	
0	1	1	0	+18.40	$a_2 = 9.18$ $b_2 = 0.19$
1	0	0	1	+18.40	
-1	1	0	0	+18.37	
0	0	-1	1	+18.37	
0	0	1	-1	+18.37	
1	-1	0	0	+18.37	
-1	-1	0	0	-4.04	$(S_A^+ S_B^+ + S_A^- S_B^-)[a_3 + b_3 (S_A^z - S_B^z)^2]$
0	0	-1	-1	-4.04	
0	0	1	1	-4.04	$a_3 = -1.84$ $b_3 = -0.17$
1	1	0	0	-4.04	
-1	0	0	1	-3.70	
0	-1	1	0	-3.70	
0	1	-1	0	-3.70	
1	0	0	-1	-3.70	

continued

Table 1. continued

$\langle m_1, m_2 H_{\text{eff}} m'_1, m'_2 \rangle$					Equivalent spin operator
m_1	m_2	m'_1	m'_2		
-1	-1	1	1	+1.99	$b_4[(S_A^+)^2(S_B^+)^2 + (S_A^-)^2(S_B^-)^2]$; $b_4 = 0.50$
1	1	-1	-1	+1.99	
-1	1	1	-1	+3.13	$b_5[(S_A^+)^2(S_B^-)^2 + (S_A^-)^2(S_B^+)^2]$; $b_5 = 0.78$
1	-1	-1	1	+3.13	

antiferromagnetic spin coupling. The latter fact is consistent with the experimentally observed antiferromagnetic ordering in UO_2 .

The magnitude of the exchange parameters is consistent with a rather high transition point temperature, $T_N = 30.8$ K. The term H_3 corresponds to four-spin exchange interactions

$$H_3 = j_1 S_A^x S_B^x [(S_A^z)^2 + (S_B^z)^2] + j_2 S_A^y S_B^y [(S_A^z)^2 + (S_B^z)^2] + j_3 S_A^x S_B^x (S_A^z S_B^z) + j_4 S_A^y S_B^y (S_A^z S_B^z) \quad (14)$$

with $j_1 = -0.3$, $j_2 = 0.4 \text{ cm}^{-1}$, $j_3 = 2j_2$, and $j_4 = 2j_1$. The last term H_4 represents biquadratic interactions, which are written as

$$H_4 = q_1 O_A^{(1)} O_B^{(1)} + q_2 O_A^{(2)} O_B^{(2)} + q_3 O_A^{(3)} O_B^{(3)} + q_4 [O_A^{(1)} O_B^{(2)} + O_A^{(2)} O_B^{(1)}] \quad (15)$$

where $q_1 = 1.8$, $q_2 = 2.6$, $q_3 = 0.6$, and $q_4 = -0.2 \text{ cm}^{-1}$. Here $O_{A,B}^{(n)}$ are the components of the quadrupole operator expressed in terms of spin operators S_k^α of the effective spin $S = 1$.

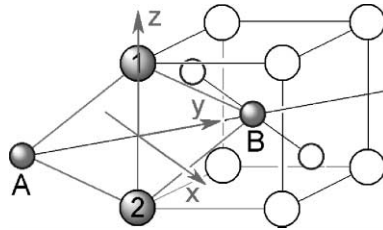


Fig. 9. Spin quantization axes x , y , and z of the neighboring $\text{U}^{4+}(\text{A})-\text{U}^{4+}(\text{B})$ exchange pair in the UO_2 crystal lattice.

$$O_k^{(1)} = (S_k^z)^2 - S(S+1)/3 \quad (16a)$$

$$O_k^{(2)} = (S_k^x)^2 - (S_k^y)^2 \quad (16b)$$

$$O_k^{(3)} = (S_k^x S_k^y + S_k^y S_k^x) \quad (16c)$$

where $k = A, B$.

The four-spin terms H_3 and H_4 are of special interest, since they have no analogs in usual spin-only $S = 1$ exchange systems. It is important that the spin operators entering H_4 are represented by products of the components of single-ion quadrupole operator $O_k^{(i)}$ (16) and thus they correspond to a quadrupole–quadrupole (Q – Q) interaction. This interaction can be called exchange-induced Q – Q interaction. By contrast to $3d$ exchange systems, in which biquadratic terms are generally very small as compared to the leading isotropic exchange interaction, the biquadratic Q – Q interaction in UO_2 is quite pronounced. Indeed, the q_1 and q_2 parameters at the $O_A^{(1)} O_B^{(1)}$ and $O_A^{(2)} O_B^{(2)}$ quadrupole operators are about 2 cm^{-1} ; being multiplied by the number of neighboring metal centers (12 in the UO_2 lattice), they can give a considerable contribution to the effective molecular field causing the quadrupolar orbital ordering. These results indicate that the U^{4+} – U^{4+} superexchange interaction in UO_2 differ considerably from that described by the conventional isotropic Heisenberg model. It has a strong influence on the character of the magnetic ordering in UO_2 . This is discussed below in more detail.

3. JAHN–TELLER EFFECT FOR THE GROUND Γ_5 STATE OF U^{4+} IONS: CALCULATIONS OF VIBRONIC COUPLING CONSTANTS FOR THE e_g , $t_{2g}(1)$ AND $t_{2g}(2)$ JAHN–TELLER MODES

Now we estimate the strength of the JT effect in UO_2 . For this, we calculated the linear vibronic coupling constants $\Gamma_5 \otimes e_g$, $\Gamma_5 \otimes t_{2g}(1)$, and $\Gamma_5 \otimes t_{2g}(2)$. Calculations were carried out using a semiempirical approach for CF calculations for $5f$ electrons developed in [14,15]. In this approach, the intraatomic interactions within the $5f^N$ shell are treated parametrically, while the CF splitting is calculated in terms of a microscopic model with taking into account the actual electronic structure of the $5f^N$ shell and ligand's molecular orbitals. This approach provides reasonable results for the CF energies in many tetra- and pentavalent actinide compounds, such as UX_6^- ($X = \text{F}, \text{Cl}, \text{Br}, \text{and I}$), UCl_6^{2-} , UBr_6^{2-} , NpO_2^+ , $\text{U}(\text{NCS})_8^{4-}$, UCl_4 , UO_2 , NpO_2 , etc. [14,15]. In particular, it gives good results for CF energies in UO_2 . The calculated CF energies and their comparison with the experimental data are given in Table 2.

To estimate the vibronic coupling constant, we performed CF calculations for the UO_8 cluster distorted along the e_g , $t_{2g}(1)$ and $t_{2g}(2)$ Jahn–Teller modes (Fig. 10). A similar approach was previously applied for calculations of vibronic coupling constants in a series of UX_6^- octahedral complexes ($X = \text{F}, \text{Cl}, \text{Br}, \text{and I}$) and in the $\text{U}(\text{NCS})_8^{4-}$ cubic complex in compound $(\text{NET}_4)_4\text{U}(\text{NCS})_8$ [14].

Table 2. Calculated and experimental CF splitting of the ground $^3H_4$ multiplet of U^{4+} for UO_2

Level	CF energy (cm ⁻¹)	
	Experimental [6]	Calculated [14]
Γ_5	0	0
Γ_3	1211	1288
Γ_4	1345	1600
Γ_1	1410	1774

For each mode, the amplitude of the distortion corresponds to the actual displacement of oxygen atoms, 0.014 Å. Then the vibronic coupling constants C were calculated from the splitting energy ΔE of the ground Γ_5 level.

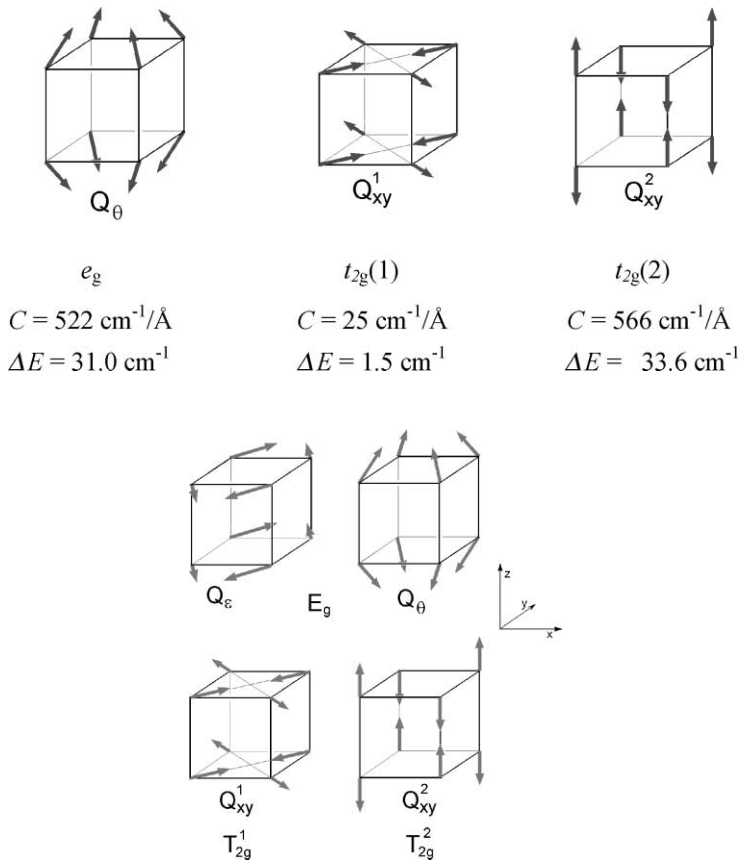


Fig. 10. The Jahn–Teller active modes in the UO_8 cubic cage. Only one of three components (Q_{xy}) is shown for the $t_{2g}(1)$ and $t_{2g}(2)$ modes.

The largest vibronic coupling constants are found for the e_g and $t_{2g}(2)$ modes, while for the $t_{2g}(1)$ mode it is about one order of magnitude smaller. From these data we can also estimate the JT stabilization energy per U atom, 10 cm^{-1} for e_g , 8 cm^{-1} for $t_{2g}(2)$, and only 0.5 cm^{-1} for $t_{2g}(1)$. All these energies are smaller than the thermal energy at the transition point, $T_N/k_B \approx 20 \text{ cm}^{-1}$.

4. DISCUSSION: THE RELATIONSHIP BETWEEN THE $5f^2-5f^2$ SUPEREXCHANGE INTERACTION AND JAHN–TELLER EFFECT

Using these results, now we discuss the competition between the $5f^2-5f^2$ superexchange interaction and the cooperative JT effect in the phase transition in UO_2 . We discuss first the type of the lattice distortions in UO_2 , which can be expected from the cooperative JT effect. It is well known that there are two types of the minima in the linear $T \otimes (e + t)$ JT problem, three equivalent tetragonal e_g minima and four trigonal t_{2g} minima. Since the local e_g and $t_{2g}(2)$ modes have the largest vibronic coupling constants, one can expect that lattice distortions in UO_2 below T_N should be related to these JT modes. The corresponding distortions of UO_8 cubic cage are shown in Fig. 11. In principle, due to the cooperative character of JT distortions in the extended crystal lattice, local distortions can be of the mixed type $e_g + t_{2g}(1) + t_{2g}(2)$, but at least one of the JT components with the largest coupling constant should be present. It is therefore surprising that the actual triple- $\mathbf{k}$ distortion of the UO_8 cage does not contain e_g or $t_{2g}(2)$ JT components.

Instead, the actual distortion of the UO_8 cage in UO_2 just corresponds to the trigonal JT minimum of the $t_{2g}(1)$ mode, which has the vibronic coupling constant being more than 20 times smaller than those for the e_g or $t_{2g}(2)$ modes. In fact, the distortion shown in Fig. 11 can be represented by the sum $(Q_{xy}^{(1)} + Q_{zx}^{(1)} + Q_{yz}^{(1)})/\sqrt{3}$ of $t_{2g}(1)$ coordinates combined with some rotation around the $\langle 111 \rangle$ diagonal.

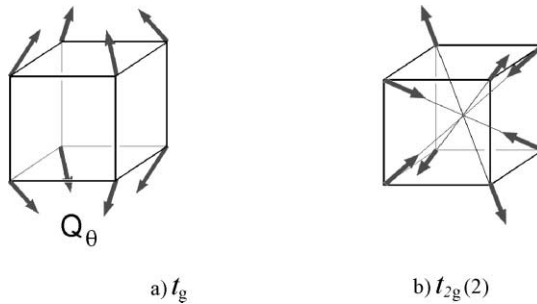


Fig. 11. Distortions of the UO_8 cubic cage in a) e_g tetragonal minimum (with the JT stabilization energy of $\Delta E_{JT} \approx 8 \text{ cm}^{-1}$ per U atom) and b) $t_{2g}(2)$ trigonal JT minimum ($\Delta E_{JT} \approx 10 \text{ cm}^{-1}$).

This is a strong indication of the fact that the orbital ordering and lattice distortions are not due to the cooperative JT effect. Indeed, the stabilization energy per U atom for the actual 3- $\mathbf{k}$ type distortion shown in Fig. 12 is as small as 0.5 cm^{-1} , which is much smaller than the characteristic thermal energy at the transition point temperature, $T_N/k_B \approx 20 \text{ cm}^{-1}$. Therefore, the lattice distortions in UO_2 seem to be induced by an orbital ordering related to the exchange interactions and/or Q - Q interaction. This is due to the fact that the degeneracy of a ground state with an even number of electrons per magnetic ion can be lifted by magnetic or quadrupolar ordering at low temperatures. There are therefore three sources of the Q - Q interaction in UO_2 , (a) the direct Q - Q interaction which is generally small and can safely be neglected, (b) the indirect Q - Q interaction related to the spin-lattice interaction and the cooperative JT effect [7,8], and (c) the exchange-induced Q - Q interaction, which is described by the H_4 term (15) of the effective spin Hamiltonian of the $5f^2$ - $5f^2$ superexchange interaction. The latter mechanism of the Q - Q interaction seems to be the most important, since the mechanism (b) should lead to the e_g or $t_{2g}(2)$ types of the lattice distortion, which are not actually observed in UO_2 . This is also consistent with a large value of the q_1 and q_2 parameters at the $O_A^{(1)}O_B^{(1)}$ and $O_A^{(2)}O_B^{(2)}$ components of the Q - Q interaction. It is important to note that the JT-induced Q - Q interaction (b) and the exchange-induced Q - Q interaction (c) can be represented by quite different quadrupole components, as evidenced from the comparison of the Q - Q operator (b) obtained in [7,8] and the Q - Q operator H_4 , equations (15) and (16a-c). As a result, the orbital ordering caused by the Q - Q interactions (b) and (c) may be quite different resulting in different types of the lattice distortion.

The fact that the phase transition in UO_2 has the first-order character and the ordered magnetic moment of $1.74 \mu_B$ is considerably lower than the paramagnetic moment (about $3 \mu_B$) is qualitatively consistent with the ratio of the strength of the bilinear and biquadratic parts of the effective spin Hamiltonian (8) of the $5f^2$ - $5f^2$

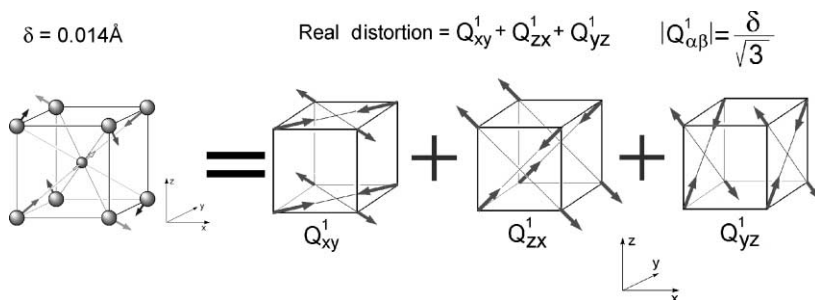


Fig. 12. The actual distortion of each UO_8 cubic cage in UO_2 is represented by the $(Q_{xy}^{(1)} + Q_{zx}^{(1)} + Q_{yz}^{(1)})/\sqrt{3}$ linear combination of the components of the $t_{2g}(1)$ mode combined with some rotation around the $\langle 111 \rangle$ space diagonal. This distortion corresponds to the trigonal minimum of the $t_{2g}(1)$ JT mode with the stabilization energy of about 0.5 cm^{-1} per U atom.

superexchange interaction. Quadrupole interactions compete with exchange interactions and can completely suppress the ordered magnetic moment, although the quadrupole order can always coexist with the magnetic order [8]. According to the Allen model [8], the first-order phase transition in UO_2 occurs in a rather narrow range of the ratio between the strength of $Q-Q$ and exchange interactions (between $2/7$ and $1/2$). This is compatible with our estimate given by the spin Hamiltonian (8).

Although the quantitative details of the competition between the spin and orbital ordering are not clear yet, our results allow one to conclude that the $5f^2-5f^2$ superexchange interaction dominates in the mechanism of the phase transition. The $Q-Q$ interaction induced by the $5f^2-5f^2$ superexchange interaction is responsible for the orbital ordering which causes the lattice distortions of the $t_{2g}(1)$ type, which cannot be ascribed to the cooperative JT effect due to a very low vibronic coupling constant. Distortion of the oxygen sublattice in UO_2 is therefore a secondary effect. These findings can serve as a basis for the development of the microscopic model explaining the origin of the 3-k character of the magnetic ordering and lattice distortions.

5. CONCLUSIONS AND FURTHER OUTLOOK

We have analyzed the interplay between the superexchange interaction and the cooperative JT effect in UO_2 . Our calculations show that the $5f^2-5f^2$ superexchange interaction in UO_2 is anisotropic and essentially non-Heisenberg. The biquadratic part of the spin Hamiltonian is comparable in magnitude with the bilinear part, and it corresponds to a strong exchange-induced quadrupole–quadrupole interaction between $5f$ states of U^{4+} ions. The linear vibronic coupling constants $\Gamma_5 \otimes e_g$, $\Gamma_5 \otimes t_{2g}(1)$, and $\Gamma_5 \otimes t_{2g}(2)$ are calculated. Despite $\Gamma_5 \otimes e_g$ and $\Gamma_5 \otimes t_{2g}(2)$ are found to be much larger than $\Gamma_5 \otimes t_{2g}(1)$, the actual lattice distortion in UO_2 is of the pure $t_{2g}(1)$ type. Exchange interactions between U^{4+} ions play the primary role in the mechanism of the phase transition in UO_2 . The magnetic ordering and related orbital ordering and lattice distortions are determined by the superexchange interaction. The most important e_g and $t_{2g}(2)$ Jahn–Teller distortions are completely suppressed by the competing exchange interactions. Although the complete solution of the problem is not yet obtained, our results elucidate a number of points, which remained unclear before. The most important finding is that there is a strong exchange-induced $Q-Q$ interaction in UO_2 , which is represented by the biquadratic part of the $5f^2-5f^2$ superexchange interaction. This $Q-Q$ interaction, which is different from the $Q-Q$ interaction related to the cooperative JT effect and spin-lattice interaction, seems to be responsible for the orbital ordering and a considerable reduction of the ordered magnetic moment. The development of a microscopic model of the phase transition in UO_2 for a consistent explanation of the origin of the triple- $\mathbf{k}$ magnetic structure, lattice distortions, and orbital ordering below T_N will therefore be the next step.

ACKNOWLEDGEMENTS

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REFERENCES

- [1] B. C. Frazer, G. Shirane, D. E. Cox and C. E. Olsen, *Phys. Rev.*, 1965, **140**, A1448; B. T. M. Willis and R. I. Taylor, *Phys. Lett.*, 1965, **17**, 188.
- [2] R. A. Cowley and G. Dolling, *Phys. Rev.*, 1968, **167**, 464.
- [3] K. Sasaki and Y. Obata, *J. Phys. Soc. Jpn*, 1970, **28**, 1157.
- [4] J. Faber and G. H. Lander, *Phys. Rev. B*, 1976, **14**, 1151.
- [5] P. Burlet, J. Rossat-Mignod, S. Quezel, O. Vogt, J. C. Spirlet and J. Rebizant, *J. Less-Common Met.*, 1986, **121**, 121.
- [6] G. Amoretti, A. Blaise, R. Caciuffo, J. M. Fournier, M. T. Hutchings, R. Osborn and A. D. Taylor, *Phys. Rev. B*, 1989, **40**, 1856.
- [7] S. J. Allen, *Phys. Rev.*, 1968, **166**, 530.
- [8] S. J. Allen, *Phys. Rev.*, 1968, **167**, 492.
- [9] S. Kern, C.-K. Loong and G. H. Lander, *Phys. Rev. B*, 1985, **32**, 3051.
- [10] W. Kopmann, F. J. Litterst, H.-H. Klauß, M. Hillberg, W. Wagener, G. M. Kalvius, E. Schreier, F. J. Burghart, J. Rebizant and G. H. Lander, *J. Alloys Comp.*, 1998, **271–273**, 463.
- [11] L. Paolasini, R. Caciuffo, B. Roessli and G. H. Lander, *Physica B*, 1998, **241–243**, 681; L. Paolasini, R. Caciuffo, B. Roessli and G. H. Lander, *Phys. Rev. B*, 1999, **59**, 6867.
- [12] K. Ikushima, S. Tsutsui, Y. Haga, H. Yasuoka, R. E. Walstedt, N. M. Masaki, A. Nakamura, S. Nasu and Y. Onuki, *Phys. Rev. B*, 2001, **63**, 104404.
- [13] P. W. Anderson, *Phys. Rev.*, 1959, **115**, 2; P. W. Anderson, in *Magnetism I* (eds G. T. Rado and H. Suhl), Academic Press, New York, 1963.
- [14] V. S. Mironov and S. P. Rosov, *Phys. Status Solidi (b)*, 1992, **169**, 463; V. S. Mironov and S. P. Rosov, *Phys. Status Solidi (b)*, 1992, **170**, 199; V. S. Mironov and S. P. Rosov, *Phys. Status Solidi (b)*, 1992, **170**, 509.
- [15] V. S. Mironov and S. P. Rosov, *J. Alloys Comp.*, 1992, **189**, 163–168.
- [16] V. S. Mironov, L. F. Chibotaru and A. Ceulemans, *Phys. Rev. B*, 2003, **67**, 014424.
- [17] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, 1952, **20**, 827.
- [18] L. L. Lohr and P. Pykkö, *Chem. Phys. Lett.*, 1979, **62**, 333.
- [19] J. W. Lauher, M. Elian, R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 3219.

Dynamic Jahn–Teller Character of Manganese(III) Spin-Crossover Complex [Mn(taa)] ($H_3taa = \text{tris}(1-(2\text{-azoly})\text{-}2\text{-azabuten-4-yl})\text{amine}$)

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Abstract

Paraelectric behavior due to a dynamic Jahn–Teller effect has been found in the high-spin (HS) phase above $T_c = 48$ K of the manganese(III) spin-crossover complex [Mn(taa)] ($H_3taa = \text{tris}(1-(2\text{-azoly})\text{-}2\text{-azabuten-4-yl})\text{amine}$). The dielectric constant obeys the Curie–Weiss law with an asymptotic Curie temperature of 26 K, suggesting competition between a low-spin (LS) phase and a ferroelectric-ordered (FO) phase at low temperatures. A phase diagram based on a four-state Ising–Potts model incorporating both a virtual cooperative Jahn–Teller transition ($HS \rightleftharpoons FO$) and a spin-crossover transition ($HS \rightleftharpoons LS$) is proposed to elucidate the interrelation of the HS, LS, and FO phases.

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1. INTRODUCTION

Spin-crossover complexes contain octahedrally coordinate d^4 – d^7 transition metal ions and have two nearly degenerate electron configurations with different spin multiplicities, i.e., high-spin (HS) and low-spin (LS) states [1–5]. The ground state configuration of these complexes can be switched from one to the other by varying ligand-field strength. This bistability is usually accomplished by coupling with molecular deformations, especially metal–ligand stretching modes, and known to be controllable through external fields including temperature, pressure, magnetic field, and so on. In many theoretical models, only totally symmetric breathing mode is taken into account as the interaction mode relevant to spin-crossover phenomena. However, lower-symmetry modes may play an important role when the orbital degeneracy is not fully quenched. Such low-symmetry deformations are sometimes noted in experimental works [6–10]. In this paper, a manganese(III) spin-crossover complex, where the anisotropic deformation induced by the Jahn–Teller effect provides a rich variety of phase behavior, is discussed based on a simple mean-field model.

The title compound [Mn(taa)] (H_3taa = tris(1-(2-azoly)-2-azabuten-4-yl)amine) is known to have an abrupt spin-crossover phase transition [11,12]. The LS phase consisting of $^3T_{1g}$ ($t_{2g}^4e_g^1; S=1$) molecules transforms into the HS phase consisting of ^5E_g ($t_{2g}^3e_g^2; S=2$) molecules at above $T_c = 48$ K. The crystal structure of the HS phase has cubic symmetry: space group $I\bar{4}3d$, lattice constant $a = 2.031$ nm, cell volume $V = 8.377$ nm³, and number of formula unit per unit cell $Z = 16$ [11]. The HS molecule in the cubic lattice has a C_3 axis penetrating the central Mn(III) ion and the non-ligating N(amino) atom of the taa^{3-} ligand (Fig. 1(a)). The coordination environment of the central Mn(III) ion is approximately octahedral with small twisting (9.2°) around the C_3 axis from the C_{3v} symmetry.

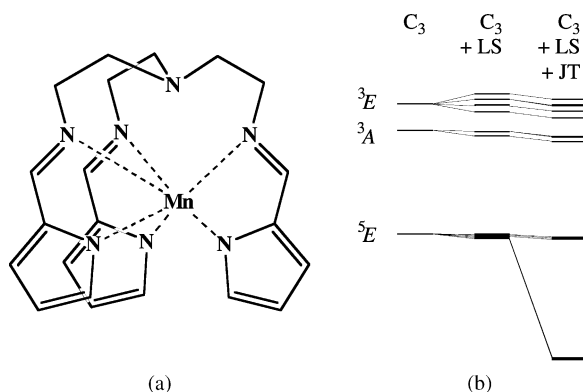


Fig. 1. (a) Molecular structure of [Mn(taa)] and (b) splitting of ground multiplet under perturbations; C_3 twist (C_3), spin–orbit coupling (LS), and $E \otimes e$ Jahn–Teller distortion (JT).

2. EXPERIMENTAL

Polycrystalline [Mn(taa)] samples were prepared according to the literature method [11,12] and tetrahedron-shaped single crystals were obtained by recrystallization from CH_2Cl_2 /hexane solutions.

Variable-temperature laser Raman spectra between 15 and 70 K were measured for a polycrystalline sample mounted in an Oxford CF1204 cryostat using a Jasco NR-1800 Raman spectrophotometer.

The dielectric permittivity was measured on a compacted disk, 0.55 mm thick and 9.0 mm in diameter, with vacuum-deposited electrodes on the circular faces, using an HP 4284A precision LCR meter. The frequency and temperature ranges were 10^2 – 10^6 Hz and 15–300 K, respectively. Temperature measurements were made by an Rh–Fe resistance thermometer fixed on the sample holder, which was calibrated against the ITS90. For the aid of thermal equilibration, a small amount of He gas (~ 10 Pa) was introduced in the sample chamber of the lab-made vacuum cryostat. Degradation of the sample by thermal cycling, e.g. crack of the disk or strip-off of the Au electrodes, was negligible since no thermal hystereses of dielectric constants were detected.

3. RESULTS AND DISCUSSION

3.1. Raman Spectra of [Mn(taa)]

The Raman spectrum of [Mn(taa)] recorded at 50 K is plotted in Fig. 2, together with a quantum-chemical simulation spectrum. The details of the theoretical method are presented in Section 3.3. Although the simulation curve is not corrected with any scaling factors of vibrational frequencies, it is still useful for peak assignment. Temperature dependences of the Raman spectra are shown in Fig. 3. Some peaks showing remarkable intensity changes at around T_c are indicated by arrows. An important feature of these spectra is that most of Raman-active vibrational modes show negligible frequency shifts across T_c , while the intensities vary due to probable site-symmetry changes are observed. This behavior is in clear contrast to ordinary Fe spin-crossover complexes, where vibrational frequencies shift to lower as the sample changes from the LS to HS species [1–5,13–18].

The shifts in vibrational frequencies between the LS and HS species are responsible for the major parts of the entropy changes ΔS in spin transitions [13]. This has been repeatedly confirmed by infrared [13–15], Raman [14–17], and inelastic neutron scattering spectroscopies [18]. Since the observed entropy change $13.8 \text{ J K}^{-1} \text{ mol}^{-1}$ [12] in the present compound is not explained adequately solely by the entropy of the spin multiplicity ($R \ln(5/3) = 4.25 \text{ J K}^{-1} \text{ mol}^{-1}$). However, we cannot assign the extra entropy change to a vibrational origin, since the Raman spectra of the two phases differ only in intensities.

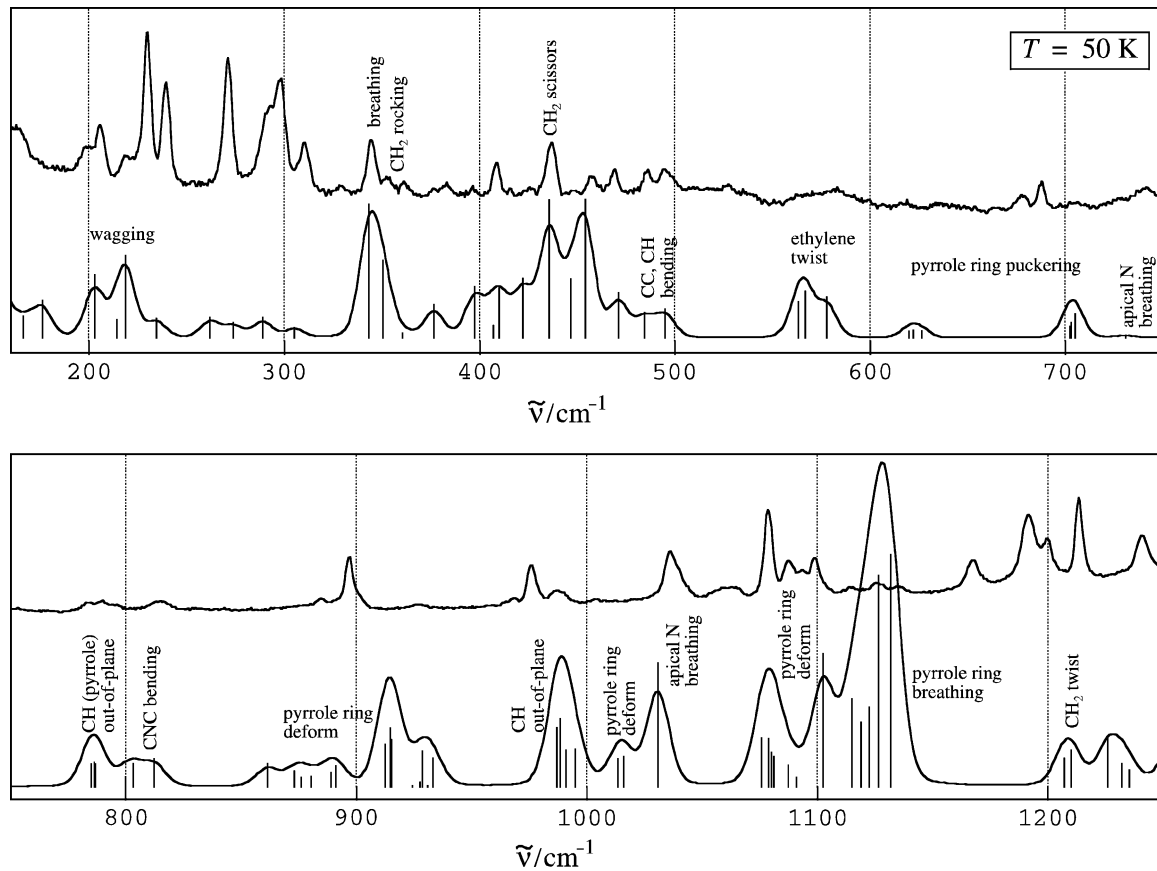


Fig. 2. Raman spectrum of [Mn(taa)] at 50 K (upper curve) and simulations for the geometry-optimized high-spin (HS) species by B3PW91/LANL2DZ.

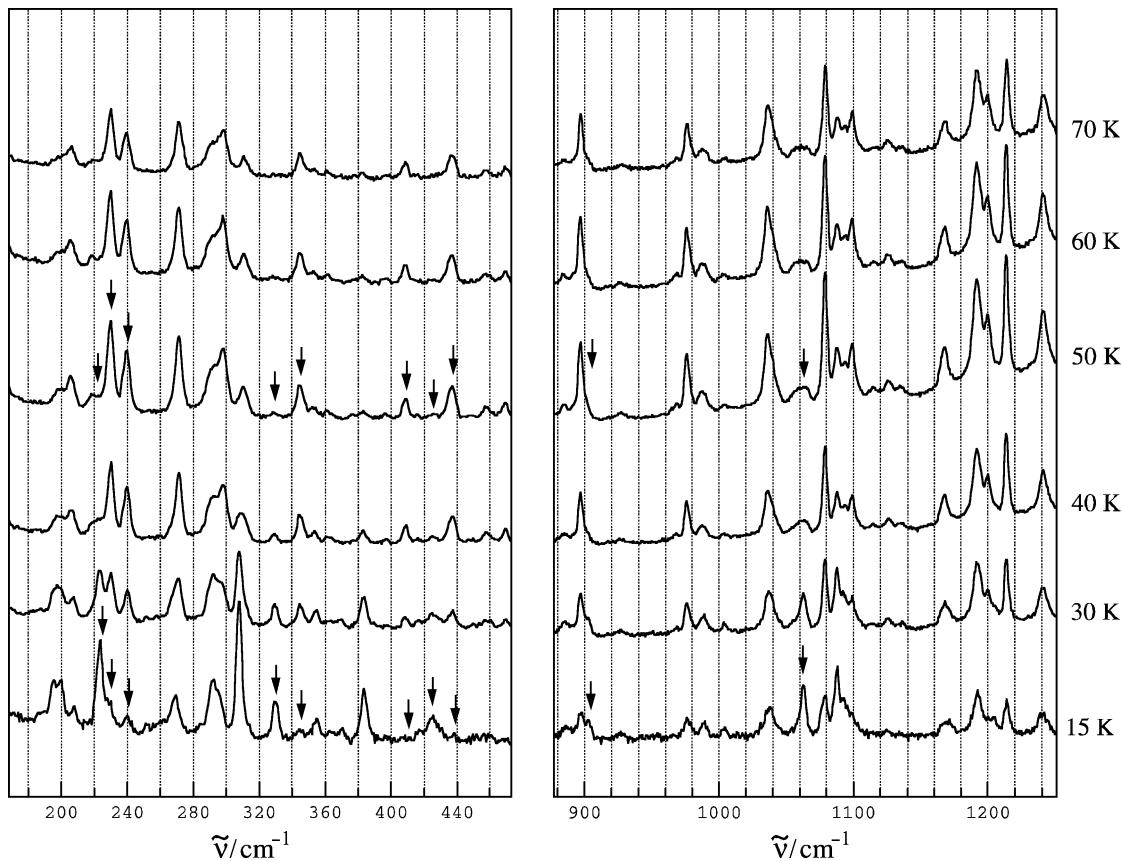


Fig. 3. Temperature dependence of Raman spectra of [Mn(taa)]. Arrows indicate peaks showing remarkable intensity changes at around spin-crossover transition $T_c = 48$ K.

One of plausible candidates for the entropy source is a dynamic structural disorder in the HS phase, which should be settled down in the LS phase. The crystallographic data for [Mn(taa)] [11] provide a clue, i.e., the presence of C_3 axis in the HS molecule. An Mn(III) ion in the ^5E state is a well-known Jahn–Teller ion [19]. Since the C_3 site-symmetry cannot lift the orbital degeneracy of the ^5E term (Fig. 1(b)), it is likely that the Mn ion is subjected to the $E \otimes e$ Jahn–Teller effect, which gives rise to three energetically equivalent deformation structures. The apparent C_3 symmetry should be observed in a time-averaged structure over three deformed structures.

3.2. Dielectric behavior of [Mn(taa)]

The temperature dependence of dielectric constant at 1.0 kHz is plotted in Fig. 4. The HS phase above the spin-crossover transition at $T_c = 48$ K shows a characteristic Curie–Weiss behavior, $\varepsilon_\infty + C/(T - \theta)$, indicating the presence of dynamically disordering electric dipoles. The high-frequency dielectric constant is $\varepsilon_\infty = 3.0$, the Curie constant $C = 91$ K, and the asymptotic Curie temperature $\theta = 26$ K. The positive value of θ suggests a ferroelectric interaction between reorienting dipoles in the HS phase. Such an interaction has a possibility of providing a ferroelectric phase at low temperatures, if the spin-crossover phase transition would not prevent the development of ferroelectric long-range order.

On the other hand, the Curie–Weiss behavior is fully suppressed in the LS phase below 48 K. It suggests that the complete C_3 -symmetry is recovered in the LS molecule and the reorienting dipoles, which are required to guarantee the apparent C_3 -symmetry in the dynamically disordered HS phase, disappear. A slight growth of ε observed between 15 and 40 K arises from a small fraction of thermally excited HS species. Analysis of this part assuming a temperature dependence of the

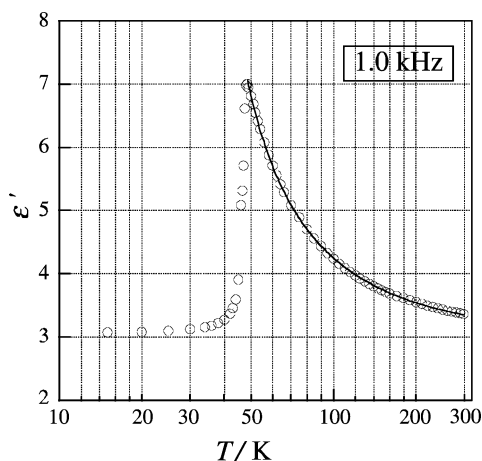


Fig. 4. Temperature dependence of dielectric constant of [Mn(taa)] at 1.0 kHz. Full curve is the Curie–Weiss law, $C/(T - \theta)$, where $C = 91$ K and $\theta = 26$ K.

form $T^{-1}\exp(-\Delta_{\text{eff}}/k_{\text{B}}T)$ for the permittivity gives the effective LS–HS gap $\Delta_{\text{eff}}/k_{\text{B}} = 340$ K. This gap Δ_{eff} is the energy difference between the LS and HS states of a [Mn(taa)] molecule embedded in the LS molecules. Thus, it should differ from the LS–HS gap Δ of an isolated molecule in vacuum by the van der Waals' interaction exerted by the surrounding LS molecules. This interaction is expected to enhance the energy gap Δ because of mismatched molecular packing disturbing the uniform and equilibrium molecular array of the LS phase.

A simple electrostatic model facilitates understanding the physical meaning of the Curie behavior of [Mn(taa)] in the HS phase. Electric polarization $\mathbf{P}$ produced by a number of reorienting molecular dipoles μ under a local field $\mathbf{E}_{\text{loc}}$ obeys a simple Curie law,

$$\mathbf{P} = (N\mu^2/3k_{\text{B}}T)\mathbf{E}_{\text{loc}}$$

where N stands for the number density of molecular dipoles. The local field $\mathbf{E}_{\text{loc}}$ consists of the external field $\mathbf{E}_{\text{ext}}$ and the Lorentz field $\mathbf{E}_{\text{Lorentz}}$ exerted from neighboring molecular dipoles,

$$\mathbf{E}_{\text{loc}} = \mathbf{E}_{\text{ext}} + \mathbf{E}_{\text{Lorentz}} = \mathbf{E}_{\text{ext}} + \mathbf{P}/(3\varepsilon_{\infty}\varepsilon_0)$$

where ε_{∞} is the high-frequency dielectric constant. From the definition of dielectric constant $\mathbf{P} = (\varepsilon - \varepsilon_{\infty})\varepsilon_0\mathbf{E}_{\text{ext}}$, the Curie–Weiss law is provided:

$$\varepsilon = \varepsilon_{\infty} + C/(T - \theta_{\text{es}})$$

where $C = N\mu^2/(3k_{\text{B}}\varepsilon_0)$, $\theta_{\text{es}} = C/(3\varepsilon_{\infty})$, and ε_0 means the permittivity of vacuum. Based on the experimental values, $C = 91$ K, $\varepsilon_{\infty} = 3.0$, and $N = 1.91 \text{ nm}^{-3}$ [11], the calculated value of the reorienting molecular dipole moment is $\mu = 1.25$ D. The asymptotic Curie temperature in this electrostatic model is deduced to $\theta_{\text{es}} = C/(3\varepsilon_{\infty}) \cong 10$ K, which is much smaller than the observed value, $\theta = 26$ K. If we attribute the discrepancy between the calculated θ_{es} and the experimental θ solely to the van der Waals energy, we conclude that a neighboring pair of HS molecules prefers parallel deformation between them. Thus, the electrostatic contribution is about 40% of whole ferroelectric interaction between HS molecules, while the van der Waals interaction contributes up to 60%.

3.3. DFT-optimized structure of HS [Mn(taa)] species

The geometry optimization of the HS [Mn(taa)] molecule was carried out by a hybrid DFT quantum chemical calculation using GAUSSIAN98 program suite [20]. In the calculation, the effective core-potential (ECP) basis functions LANL2DZ were adopted for all atoms and a hybrid density functional UB3PW91 was used. Since the C_3 -symmetry constraint is released, the optimized molecular structure is quite skewed (Fig. 5), so that three Mn–N(pyrrole) bond lengths are 1.9785, 1.9778, and 2.2032 Å, and three Mn–N(imino) bond lengths are 2.0642, 2.0365, and 2.3144 Å. Typical Jahn–Teller elongations along a coordination axis are found. Averaged bond lengths

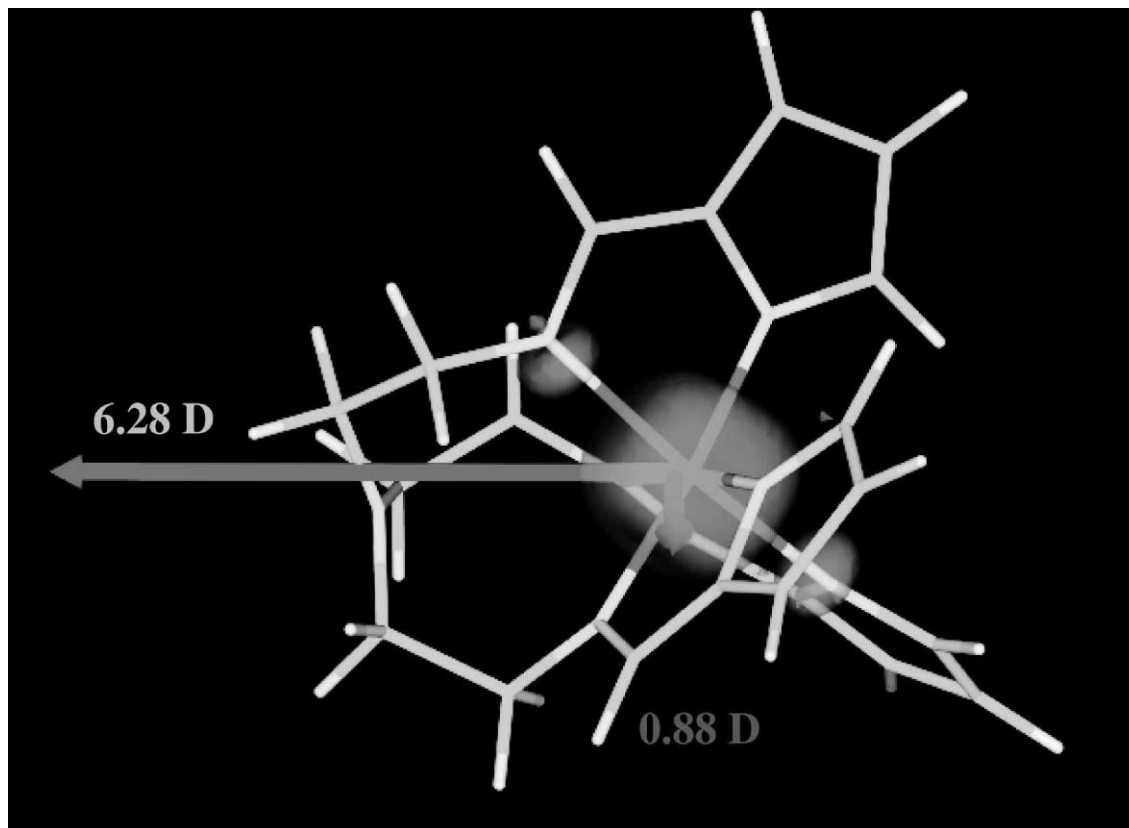


Fig. 5. DFT-optimized molecular structure of high-spin (HS) [Mn(taa)]. Two solid arrows mean the longitudinal and transverse electric dipole moment. Spin-density isosurface at $0.005e/a.u.^3$ is also shown.

are 2.053 and 2.138 Å for Mn–N(pyrrole) and Mn–N(imino) bonds, respectively, which correspond very well to the experimental values of 2.054 and 2.148 Å [11].

If the complex molecule maintains C_3 symmetry, it carries only longitudinal electric dipole parallel to the C_3 axis. Symmetry lowering of the HS molecule produces the transverse component of electric dipole moment. Based on the optimized structure and the electron distribution, the longitudinal and transverse dipole moments are estimated to be 6.28 and 0.88 D, respectively. In the crystal lattice, reorientation of a whole molecule is prevented by dense packing, and only pseudo-rotation of the transverse moment is allowed. If we remember that the choice of the pseudo- C_3 axis, which affects separation of the longitudinal and transverse components, is not unique, the value obtained for the transverse moment may be regarded close to the experimental value of the reorienting dipole 1.25 D estimated from the dielectric constant. This good agreement verifies the idea of pseudo-rotating distortion dipoles attributable to the $E \otimes e$ Jahn–Teller effect.

Since the 16 molecules in a unit cell are grouped into four sublattices in terms of their longitudinal moments, which align to four body-diagonals of the cubic unit cell, the Jahn–Teller distortions in the same direction generate non-collinear electric dipoles on different sublattices. The mutual relation of four sublattices is depicted in Fig. 6. Each octant of a unit cell contains two molecules belonging to a same sublattice, placed on the body-diagonal. Any two octants sharing a single corner are equivalent. Coordination axes (N–Mn–N) of a molecule are approximately parallel to the lattice vectors a , b , and c , and the tetragonal elongations of coordination octahedra by $E \otimes e$ Jahn–Teller effect are regarded to take place along the lattice vectors. A transverse electric dipole is induced perpendicular to the molecular C_3 axis on a coplane of the C_3 and elongation axes. The lost collinearity suggests

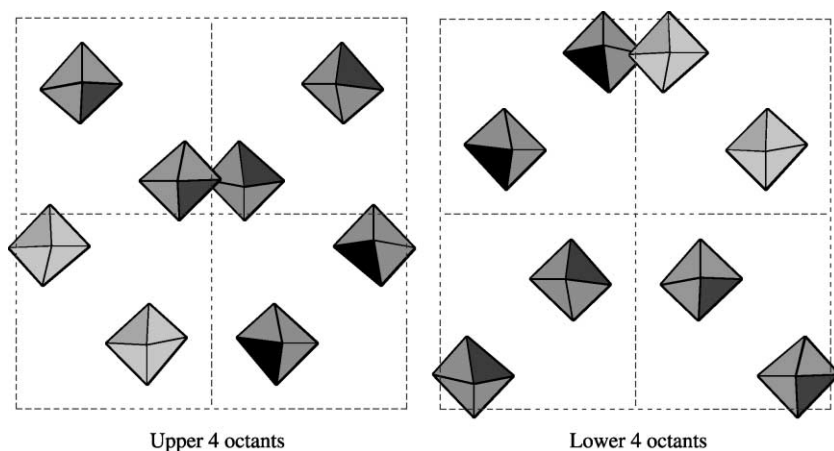


Fig. 6. Molecular packing in [Mn(taa)] crystal. Coordination octahedra are colored according to four sublattices discriminated by mapping a body-diagonal of the unit cell to C_3 axes of member molecules. Darken side of each octahedron faces to the C_3 axis.

inequivalency of ferrodistorive and ferroelectric interactions between the HS molecules. For example, a ferrodistorive order with z -axis elongations makes electric polarizations of different sublattices cancel out each other resulting in an antiferroelectric order.

In Fig. 5 the spin-density isosurface of $0.005e/a.u.^3$ of [Mn(taa)] is also shown. Taking the Jahn–Teller elongation axis as z , the electron configuration is approximately described to be $(d_{yz})^1(d_{zx})^1(d_{xy})^1(d_{z^2})^1$. Most of the spin densities sit on t_{2g} orbitals and around the z -axis, consistent with the electron configuration. A small amount of spin densities appears on the pyrrole ring perpendicular to the z -axis, suggesting delocalization of t_{2g} electrons over pyrrole π orbitals sharing the nodal plane. It induces energy splitting between d_{yz} and d_{zx} orbitals and may cause rhombic zero-field splitting term in the spin Hamiltonian.

3.4. Phase diagram based on a four-state Ising–Potts model

A four-state Ising–Potts model is applied to the [Mn(taa)] system to elucidate thermodynamic relations [21]. An [Mn(taa)] molecule is assumed to take four different microscopic states: state 0 is the LS state and states 1–3 are the HS states with the elongation axis parallel to x , y , and z , respectively. Interactions are assumed only between nearest neighbor molecules. Under a mean-field approximation [22], the internal energy of the [Mn(taa)] system is expressed in terms of populations ρ_i ($i = 0, 1, 2, 3$) of four microscopic states,

$$U = \Delta(1 - \rho_0) + J_0(\rho_1^2 + \rho_2^2 + \rho_3^2) + 2J_1\rho_0(1 - \rho_0)$$

where Δ (> 0) is the LS–HS gap, J_0 (< 0) is the Potts-type ferroelectric interaction between the HS species, and J_1 (> 0) is the Ising-type demixing interaction between HS and LS species [23]. The entropy S of the system consists of the contribution of spin-multiplicity and the entropy of mixing,

$$S/k_B = \rho_0 \ln(2S_{LS} + 1) + (1 - \rho_0) \ln(2S_{HS} + 1) - \sum_{i=0}^3 \rho_i \ln \rho_i$$

where $S_{LS} = 1$ and $S_{HS} = 2$ are spin quantum numbers of the LS ($i = 0$) and HS ($i = 1, 2, 3$) states, respectively. By minimizing the free energy of the system $F = U - TS$ under a normalization condition $\rho_0 + \rho_1 + \rho_2 + \rho_3 = 1$, i.e., solving

$$\partial F / \partial \rho_i = 0, \quad \partial^2 F / \partial \rho_i \partial \rho_j > 0, \quad i, j = 1, 2, 3$$

three stable solutions are obtained: an LS phase ($\rho_0 \gg \rho_1 = \rho_2 = \rho_3$), an HS phase ($\rho_0 \ll \rho_1 = \rho_2 = \rho_3$), and a ferroelectric-ordered (FO) phase ($\rho_0 \ll \rho_1 = \rho_2 < \rho_3$). These three phases are shown in a T – J_0 phase diagram (Fig. 7). The HS phase has the highest entropy and occupies high-temperature regions. Two distinct ordered phases, LS and FO, appear at lower temperatures, and the most stable phase

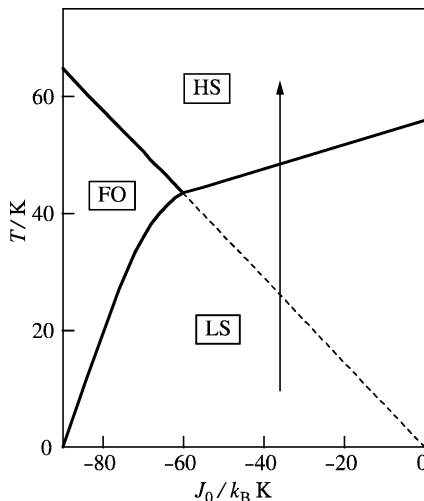


Fig. 7. Mean-field phase diagram of the four-state Ising–Potts model ($\Delta/k_B = 90$ K, $J_1/k_B = 125$ K). The high-spin (HS) phase, the low-spin (LS) phase, and the ferroelectric-ordered (FO) phase are shown. The arrow line corresponds to $J_0/k_B = -36$ K, appropriate to the [Mn(taa)] system.

observable near 0 K switches from one to the other at a critical value $J_0 = -\Delta$. The phase boundary between the HS and LS phases is given by

$$T_c(J_0) = (\Delta + J_0/3)/k_B \ln[3(2S_{\text{HS}} + 1)/(2S_{\text{LS}} + 1)]$$

Both spin-crossover transitions ($\text{HS} \rightleftharpoons \text{LS}$, $\text{FO} \rightleftharpoons \text{LS}$) are first order accompanied by definite jumps of populations, while the cooperative Jahn–Teller transition ($\text{HS} \rightleftharpoons \text{FO}$) is weak first-order (very close to a second-order transition). It suggests a possibility of observation of hidden cooperative Jahn–Teller transition (the broken line in Fig. 7) between the metastable HS and FO phases, if the HS phase could be supercooled enough below the spin-crossover transition temperature T_c by a rapid cooling.

The three adjustable parameters are determined, $\Delta/k_B = 90$ K, $J_0/k_B = -36$ K, and $J_1/k_B = 125$ K, so as to reproduce the spin-crossover transition temperature $T_c = 48$ K, the virtual Jahn–Teller transition temperature $T_{\text{JT}} \cong \theta = 26$ K, and the effective LS–HS gap in the LS phase $\Delta_{\text{eff}}/k_B = 340$ K. (Note Δ_{eff} is approximated by $\Delta + 2J_1$ in this mean-field model.) This choice of model parameters gives a phase sequence from the LS to HS with increasing temperature, corresponding to the arrow path in Fig. 7. Temperature dependence of thermodynamic quantities (Fig. 8) is calculated along the path indicated by the arrow in Fig. 7, where the discontinuities arising from the first-order spin-crossover transition are recognized: $\Delta\rho_0 = 0.99$, $\Delta H = 0.64$ kJ mol $^{-1}$, and $\Delta S = 13.3$ J K $^{-1}$ mol $^{-1}$. These theoretical

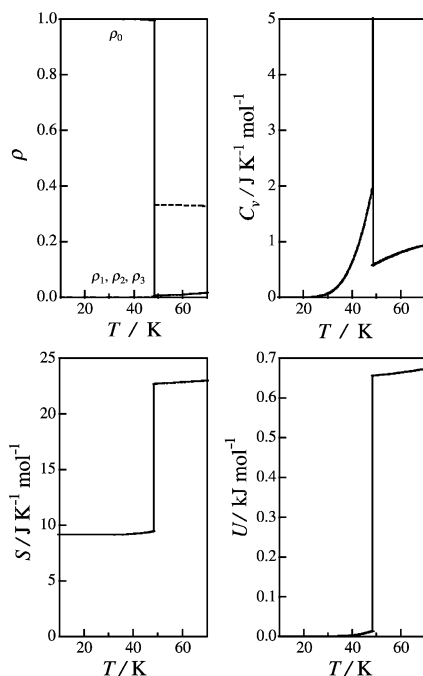


Fig. 8. Thermodynamic quantities of the four-state Ising–Potts model along the heating path (arrow line) in Fig. 7.

values compare well with the experimental ones, $\Delta H = 0.60 \text{ kJ mol}^{-1}$ and $\Delta S = 13.8 \text{ J K}^{-1} \text{ mol}^{-1}$ [12]. The good agreement supports the validity of the four-state Ising–Potts model in the spin-crossover [Mn(taa)] system.

Jahn–Teller effects are rarely adopted in theoretical treatments of spin-crossover phenomena, except Kambara’s model for Fe(II) complexes [24] and Bersuker’s for Fe(III) complexes [19,25]. In the Kambara theory, abrupt spin-crossover transitions are given an FO $\rightleftharpoons$ LS character, while gradual transitions are of the HS $\rightleftharpoons$ LS type. However, experimental evidences of cooperative Jahn–Teller transitions (FO $\rightleftharpoons$ HS) have not yet been reported for Fe(II) spin-crossover complexes. Kambara’s theory ignores the spin–orbit interaction and appears to overestimate the Jahn–Teller coupling, producing an unphysical (for Fe(II) complexes) FO $\rightleftharpoons$ HS transition.

The most interesting possibility indicated by this phase diagram is that the FO phase may be present as a metastable phase below $T_{JT} \approx 26 \text{ K}$, instead of the HS phase above T_{JT} . It suggests that physical properties of the metastable phase may change at T_{JT} . Recently, a photo-induced metastable phase of an Fe(II) spin-crossover complex [Fe(2-pic)₃]Cl₂ · EtOH (2-pic = 2-aminomethylpyridine) was reported [26–28]. Its properties are remarkably different from those of the metastable HS phase quenched by rapid cooling. Lowered symmetry accompanying the Jahn–Teller deformation has

been invoked to explain the difference. The situation has close similarity to the present compound. Thus, [Mn(taa)] may be driven into a Jahn–Teller distorted FO phase by irradiation of light. The strong cooperativity indicated by the large value of $J_1/k_B = 125$ K is a favorable factor [29], even though the $HS \rightleftharpoons LS$ transition has very small thermal hysteresis.

Recently high-field/high-frequency EPR spectra of [Mn(taa)] were recorded for a powder sample at 1017.6 GHz. Analysis of the spectra showed the presence of a rhombic zero-field splitting in the HS molecule [30], which is consistent with the symmetry lowering by $E \otimes e$ Jahn–Teller distortions and the dynamic reorientation of deformation dipoles slower than the time scale of $\sim 10^{-12}$ s.

4. CONCLUSION

Spin-crossover phase transition of a manganese(III) complex [Mn(taa)] was studied by variable-temperature laser Raman spectroscopy and it was found that the vibrational contribution in the transition entropy is not dominant in contrast to the cases of ordinary iron spin-crossover systems. The discovery of a dynamic disorder in the HS phase by means of dielectric measurements provided an alternative entropy source to explain the thermally induced spin-crossover transition. This dynamic disorder was attributed to the reorienting distortion dipoles accompanying the $E \otimes e$ Jahn–Teller effect in HS manganese(III) ions.

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REFERENCES

- [1] O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993, Chapter 4.
- [2] P. Gülich, A. Hauser and H. Spiering, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 2024.
- [3] O. Kahn, *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 547.
- [4] A. Hauser, J. Jeftić, H. Romstedt, R. Hinek and H. Spiering, *Coord. Chem. Rev.*, 1999, **190–192**, 471.
- [5] P. Gülich, Y. Garcia and H. A. Goodwin, *Chem. Soc. Rev.*, 2000, **29**, 419.
- [6] J. K. McCusker, A. L. Rheingold and D. N. Hendrickson, *Inorg. Chem.*, 1996, **35**, 2100.
- [7] M. Nakano, S. Okuno, G. Matsubayashi, W. Mori and M. Katada, *Mol. Cryst. Liq. Cryst.*, 1996, **286**, 83.
- [8] M. Nakano, A. Nakahama, S. Okuno, G. Matsubayashi, W. Mori and M. Katada, *Mol. Cryst. Liq. Cryst.*, 2002, **376**, 399.

- [9] J. M. Holland, J. A. McAllister, C. A. Kilner, M. Thornton-Pett, A. J. Bridgeman and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 2002, 548.
- [10] D. L. Reger, C. A. Little and M. D. Smith, *Inorg. Chem.*, 2002, **41**, 4453.
- [11] P. G. Sim and E. Sinn, *J. Am. Chem. Soc.*, 1981, **103**, 241.
- [12] Y. Garcia, O. Kahn, J.-P. Ader, A. Buzdin, Y. Meurdesoif and M. Guillot, *Phys. Lett. A*, 2000, **271**, 145.
- [13] M. Sorai and S. Seki, *J. Phys. Chem. Solids*, 1974, **35**, 555.
- [14] M. Sorai, *Bull. Chem. Soc. Jpn*, 2001, **74**, 2223.
- [15] G. Molnár, V. Niel, A. B. Gaspar, J.-A. Real, A. Zwick, A. Bousseksou and J. J. McGarvey, *J. Phys. Chem. B*, 2002, **106**, 9701.
- [16] A. Bousseksou, J. J. McGarvey, F. Varret, J. A. Real, J.-P. Tuchagues, A. C. Dennis and M. L. Boillot, *Chem. Phys. Lett.*, 2000, **318**, 409.
- [17] N. Suemura, M. Ohama and S. Kaizaki, *Chem. Commun.*, 2001, 1538.
- [18] H. Paulsen, R. Benda, C. Herta, V. Schünemann, A. I. Chumakov, L. Duelund, H. Winkler, H. Toftlund and A. X. Trautwein, *Phys. Rev. Lett.*, 2001, **86**, 1351.
- [19] I. B. Bersuker, *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry*, Plenum Press, New York, 1983.
- [20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M.W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, GAUSSIAN98, Revision A.11, Gaussian, Inc., Pittsburgh, PA, 2001.
- [21] R. M. Strat and H. Adachi, *J. Chem. Phys.*, 1987, **86**, 7156.
- [22] M. Nakano, N. Fujita, G. Matsubayashi and W. Mori, *Mol. Cryst. Liq. Cryst.*, 2002, **379**, 365.
- [23] C. P. Slichter and H. G. Drickamer, *J. Chem. Phys.*, 1972, **56**, 2142.
- [24] T. Kambara, *J. Chem. Phys.*, 1979, **70**, 4199. T. Kambara, *J. Chem. Phys.*, 1981, **74**, 4557.
- [25] N. Sasaki and T. Kambara, *J. Chem. Phys.*, 1981, **74**, 3472.
- [26] T. Tayagaki and K. Tanaka, *Phys. Rev. Lett.*, 2001, **86**, 2886.
- [27] T. Tayagaki, K. Tanaka, N. Yonemura, M. Shirai and K.-I. Kan'no, *Int. J. Mod. Phys. B*, 2001, **15**, 3709.
- [28] L. X. Chen, Z. Y. Wang, J. K. Burdett, P. A. Montano and J. R. Norris, *J. Phys. Chem.*, 1995, **99**, 7958.
- [29] X.-J. Liu, Y. Moritomo, A. Nakamura, T. Hirao, S. Toyozaki and N. Kojima, *J. Phys. Soc. Jpn*, 2001, **70**, 2521.
- [30] S. Kimura, T. Otani, Y. Narumi, K. Kindo, M. Nakano and G. Matsubayashi, *J. Phys. Soc. Jpn Suppl.*, in press; S. Kimura, private communication.

Ground State of Quantum Jahn–Teller Model: Selftrapping vs. Correlated Phonon-assisted Tunneling

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Abstract

Ground state of the quantum Jahn–Teller model with broken rotational symmetry was investigated by the variational approach in two cases: a lattice and a local one. Both cases differ by the way of accounting for the nonlinearity hidden in the reflection-symmetric Hamiltonian. In spite of that the ground state energy in both the cases shows the same features, namely, there appear two regions of model parameters governing the ground state: the region of dominating selftrapping modified by the quantum effects and the region of dominating phonon-assisted tunneling (antiselftrapping). In the local case (i) the effect of quantum fluctuations and anharmonicity due to the two-mode correlations is up to two orders larger than contributions due to the reflection effects of two-center wave function; (ii) the variational results for the ground state energy were compared with exact numerical results. The coincidence is the better the more far away from the transition region at the $E \otimes e$ symmetry where the variational approach fails.

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1. INTRODUCTION

Jahn–Teller model as a prototype model for phonon removal of degeneracy of electron levels in complex molecules [1] was investigated mainly in its rotational symmetric $E \otimes e$ local version with electron coupling to two degenerate intramolecular phonon modes, one antisymmetric and one symmetric against reflection. Importance of focusing on the lattice version of the model increased due to JT-based structural phase transitions in some recently discovered high- T_c superconductors and manganese-based perovskites [2,3].

For the reflection symmetric two-level electron–phonon models with linear coupling to one phonon mode (exciton, dimer) Shore *et al.* [4] introduced variational wave function in a form of linear combination of the harmonic oscillator wave functions related with two levels. Two asymmetric minima of effective polaron potential turn coupled by a variational parameter (VP) respecting its anharmonism by assuming two-center variational phonon wave function. This approach was shown to yield the lowest ground state energy for the two-level models [4,5].

The peculiarities due to reflection phenomena are expected also in the case of linear coupling with two phonon modes. In contrast to the model with coupling to one phonon mode, the oscillations mediated by the antisymmetric mode are nonlinearly coupled to the symmetric phonon mode. Therefore, in order to improve the harmonic oscillator variational ansatz for this model, it was necessary to introduce additional considering *correlation* of both the phonon modes. This was performed by Lo [6] for the $E \otimes e$ JT model and by Lo and Sollie [7] for the dimer model. The correlation was found most effective in the region of parameters where the competing localization (polaron) energy and the delocalization transfer energy (tunneling) were comparable.

In crystals exhibiting high space anisotropy the rotational symmetry of Jahn–Teller molecules can be broken. Therefore, it is reasonable to investigate JT model generalized by breaking the rotational symmetry (while saving the reflection symmetry): we assume different coupling strengths for the onsite (intralevel) and interlevel electron–phonon couplings. Such a model can also be considered as a generalization of the exciton–phonon or the dimer–phonon model by assuming that the electron tunneling is phonon assisted. JT model with the broken rotational symmetry will involve the coupling of two minima as well as the coupling of the symmetric and antisymmetric phonon modes. In the lattice model, however, in contrast to the local case, the mode correlation appears to be of a marginal importance (Section 3). As a consequence, our ansatz for the variational wave function of the local model will involve (i) the reflection VP introduced by the construction of the two-center phonon wave function, and (ii) correlation VP respecting coupling of the symmetric and antisymmetric phonon modes. The question arises of the importance of these VPs and respective effects regarding their relevance in different regions of the model parameters. Formulation of the variational ansatz of the local case is presented in Section 4. Calculation of the ground state energy of the lattice model and related discussions

are the contents of Sections 3 and 5. Reliability of different variational alternatives was checked by comparison with results of exact numerical simulations for the local model.

2. EXTENDED (LATTICE) GENERALIZED JAHN–TELLER MODEL

We investigate 1D lattice of spinless double degenerated electron states linearly coupled to two intramolecular phonon modes described by Hamiltonian

$$H = \Omega \sum_{n,i=1,2} (b_{i,n}^\dagger b_{i,n} + 1/2) + \sum_n (\alpha(b_{1,n}^\dagger + b_{1,n})\sigma_{zn} - \beta(b_{2,n}^\dagger + b_{2,n})\sigma_{xn}) - \frac{T}{2} \sum_{n,j=1,2} (R_{1,j} + R_{-1,j})I_n \quad (1)$$

where $b_{i,n}$, $i = 1, 2$ are phonon annihilation operators, and Pauli's matrices σ_{ln} represent two-level electron system. They satisfy identities $[\sigma_{ln}, \sigma_{jn}] = i\sigma_{kn}$, $l = x, y, z$, representing 1/2-pseudo-spins related to the electron densities in a usual way, i.e., $\sigma_{xn} = \frac{1}{2}(c_{1,n}^\dagger c_{2,n} + c_{2,n}^\dagger c_{1,n})$, $\sigma_{yn} = \frac{1}{2i}(c_{1,n}^\dagger c_{2,n} - c_{2,n}^\dagger c_{1,n})$, $\sigma_{zn} = \frac{1}{2}(c_{1,n}^\dagger c_{1,n} - c_{2,n}^\dagger c_{2,n})$, $I_n = \frac{1}{2}(c_{1,n}^\dagger c_{1,n} + c_{2,n}^\dagger c_{2,n})$ is a unit matrix, and $c_{j,n}$ are electron annihilation operators. The operator $R_{\pm 1,j} = e^{\pm ipa}$ of the displacement by a lattice constant $\pm a$ acts in both the electron and phonon space, $R_{\pm 1,j}f_n = f_{n\pm 1}R_{\pm 1,j}$.

In terms of the creation–annihilation electron and phonon operators the Hamiltonian can be cast as follows:

$$H = \sum_n \left[\Omega \sum_{i=1,2} \left(b_{i,n}^\dagger b_{i,n} + \frac{1}{2} \right) + \frac{\alpha}{2} (c_{1,n}^\dagger c_{1,n} - c_{2,n}^\dagger c_{2,n}) (b_{1n}^\dagger + b_{1n}) - \frac{\beta}{2} (c_{1n}^\dagger c_{2n} + c_{2n}^\dagger c_{1n}) (b_{2n}^\dagger + b_{2n}) - \frac{T}{2} \sum_{n=1,2} (c_{j,n}^\dagger c_{j,n+1} + \text{H.c.}) \right] \quad (2)$$

For $\beta = -\alpha$, the interaction part of equation (1)

$$\alpha \begin{pmatrix} b_{1n}^\dagger + b_{1n} & b_{2n}^\dagger + b_{2n} \\ b_{2n}^\dagger + b_{2n} & -(b_{1n}^\dagger + b_{1n}) \end{pmatrix} \quad (3)$$

yields the rotationally symmetric $E \otimes e$ form [1] with a pair (an antisymmetric and a symmetric under reflection) of double degenerated vibrations. This is, e.g. the case of Cu^{++} ions with d^9 configurations in high- T_c cuprates [1,2].

Taking $\alpha \neq \beta$ removes the degeneration of the vibronic states breaking the rotational symmetry of the electron–phonon interactions, the model still staying within the class of JT models [1,2].

The dispersionless optical phonon mode b_1 splits the degenerated unperturbed electron level ($j = 1, 2$) while the mode b_2 mediates the electron transitions between the levels. This latter term represents phonon-assisted tunneling, a mechanism of the

nonclassical (nonadiabatic) nature as well as the pure tunneling in related exciton and dimer models.

Evidently, Hamiltonian (1) ($\alpha \neq \beta$) is reflection-symmetric, $G^{(\text{el})} G_1^{(\text{ph})} H = H$,

$$\begin{aligned} |2\rangle &= G^{(\text{el})} |1\rangle, & (G^{(\text{el})})^2 &= 1, \\ G_{1n}^{(\text{ph})} (b_{1n}^\dagger \pm b_{1n}) &= -(b_{1n}^\dagger \pm b_{1n}) G_{1n}^{(\text{ph})}, & (G_{1n}^{(\text{ph})})^2 &= 1 \end{aligned} \quad (4)$$

where $G_{1n}^{(\text{ph})} = \exp(i\pi b_{1n}^\dagger b_{1n})$ is the phonon reflection operator. While phonon 1 is antisymmetric under the reflection, phonon 2 remains symmetric.

In addition, the transfer part of equation (2) exhibits SU(2) symmetry of the left- and right-moving electrons (holes).

Let us note that the quantum phonon assistance of the electron tunneling (β -term in equations (1) and (2)) constitutes the difference of the model from the related dimer and exciton quantum models where instead of $\beta \sum_n (b_{2n}^\dagger + b_{2n}) \sigma_{xn}$ of equation (1) there stands $\Delta \sigma_{xn}$, where Δ is the distance between the levels [4,5].

The local part of equation (1) can be diagonalized in electron subspace by the Fulton–Gouterman unitary operator [8] $U_n \equiv U_{2,n} U_{1,n}$, where

$$U_{i,n} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & G_{i,n} \\ 1 & -G_{i,n} \end{pmatrix}, \quad G_{i,n} = \exp(i\pi b_{in}^\dagger b_{in}) \equiv G_{i,n}^{(\text{ph})} \quad (5)$$

as follows

$$\begin{aligned} \tilde{H}_L &= \sum_n U_n H_{0n} U_n^{-1} \\ &= \Omega \sum_{n,i=1,2} \left(b_{in}^\dagger b_{in} + \frac{1}{2} \right) + \frac{1}{2} \sum_n [\alpha (b_{1n}^\dagger + b_{1,n}) - \beta (b_{2n}^\dagger + b_{2n}) G_{1,n}] I_n \end{aligned} \quad (6)$$

On the other hand, in the transfer term

$$\tilde{H}_T = -\frac{T}{2} \sum_n (V_{n,1} R_1 + V_{n,-1} R_{-1}) \quad (7)$$

there appears a nondiagonality

$$\begin{aligned} V_{n,\pm 1} &= [(1 + G_{1n} G_{1n\pm 1}) I_n + (1 - G_{1n} G_{1,n\pm 1}) G_{2n} \sigma_{zn}] \\ &\quad \times [(1 + G_{2n} G_{2n\pm 1}) I_n + (1 - G_{2n} G_{2,n\pm 1}) \sigma_{xn}] \end{aligned} \quad (8)$$

Here, Pauli's matrices transform as $U_i \sigma_x U_i^{-1} = G_i \sigma_z$, $U_i \sigma_z U_i^{-1} = \sigma_x$, and $U_i (b_i^\dagger + b_i) U_i^{-1} = (b_i^\dagger + b_i) 2\sigma_x$.

The diagonal terms of equation (8) represent the polaron transfer within one level while the off-diagonal ones represent the interlevel polaron transfer through the lattice. Evidently, the contribution of the off-diagonal terms proportional to $1 - G_{in} G_{i,n+1}$ is much smaller when compared with those proportional to $1 + G_{in} G_{i,n+1}$.

Because of nonconservation of the number of coherent phonons, they are able even in the ground state to assist electron transitions between the levels. In the

Hamiltonian (6), the operator $G_{1n} = (-1)^{b_{1n}^\dagger b_{1n}}$ (equation (5)) highly nonlinear in the phonon-1 appears mediated by phonons 2. It introduces multiple electron oscillations between the split levels mediated by *continuous virtual absorption and emission of the phonons* 1. The effect is analogous to Rabi oscillations in quantum optics due to photons [9]. Let us note that Rabi oscillations assist both the interlevel onsite and intersite electron transitions mediated by the electron transfer T .

Further we shall investigate by variational approach the two variants of the model (1) – the lattice and the local one (considering $T = 0$).

Shore *et al.* [4] and Wagner *et al.* [5] proved for exciton or dimer models coupled to one phonon mode that the two-center wave function generalized to an asymmetric nonunitary ansatz with a VP η of the form

$$\Psi^{(p)} = \frac{1}{\sqrt{C}}(1 + \eta p G)|1\rangle\phi^{(p)} \quad (9)$$

(where C is a normalization constant), yields lower ground state [4,5].

So, rather generally we define phonon wave functions $\phi^{(p)}$

$$\phi^{(\pm)} = D_1(\pm\zeta_1)D_2(\zeta_2)S_2(r_2)S_1(r_1)S_{12}(\pm\lambda)|0\rangle \quad (10)$$

Here, the generators of variational displacements are defined

$$D_i(\eta) = \exp[\zeta_i(b_i^\dagger - b_i)] \quad (11)$$

and those of squeezing

$$S_i(r_i) = \exp[r_i(b_i^{\dagger 2} - b_i^2)] \quad (12)$$

for $i = 1, 2$. In equation (6) coupling of the phonon modes 1 and 2 occurs, therefore, one includes into the ansatz (10) also the correlation generator

$$S_{12}(\lambda) = \exp[\lambda(b_1^\dagger b_2^\dagger - b_1 b_2)] \quad (13)$$

with a correlation VP λ .

The form (10) is written here seemingly for the local case, while the most general form of it should contain the dependencies of all VPs on n (site number in the lattice): $\gamma_1 \rightarrow \gamma_{1m}(n)$, etc., showing the displacement of the mode 1 at site m due to the electron at site n , $\gamma_{jm}(n) = (1/\sqrt{N}) \sum_q \gamma_{jq}(n) \exp(-iqma)$. We take

$$\gamma_{jq}(n) = \frac{\gamma_j}{\sqrt{N}} \exp(iqna) \rightarrow \gamma_{jm}(n) = \gamma_j \delta_{m,n} \quad (14)$$

where γ_j are independent of n . Equation (14) indicates that the phonon displacement accompanies the electron at site n . The same is valid for the squeezing, $r_m(n) = r \delta_{m,n}$ and mixing parameter λ . When we consider the ground state of the lattice model, we omit the electron and phonon dynamic terms by setting $k = 0$, $q = 0$, thus even in the lattice case we are left with the effective local molecule Hamiltonian, the only

difference being the additional contribution of the transfer terms (those containing T). As it is shown later, in the lattice model we can set $\lambda = 0$ without worsening considerably the variational results, while for the local case $T = 0$ introducing this parameter considerably improves the results. In what follows the ground state energy as a function of optimized VPs η , γ_1 , γ_2 , r , λ will be determined.

3. GROUND STATE OF THE LATTICE MODEL

First we consider the lattice model setting $\lambda = 0$.

By averaging $\tilde{H} = \tilde{H}_L + \tilde{H}_T$ (equations (6) and (7)) over the phonon wave functions (9) with equation (10) one obtains for the site Hamiltonian (6) the local part in the form

$$\frac{\langle \tilde{H}_L \rangle}{N} \equiv H_{\text{ph}} + H_{\text{int}} \quad (15)$$

where

$$H_{\text{ph}} = \frac{\Omega}{2} (\cosh 4r + 1)I + \Omega \frac{1 + \eta^2 - 2\eta e^{-8r_1} \exp(-2|\tilde{\gamma}_1|^2)}{1 + \eta^2 + 2\eta \exp(-2|\tilde{\gamma}_1|^2)} |\gamma_1|^2 I + \Omega |\gamma_2|^2 I \quad (16)$$

$$H_{\text{int}} \equiv H_\alpha + H_\beta = \frac{\alpha(1 - \eta^2)}{1 + \eta^2 + 2\eta \exp(-2|\tilde{\gamma}_1|^2)} \gamma_1 \sigma_z - \frac{\beta[(1 + \eta^2) \exp(-2|\tilde{\gamma}_{1q}|^2) + 2\eta]}{1 + \eta^2 + 2\eta \exp(-2|\tilde{\gamma}_1|^2)} \gamma_2 I \quad (17)$$

where H_α and H_β are α - and β -dependent parts of the interaction H_{int} (equation (17)). From the transfer Hamiltonian $\tilde{H}_T$ (equation (7)) there remains

$$\frac{\langle \tilde{H}_T \rangle}{N} = -T \exp(-W)M \equiv 2(H_{T1}I + H_{T2}i\sigma_y + H_{T3}\sigma_z + H_{T4}\sigma_x) \quad (18)$$

where M :

$$M = [(1 + E_1^2)I + (1 - E_1^2)E_2\sigma_{zn}] \cdot [(1 + E_2^2)I + (1 - E_2^2)\sigma_x] \quad (19)$$

and E_i are given by

$$E_1 \equiv \exp(-2|\tilde{\gamma}_2|^2), \quad E_2 \equiv \exp(-2|\gamma_2|^2) \quad (20)$$

Expressions E_i (equation (20)) in the ground state are independent of q and n because of the form of $\gamma_{iq}(n) = \gamma_i \exp(-iqna)$ (14). This substantially simplifies subsequent calculations leaving E_i and C_1 as functions of γ_i^2 independent on n . The transfer terms H_{Ti} , $i = 1, 2, 3, 4$ in equation (18) with equation (19) are

expressed as

$$\begin{aligned} H_{T1} &= -\frac{T}{4}(1 + E_1^2)(1 + E_2^2), & H_{T2} &= -\frac{T}{4}(1 - E_1^2)(1 - E_2^2)E_2, \\ H_{T3} &= -\frac{T}{4}(1 - E_1^2)(1 + E_2^2)E_2, & H_{T4} &= -\frac{T}{4}(1 + E_1^2)(1 - E_2^2) \end{aligned} \quad (21)$$

Here, H_{T1} , H_{T3} and H_{T2} , H_{T4} are diagonal and off-diagonal terms of equation (18), respectively.

The effective polaron potential in equation (15) (with equations (16)–(20)) as a highly nonlinear function of γ_1 and γ_2 is visualized in Fig. 1.

The potential exhibits two sets of minima related to two competing ground states:

- (i) Two nonequivalent broad minima related to both the levels (equation (10)) at $\pm\gamma_1 \neq 0$ and γ_2 close to 0;
- (ii) One narrow minimum at γ_1 close to 0, $\gamma_2 > 0$, where both levels approach close together. This minimum develops at growing β ; evidently its behaviour depends also on T value because of nonlinearity of the Debye–Waller factor M (equations (19) and (20)).

The ground state energies related to these two sets of competing minima were calculated numerically. The result of the numerical minimalization of the

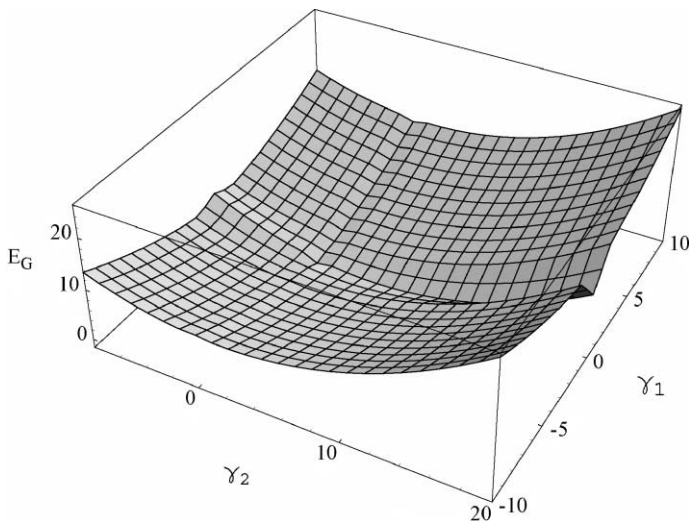


Fig. 1. The effective potential for $\chi = \beta/\alpha = 0.5$, $\mu = 2$ and $T = 1$, $\Omega = 0.05$ as a function of γ_1 , γ_2 .

diagonalized form of energy (equation (15))

$$E = H_{\text{ph}} + H_{\beta} + H_{\text{T1}} - [(H_{\alpha} + H_{\text{T3}})^2 + H_{\text{T4}}^2 - H_{\text{T2}}^2]^{1/2} \quad (22)$$

can be written symbolically as

$$E_{\text{G}}(\mu, \chi, \Omega/T) = E(\{\gamma_{1q}, \gamma_{2q}, r, \eta\}_{\text{min}})/T \quad (23)$$

Here, the index ‘min’ denotes the optimized values. The model parameters

$$\mu = \frac{\alpha^2}{2\Omega T}, \quad \chi = \frac{\beta}{\alpha}, \quad \frac{\Omega}{T} \quad (24)$$

are parameters of the effective interaction, asymmetry and nonadiabaticity, respectively. Energy E_{G} (equation (23)) is in scaled units, renormalized by T . The results of the numerical evaluations of the ground state energy (equation (23)) are depicted in Figs 2a and b for various model parameters.

One can distinguish there two regions depending on the value of χ with different behaviour of ground state in each of them:

- (i) The ground state pertaining to the lower broad minimum at $\gamma_1 < 0$ and $\gamma_2 \approx 0$ with a small reflection part at $\gamma_1 > 0$ is referred to as a ‘heavy’ region. It corresponds to predominantly intralevel ‘heavy’ polaron which is represented by a two-peak wave function, both peaks representing a harmonic oscillator ($\sim \exp[-(x \mp \gamma_1)^2]$) displaced by the value $\pm \gamma_1$ (as it is seen from the form of the ansatz (equation (10))). The ‘heavy’ polaron is dominant at $\chi < 1$ where the broad minimum $\gamma_1 < 0$ is dominating.
- (ii) Close to $\chi = 1$, the energies of two minima go very close to each other (their difference is of the order of the phonon energy Ω). They drop to one narrow minimum which represents a new ground state. *Close to $\chi = 1$, continuous transition to a new ground state occurs.* It stabilizes at $\chi > 1$, where (optimized)

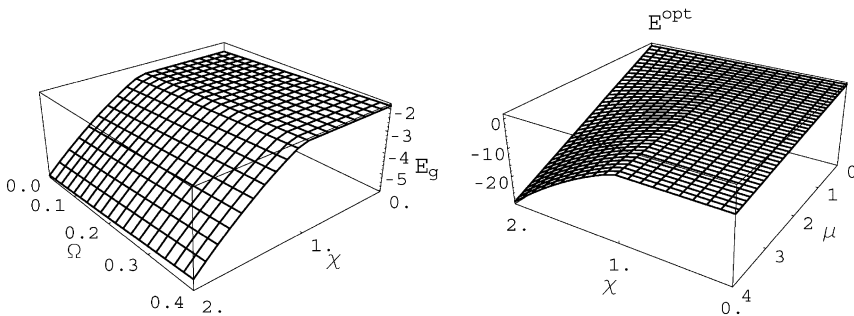


Fig. 2. The ground state energy (equation (28)) in the χ – Ω plane at $\mu = 2.5$ (a) and in the plane χ – μ ($\Omega = 1$) (b). The selftrapping dominated phase at $\chi < 1$ and the tunneling dominated phase at $\chi > 1$.

γ_1 value is close to 0 and $\gamma_2 > 0$. This region is referred to as a ‘light’ polaron region because, owing to the abrupt decrease of $\gamma_1 \approx 0$ at $\chi > 1$, the effective mass of the intralevel polaron drops to almost its free-electron value, i.e., *the polaron selflocalization vanishes in the ‘light’ region*. Because of this ‘undressing’, the transport characteristics of the excited electron would increase. Moreover, due to the very small distance between the levels, their coupling takes place by the exchange of virtual phonons 1. At suitable conditions, in the excited state, when both levels are occupied by electrons of opposite spins, *the mechanism of virtual phonon exchange implies the pairing of electrons, i.e., formation of ‘light’ bipolarons*.

The ground state energy, especially its behavior dependent on pairs of parameters χ , Ω and χ , μ is illustrated in detail in Fig. 2. While being weakly Ω -dependent, the energy strongly decreases with χ inside the ‘light’ phase (Fig. 2a). The position of the phase line is slightly shifted from $\chi = 1$ at $\Omega = 0$ to higher values of χ with increasing Ω . This is consistent with the fact that the phonon fluctuations are most effective when the difference of the energies of the phases is of the order of the phonon energy.

The ground state energy in the ‘heavy’ region ($\chi < 1$) is independent of χ , its decrease inside the ‘light’ region ($\chi > 1$) is dependent on the effective coupling μ (Fig. 2b). The energy decrease due to μ is stronger in the ‘light’ phase (depending on χ) than in the ‘heavy’ phase.

The region of importance of reflection measure η and r is illustrated in Fig. 3. There we show the difference between the ground state energy with r and η omitted and ground state with four VPs calculated numerically. However, contribution due to r , $E_G(\eta, r = 0) - E_G \sim 2 \times 10^{-3}$ of the maximum value in Fig. 3. The said parameters turn out to be most relevant in $E \otimes e$ JT case ($\chi = 1$).

The effects of η and r on the ground state is apparent only at moderate couplings in the ‘heavy’ region, reaching their maximum at $\chi = 1$. The narrow minimum (the ‘light’ region) is resistant against η .

In order to demonstrate important properties of displacements (μ and Ω dependence) it is sufficient, except for the region of importance of the reflection (Fig. 3) inside the ‘heavy’ region apparent for γ_2 , to calculate them in the limit $\eta = 0$. We shall use equation (22) approximated for the cases of both ‘heavy’ and ‘light’ polaron and obtain implicit expressions for γ_i , which, however, are good to visualize their behaviour in both regions:

- (i) ‘heavy’ polaron (γ_2 small, $E_2 \approx 1$; H_{T2} ; $H_{T4} \approx 0$):

$$\gamma_1 \approx \frac{-\alpha e^{4r}}{2T E_1^2 \left[2 + \frac{\Omega e^{4r}}{T E_1^2} \right]} \quad (25)$$

γ_2 is small except for the region of fluctuations visualized in Fig. 4. One can see that the selflocalization due to phonons 2 in the ‘heavy’ region $\sim -\gamma_2^2$ clearly

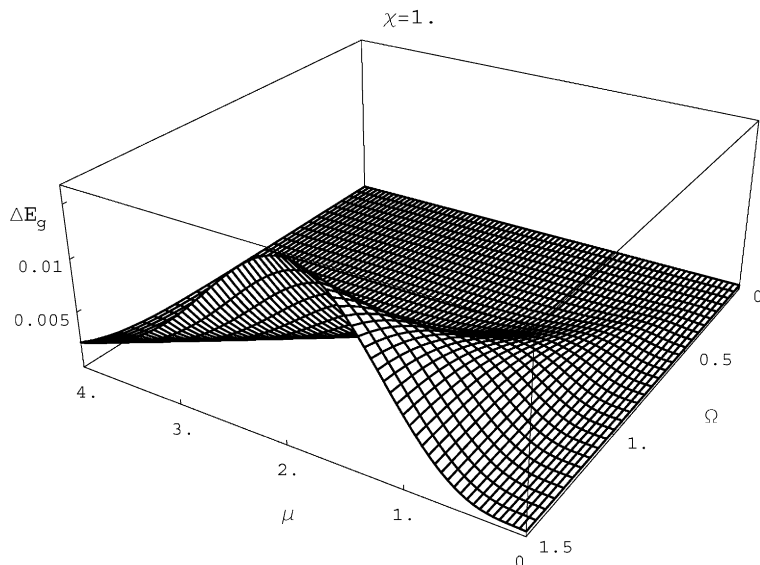


Fig. 3. The range of relevance of the reflection parameter η : difference $\Delta E_G = E_G(\eta = 0, r = 0) - E_G$, for $\chi = 1$, E_G is the exact ground state (equation (23)). For $\chi < 1$, the difference increases with χ reaching its maximum at $\chi = 1$. At $\chi > 1$ it drops to zero, i.e., the narrow minimum ‘light’ phase is resistant against η .

implies the ‘cave’ in the ground state energy due to the reaction measure η (anharmonicity) of the ground state (Fig. 3).

(ii) ‘light’ polaron (γ_1 small, $E_1 \approx 1$, $H_{T2}, H_{T3} \approx 0$):

$$\gamma_1 \approx \frac{-\alpha e^{4r}}{2T E_1^2 \left(1 + \frac{\beta^2}{2\Omega T} + \frac{\Omega e^{4r}}{T E_1^2} \right)} \approx 10^{-8},$$

$$\gamma_2 \approx \frac{\beta}{2T E_2^2 \left(2 + \frac{\Omega}{T E_2^2} \right)}$$
(26)

In the ‘light’ region the fluctuations of γ_1 are missing as well as the fluctuations of the energy. This is consistent with the above result of the resistance of the narrow minimum against η .

For both ‘heavy’ and ‘light’ polaron a dependence of γ_i on the nonadiabaticity parameter Ω/T appears. It implies the dependence of the Debye–Waller factor and consequently of the polaron mass on the phonon frequency Ω . This can be thought of as an analogy of the *isotope effect* at zero temperature.

In the ‘heavy’ phase, electron transitions mediated by phonons 2 to the upper level enhance fluctuations $\sim \gamma_2$ which mix phonons 2 with phonons 1 and contribute to

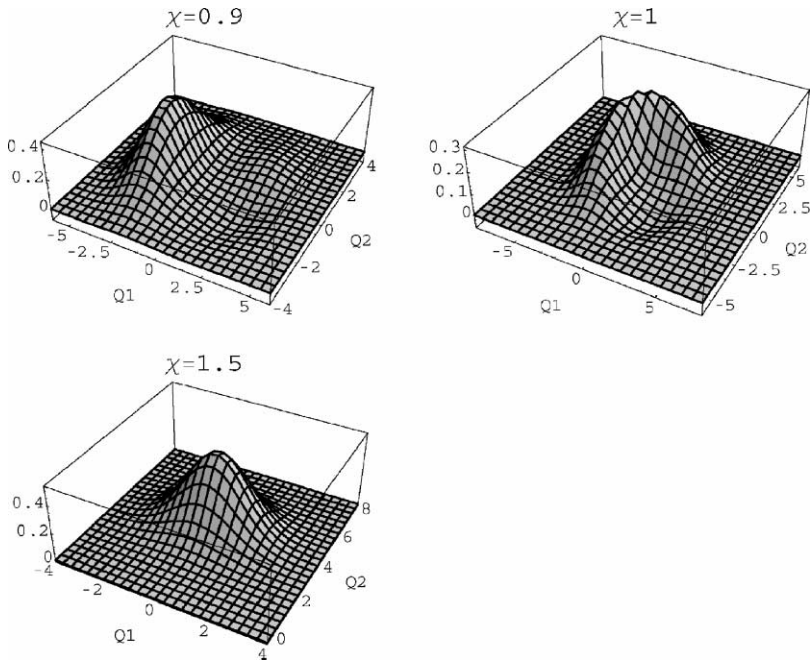


Fig. 4. The numerical ground state wave functions at $\mu = 2$ and $\chi = 0.9$ (a) $\chi = 1$ (b) and $\chi = 1.5$ (c).

the fluctuations of the ground state energy of the heavy region. This is the reason for the similarity of the results in Fig. 3.

4. GROUND STATE OF THE LOCAL MODEL

Now we consider the same Hamiltonian, but taken for the local molecule ($T = 0$). From the outset we include the additional variational mixing parameter λ into the Ansatz. The understanding of the importance of introducing the mixing parameter in the local model in the contrast to the lattice one can be gained if one examines the expressions for Hamiltonians, in particular, those terms, which contain the mixing of two phonon modes. The mixing is contained mostly in the ‘local’ term with β ,

$$\beta Q_2 \exp i\pi(b_1^+ b_1)$$

The transfer term T also contains the mixing, but it always enters the expression in the form $T(1 + E_1 E_2)$, thus for the transfer term its contribution is always shadowed by the larger term ~ 1 . Thus, if $T \neq 0$ and large enough, its contribution is always dominant over mixing term β . But if $T = 0$, we are left with the only nonlinear coupling term $\beta Q_2 \varepsilon$ and accurate accounting for mode mixing becomes crucial.

The variational mean value of the part of the Hamiltonian (6) in the state (9) renormalized by Ω yields (Appendix A)

$$\begin{aligned}
 \frac{\langle H \rangle}{\Omega} = & \frac{1}{2}(\cosh 4r_1 + \cosh 4r_2) \cosh 2\lambda + (\xi_1^2 + \xi_2^2) + \frac{2\eta}{C} \frac{\exp\left[-\frac{2\tilde{\xi}_1^2}{\cosh 2\lambda}\right]}{\cosh 2\lambda} \\
 & \times \left\{ -\tanh 2\lambda \sinh 2\lambda \cosh 2(r_1 + r_2) \cosh 2(r_1 - r_2) \right. \\
 & + \tilde{\xi}_1^2 [(\exp 2(r_1 + r_2) - \exp(-2(r_1 + r_2))) \cosh 4\lambda] (1 + \tanh^2 2\lambda) \\
 & + 2 \exp(-2(r_1 + r_2)) \sinh 4\lambda \tanh 2\lambda \cosh 2(r_1 - r_2) + \frac{\tilde{\xi}_1^2}{\cosh^2 2\lambda} \\
 & \left. \times (\sinh 4r_1 - \sinh 4r_2) - 2\xi_1 (\tanh(2\lambda) e^{2(r_2 - r_1)} \xi_2 + \xi_1) \right\} + \frac{2\alpha}{\Omega C} (1 - \eta^2) \xi_1 \\
 & - \frac{2\beta}{\Omega C} \left\{ (1 + \eta^2) [\xi_2 - \xi_1 \tanh 2\lambda \exp 2(r_2 - r_1)] \frac{\exp\left(-\frac{2\tilde{\xi}_1^2}{\cosh 2\lambda}\right)}{\cosh 2\lambda} + 2\eta \xi_2 \right\}
 \end{aligned} \tag{27}$$

where

$$\tilde{\xi}_1 = \xi_1 \exp(-2r_1), \quad C = 1 + 2\eta \frac{\exp\left(-\frac{2\tilde{\xi}_1^2}{\cosh 2\lambda}\right)}{\cosh 2\lambda} + \eta^2 \tag{28}$$

From equation (28) one can see that λ causes correlations of the selftrapping and tunneling dominated regions.

For $\lambda = 0$, equation (28) turns to

$$\begin{aligned}
 \frac{\langle H \rangle_{\lambda=0}}{\Omega} = & \frac{1}{2}(\cosh 4r_1 + \cosh 4r_2) + \frac{1}{C_0} (1 - 2\eta e^{-8r_1} \exp(-2\tilde{\xi}_1^2) + \eta^2) \xi_1^2 \\
 & + \Omega \xi_2^2 + \frac{2\alpha}{\Omega C_0} (1 - \eta^2) \xi_1 - \frac{2\beta}{\Omega C_0} [(1 + \eta^2) \exp(-2\tilde{\xi}_1^2) + 2\eta] \xi_2
 \end{aligned} \tag{29}$$

where

$$C_0 = 1 + 2\eta \exp(-2\tilde{\xi}_1^2) + \eta^2 \tag{30}$$

For $\eta = 0$, $C = 1$ and equation (28) becomes

$$\begin{aligned}
 \frac{\langle H \rangle_{\eta=0}}{\Omega} = & \frac{1}{2}(\cosh 4r_1 + \cosh 4r_2) \cosh 2\lambda + \xi_1^2 + \xi_2^2 + \frac{2\alpha}{\Omega} \xi_1 \\
 & - \frac{2\beta}{\Omega} (\xi_2 - \xi_1 \tanh 2\lambda \exp 2(r_2 - r_1)) \frac{\exp\left(-\frac{2\tilde{\xi}_1^2}{\cosh 2\lambda}\right)}{\cosh 2\lambda}
 \end{aligned} \tag{31}$$

The ground states of equations (27), (29) and (31) were found by minimalization of the expressions against the involved VPs. The respective ground state energies E^{opt} , $E_{\lambda=0}^{\text{opt}}$, $E_{\eta=0}^{\text{opt}}$, and $E_{\eta=0,\lambda=0,\text{opt}}$ will be compared mutually and with the exact value from numerical simulation in order to find out importance of the VPs η , λ in different regions of model parameters $\chi = (\beta/\alpha)$ (reflection) and $\mu = (\alpha^2/\Omega^2)$ (effective e –ph coupling). The place of $E \otimes e$ JT model will clearly come out as an important special case.

5. DISCUSSION OF THE NUMERICAL RESULTS

In lattice electron–phonon models the nonadiabaticity parameter is the ratio of phonon frequency and the band width, Ω/T . The energy is scaled by T and the effective coupling parameter (ratio of the polaron energy and of the phonon frequency) is $\mu_T = \alpha^2/2\Omega T$. In the present local model, the nonadiabaticity parameter is the ratio of the frequency and the coupling parameter Ω/α . The energy was scaled by Ω and the ratio of polaron energy and the frequency is then $\alpha^2/2\Omega^2$. Therefore, the reduction of the ground state energy of the local model due to selflocalization is stronger than that of the lattice model by the factor $\mu_L/\mu_T = T/\Omega > 1$. The energy of the tunneling β^2/Ω^2 , is comparable with the polaron energy at $\beta^2/\Omega^2 = \mu_L$. Because close to $\chi = 1$ there is $\zeta_1 \approx 0$, the effects of all VPs for $\chi > 1$ except of ζ_2 vanish. Quantum fluctuations due to r_1 , r_2 and anharmonicity due to λ are concentrated in the crossing region close to $\mu = 1$ and $\chi = 1$.

The ground state in the phase plane χ and μ shown in Fig. 4 exhibits two phases separated by the crossover line close to $\chi = 1$. It means, that the effective polaron potential exhibits two minima which reflect positions of two levels governed by the model parameters μ and χ . The minima coincide within the border of the regions close to $\chi = 1$. The phase $\chi < 1$ is χ independent, selftrapping dominated, with quantum fluctuations due to λ , η , r_1 , r_2 . The phase $\chi > 1$ is the phonon-2-assisted tunneling dominated region with continuum emission and absorption of virtual phonons-1. The phonon exchange couples the levels within one minimum. The minimum is much more sensitive to the change of model parameters μ , χ as well as to quantum fluctuations r_1 , r_2 and λ .

Electron in the selftrapping dominated region is trapped by the phonons-1 but due to the interactions mediated by phonons-2 the electron can fluctuate to the higher level. Due to the reflection symmetry of the phonons-2 continuum oscillations of the electrons at simultaneous emission and absorption of phonons-1 occurs. These oscillations couple the levels and so the electrons into pairs. This mechanism was described in a recent paper [10] for a lattice model.

From equation (31), for small χ , one can approximately take $\zeta_2 \approx 0$, $\zeta_1 \approx -\alpha/\Omega$ and for λ we are left with the result $\lambda \approx \mu\chi \exp(-2\mu)$. This dependence can be recognized in Fig. 5.

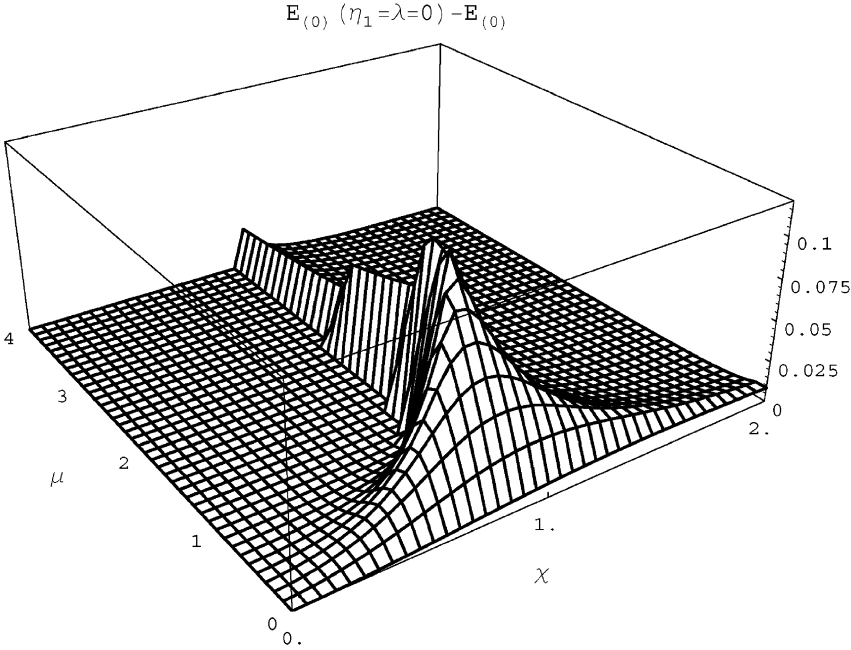


Fig. 5. The difference $E(\eta = 0, \lambda_{\text{opt}}) - E(\eta_{\text{opt}}, \lambda_{\text{opt}})$.

Comparing Figs 6a and b one can see that the mode correlation induced anharmonicity λ (Fig. 6a) is by one order larger than the contribution to the anharmonicity of the reflection level mixing η (Fig. 6b). The correlation is most effective for weak effective couplings μ at $\chi \approx 1$. For large μ it contributes only

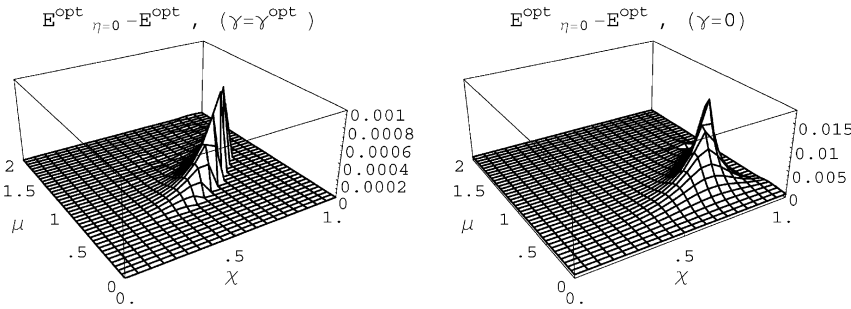


Fig. 6. The difference $E(\eta = 0, \lambda_{\text{opt}}) - E(\eta_{\text{opt}}, \lambda_{\text{opt}})$ including the mode correlation (a), without the correlation (b). Strong suppression of the reflection effects by the mode correlation at $\mu < 1$ is evident. The correlations flatten the barrier between the zones and the role of the parameter η is minorized (note the difference of the scales in (a) and (b)).

close to $\chi = 1$, where it reveals maximum for all μ . In order to check the validity of the calculations using variational approach we performed also numerical diagonalization of the Hamiltonian in the phonon-1, 2 space. We limit ourselves in N_1 phonon-1 states and N_2 phonon-2 states, thus state vector is $N_1 \times N_2$ dimensional. As numerical diagonalization results show, about 20–50 phonon states are sufficient for convergence. We show the results of numerical diagonalization of Hamiltonian matrix as function of χ for $\mu = 1$ and 4. In the first case we took 20×20 state vector, while in the latter case to achieve satisfactory convergence (especially for the tunneling-dominated region when $\chi > 1$) we had to increase the number of phonons-2 up to 50.

6. QUANTUM FLUCTUATIONS IN THE LOCAL MODEL

Fluctuations of phonon-1 coordinate $\Delta Q_1^2 = \langle Q_1^2 \rangle - \langle Q_1 \rangle^2$, $Q_1 = (1/\sqrt{2})(b_1^\dagger + b_1)$ and the conjugate momentum $P_1 = (-i/\sqrt{2})(b_1^\dagger - b_1)$ for $\eta = 0$ can be easily calculated analytically. The wave function of the phonon-1 has the Gaussian form

$$\phi(x) \sim \exp \left[-\frac{(x - \lambda_1)^2}{\cosh(2\lambda) \exp(4r_1)} \right]$$

In fact, it is squeezed displaced harmonic oscillator if one does not take into account the parameter η ; Introducing λ does not invoke higher order nonlinearities with respect to phonon-1 coordinates. Thus $\langle \Delta P_1 \rangle = 0$, like it should be for an harmonic oscillator, and the expressions for second momenta have the form:

$$\Delta Q_1^2 = \frac{1}{2} \exp 4r_1 \cosh 2\lambda, \quad \Delta P_1^2 = \frac{1}{2} \exp(-4r_1) \cosh 2\lambda \quad (32)$$

and

$$(\Delta P_1^2 \Delta Q_1^2)^{1/2} = \frac{1}{2} \cosh 2\lambda \quad (33)$$

The shape of fluctuations due to the correlation λ (equation (33)) closely follows the shape of the curve in Fig. 7, having its maximum close to $\chi = 1$ and $\mu \approx 1$.

The similarity of the product of uncertainties of phonon coordinate and momentum displayed in Fig. 7 illustrates anharmonic source of the contribution due to the mode correlation. The correlations λ manifest themselves in equations (32) and (33) as a phonon anharmonicity. It is noteworthy to emphasize its quantum origin (compare the note below equation (2)). The problem with $\eta \neq 0$ needs special consideration and will be considered elsewhere.

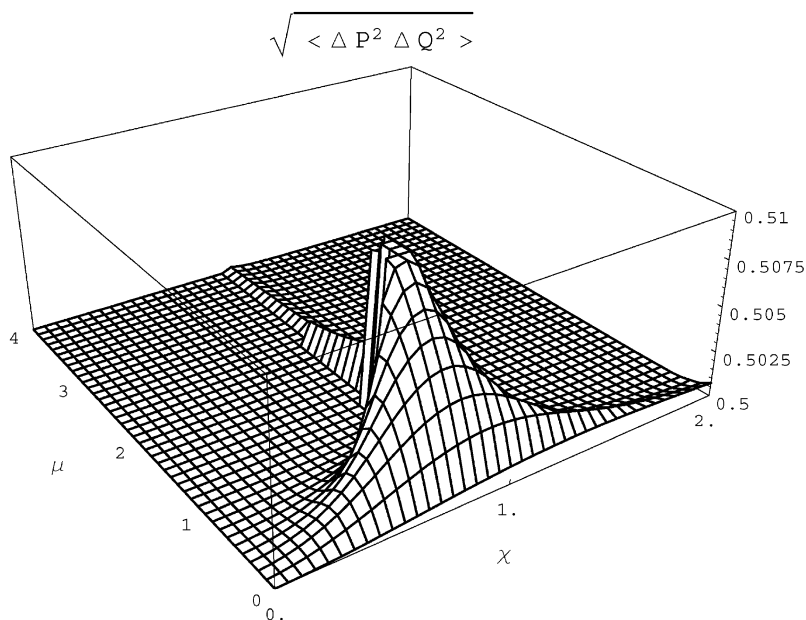


Fig. 7. The product of uncertainties of the coordinate and the conjugated momentum of the phonon 1 for $\eta = 0$.

7. CONCLUSION

A suitable choice of the variational wave functions for various electron–phonon two-level systems is a long-standing problem in solid state physics as well as in quantum optics. For two-level reflection symmetric systems with intralevel electron–phonon interaction the approach with a variational two-center squeezed coherent phonon wave function was found to yield the lowest ground state energy. The two-center wave function was constructed as a linear combination of the phonon wave functions related to both levels introducing new VP.

This symmetry implies coupling of the levels mediated by continuous virtual emission and absorption of phonons accompanying the electron tunneling between the levels. This is an analogy of Rabi oscillations in quantum optics. Investigation of referring properties (tunneling rates, Debye–Waller factors) was performed mostly for the models with onsite (Holstein) electron–phonon interactions in dimer or exciton–phonon models and also for $E \otimes e$ JT model. The methods used there were based on either combination of variational approach and unitary transformations or numerical diagonalization.

In two-level models with phonon assisted tunneling, there appears coupling of both phonon modes mediated by Rabi oscillations. Therefore, also the interlevel

quantum correlations of the phonons must be taken into account. This brings into the variational ansatz additional quantum VP.

The two-level system is characterized by strongly nonlinear effective potential provided by phonons. The nonlinearity is governed by the bare Hamiltonian parameters exhibiting a crossover from an asymmetric double potential well with two broad nonequivalent minima pertaining to the levels to a regime of one narrow minimum when the broad minima coincide into one potential well. This effect is due to the effective attraction of the levels by virtual exchange of phonons. Much effort was expended also to improve one-center variational approach by including correlations of the concerning two squeezed coherent phonon modes of the JT model. When compared to the lattice case, the local version of the model provides qualitatively similar effective potential. This conclusion was to be expected: in the symmetric case minima of the nonlinear effective potential related with two levels are close together and so the quantum fluctuations there are most effective. We considered both the mixing and squeezing correlation VP in order to find region of relevance of both parameters as functions of the interaction constants.

ACKNOWLEDGEMENTS

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APPENDIX A

We used the following formulas [11]

$$D_1(\eta_1)S_1(r_1) = S_1(r_1)D_1(\tilde{\eta}_1), \quad \tilde{\eta}_1 = \eta_1 e^{-2r} \quad (\text{A.1})$$

$$S_1^{-1}(r_1)b_1S_1(r_1) = b_1 \cosh 2r_1 + b_1^\dagger \sinh 2r_1 \quad (\text{A.2})$$

$$S_{12}^{-1}(\lambda)b_1S_{12}(\lambda) = b_1 \cosh \lambda + b_2^\dagger \sinh \lambda \quad (\text{A.3})$$

$$\begin{aligned} \langle 0|S_1^\dagger(r)D_1^\dagger(\eta)\exp(\lambda b_1^\dagger)\rangle &= \frac{1}{(\cosh 2r)^{1/2}}\exp\left[\frac{\lambda^2}{2}\tanh(2r) - \lambda\eta(\tanh 2r - 1) \right. \\ &\quad \left. - \frac{1}{2}\eta^2 + \frac{1}{2}(\tanh 2r - 1)\eta^2\right] \end{aligned} \quad (\text{A.4})$$

$$\langle 0|S_1(\zeta)D_1(\eta)b_1^{\dagger m}\rangle = \frac{d^m}{d\lambda^m}\langle 0|S_1(\zeta)D_1(\eta)\exp(\lambda b_1^\dagger)\rangle|_{\lambda=0} \quad (\text{A.5})$$

$$S_{12}(\lambda) = T^\dagger\left(\frac{\pi}{4}\right)S_1(\lambda/2)S_2(-\lambda/2)T\left(\frac{\pi}{4}\right) \quad (\text{A.6})$$

$$T\left(\frac{\pi}{4}\right)\begin{pmatrix} b_1 \\ b_2 \end{pmatrix}T^\dagger\left(\frac{\pi}{4}\right) = \frac{1}{\sqrt{2}}\begin{pmatrix} b_1 - b_2 \\ b_1 + b_2 \end{pmatrix} \quad (\text{A.7})$$

$$T^\dagger|0\rangle = T|0\rangle = |0\rangle \quad (\text{A.8})$$

REFERENCES

- [1] M. C. M. O'Brien and C. C. Chancey, *Am. J. Phys.*, 1993, **61** (8), 688.
- [2] M. D. Kaplan and B. G. Vekhter, in *Cooperative Phenomena in Jahn–Teller Crystals* (ed. J. P. Fackler), Plenum, New York, 1995.
- [3] O. Gunnarson, *Phys. Rev. Lett.*, 1995, **74**, 1875; O. Gunnarson, *Rev. Mod. Phys.*, 1997, **69**, 575.
- [4] H. B. Shore and L. M. Sander, *Phys. Rev. B*, 1973, **7**, 4537.
- [5] M. Sonnek, T. Frank and M. Wagner, *Phys. Rev. B*, 1994, **49** (22), 15637.
- [6] C. F. Lo, *Phys. Rev. A*, 1991, **43** (9), 5127.
- [7] C. F. Lo and R. Sollie, *Phys. Rev. B*, 1991, **44** (10), 5013.
- [8] R. L. Fulton and M. Gouterman, *J. Chem. Phys.*, 1961, **35**, 1059.
- [9] B. W. Shore and P. L. Knight, *J. Mod. Opt.*, 1993, **40**, 1195; I. I. Rabi, *Phys. Rev.*, 1936, **49**, 324; I. I. Rabi, *Phys. Rev.*, 1937, **51**, 652.
- [10] E. Majerníková, J. Riedel and S. Shpyrko, *Phys. Rev. B*, 2002, **65** (17), 174305.
- [11] B. L. Schumaker, *Phys. Rep.*, 1986, **133** (6), 317.

Microscopic Approach to Cooperative Jahn–Teller Effect in Crystals with Strong Intra-Site Vibronic Coupling

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Abstract

An effective Hamiltonian for a static cooperative Jahn–Teller effect acting in the space of intra-site active vibronic modes is derived on a microscopic basis, including the interaction with phonon and uniform strains. The developed approach allows for simple treatment of cooperative Jahn–Teller distortions and orbital ordering in crystals, especially with strong vibronic interaction on sites. It also allows to describe quantitatively the induced distortions of non-Jahn–Teller type.

As an example, the low-temperature structural phases of Jahn–Teller hexagonal perovskites ABX_3 with $A = \text{Cs, Rb}$; $B = \text{Cu(II), Cr(II)}$; and $X = \text{Cl, Br}$ are considered. The theory reproduces the two types of ordering of Jahn–Teller distortions observed in experiment and explains the origin of the helical ferroelectric distortions and ferromagnetic interaction within individual chains in CsCuCl_3 . It is found that orbital-dependent exchange interaction is of minor importance while both structure and magnetism in these compounds are determined by the strong second-order Jahn–Teller effect on sites.

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1. INTRODUCTION

Multicentre vibronic interactions are found in a wide number of systems such as impurity Jahn–Teller centres, molecular clusters and Jahn–Teller crystals [1]. In these compounds the localized electrons in orbitally degenerate states interact directly only with active distortions of the local environment of corresponding vibronic centres. The distortions of different centres interact *via* the common vibrational modes of the system, which thus mediate the indirect interaction between Jahn–Teller centres [2,3]. As a result the corresponding vibronic problem becomes rather involved, with many electronic states mixed by many vibrational modes.

If the vibronic interaction on the centres does not mix different electronic functions of the corresponding degenerate term, like in the case of $E \otimes b_1$, $E \otimes b_2$, and $T \otimes e$ types of vibronic coupling, the problem of cooperative Jahn–Teller effect is easily solved through a shift transformation which decouples exactly the electronic and phonon degrees of freedom [2–4]. In other cases, of essentially non-adiabatic vibronic coupling on sites (e.g. $E \otimes e$ vibronic problem) this approach cannot be applied due to non-commutative electronic operators describing the vibronic mixing on sites. Second-order vibronic interactions on centres make the problem more complicate by introducing higher order phonon terms in the potential energy function of the crystal.

In such a situation even the investigation of the equilibrium geometry of the crystal, corresponding to the low-temperature structure, presents significant difficulties.

In this chapter an effective Hamiltonian for a static cooperative Jahn–Teller effect is proposed. This Hamiltonian acts in the space of local active distortions only and possesses extrema points of the potential energy equivalent to those of the full microscopic Hamiltonian, defined in the space of all phonon and uniform strain coordinates. First we present the derivation of this effective Hamiltonian for a general case and then apply the theory to the investigation of the structure of Jahn–Teller hexagonal perovskites.

2. EFFECTIVE HAMILTONIAN FOR COOPERATIVE JAHN–TELLER EFFECT

For the sake of clarity we split the derivation in two parts. First the contribution from phonons is considered and then the effect of uniform strains is added.

2.1. Contributions from phonons

The potential energy of the Jahn–Teller crystal is described by the operator

$$\hat{H} = \sum_{\mathbf{k}j} \frac{1}{2} \omega_{\mathbf{k}j}^2 Q_{\mathbf{k}j} Q_{\mathbf{k}j}^* + \sum_{\mathbf{n}} \hat{U}_{\text{vib}}^{\mathbf{n}}(\{q_{\mu\Gamma\bar{\gamma}}^{\mathbf{n}}\}) \quad (1)$$

where $\mathbf{k}$ and j denote the wave vector and phonon branch, respectively, $Q_{\mathbf{k}j}$ is the (complex) phonon coordinate and $\omega_{\mathbf{k}j}$ the corresponding frequency. $\hat{U}_{\text{vib}}^{\mathbf{n}}$ describes

the vibronic interaction at the $\mathbf{n}$ th site of the crystal lattice. The matrix of this operator is written in the basis of a (pseudo)degenerate set of electronic functions, localized at the corresponding centre. It describes the interaction with local nuclear distortions $q_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}}$ transforming after irreducible representation $\bar{\Gamma}$ of the site symmetry group. The potential energy operator (1) can be diagonalized by performing independent unitary transformations at each centre $\mathbf{n}$ which diagonalize the corresponding vibronic operators $\hat{U}_{\text{vib}}^{\mathbf{n}}$ [5]:

$$U_{\alpha_1\alpha_2\ldots} = \sum_{\mathbf{k}j} \frac{1}{2} \omega_{\mathbf{k}j}^2 Q_{\mathbf{k}j} Q_{\mathbf{k}j}^* + \sum_{\mathbf{n}} \varepsilon_{\alpha_{\mathbf{n}}}^{\mathbf{n}} (\{q_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}}\}) \quad (2)$$

where $\alpha_{\mathbf{n}}$ numbers the eigenvalues of the vibronic operator at the $\mathbf{n}$ th centre. To find the extrema of the adiabatic potential (2), we expand the local distortions from the arguments of $\varepsilon_{\alpha_{\mathbf{n}}}^{\mathbf{n}}$ in phonon coordinates:

$$q_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}} = \sum_{\mathbf{k}j} a_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}}(\mathbf{k}j) Q_{\mathbf{k}j} \quad (3)$$

and solve the corresponding extrema equations with respect to $Q_{\mathbf{k}j}$. The relation (3) is known as the Van Vleck expansion [6].

The main complication in this extrema problem is that $\varepsilon_{\alpha_{\mathbf{n}}}^{\mathbf{n}}$ are not simple functions of local nuclear coordinates, except for cases of insignificant non-adiabaticity ($E \otimes b_1$, $E \otimes b_2$, and $T \otimes e$ vibronic coupling), where they merely lead to shifts of equilibrium phonon coordinates. Following Ref. [5] we search the extrema after both $\{q_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}}\}$ and $\{Q_{\mathbf{k}j}\}$ by using the method of Lagrange multipliers in order to satisfy the constraint in equation (3). Although the phonon coordinates are complex, the number of corresponding extrema equations is not doubled because only half of these coordinates are independent due to the relation $Q_{\mathbf{k}j} = Q_{-\mathbf{k}j}^*$ [7]. After some transformations, the details of which are given in Ref. [5], we come to the following extrema conditions:

$$\frac{\partial \varepsilon_{\alpha_{\mathbf{n}}}^{\mathbf{n}}(\{q_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}}\})}{\partial q_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}}} + \sum_{\mathbf{n}'\mu'\bar{\Gamma}'\bar{\gamma}'} K_{\mathbf{n}'\mu'\bar{\Gamma}'\bar{\gamma}'}^{\mathbf{n}\mu\bar{\Gamma}\bar{\gamma}} q_{\mu'\bar{\Gamma}'\bar{\gamma}'}^{\mathbf{n}'} = 0 \quad (4)$$

where the matrix K is defined as

$$K = \zeta^{-1}, \quad \zeta_{\mathbf{n}'\mu'\bar{\Gamma}'\bar{\gamma}'}^{\mathbf{n}\mu\bar{\Gamma}\bar{\gamma}} = \sum_{\mathbf{k}j} \frac{a_{\mu'\bar{\Gamma}'\bar{\gamma}'}^{\mathbf{n}'}(\mathbf{k}j)^* a_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}}(\mathbf{k}j)}{\omega_{\mathbf{k}j}^2} \quad (5)$$

Thus the problem of finding extrema of the potential energy of Jahn–Teller crystal is reduced to the space of active local distortions only. Having found the equilibrium values of these distortions, $q_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}(0)}$, we obtain the equilibrium values for all phonon modes:

$$Q_{\mathbf{k}j}^{(0)} = \frac{1}{\omega_{\mathbf{k}j}^2} \sum_{\mathbf{n}\mu\bar{\Gamma}\bar{\gamma}} a_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}}(\mathbf{k}j)^* \sum_{\mathbf{n}'\mu'\bar{\Gamma}'\bar{\gamma}'} K_{\mathbf{n}'\mu'\bar{\Gamma}'\bar{\gamma}'}^{\mathbf{n}\mu\bar{\Gamma}\bar{\gamma}} q_{\mu'\bar{\Gamma}'\bar{\gamma}'}^{\mathbf{n}'(0)} \quad (6)$$

The extrema equations (4) can be viewed as deriving from the following effective Hamiltonian:

$$\hat{H} = \frac{1}{2} \sum_{\mathbf{n}\mu\tilde{\Gamma}\tilde{\gamma}} \sum_{\mathbf{n}'\mu'\tilde{\Gamma}'\tilde{\gamma}'} K_{\mathbf{n}'\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mathbf{n}\mu\tilde{\Gamma}\tilde{\gamma}} q_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}} q_{\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mathbf{n}'} + \sum_{\mathbf{n}} \hat{U}_{\text{vib}}^{\mathbf{n}}(\{q_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}}\}) \quad (7)$$

This is equivalent to the initial Hamiltonian in equation (1) when the extrema are considered, but depends on active one-centre nuclear displacements only. It does not mean, however, that only these local distortions are different from zero in extrema points. Some *non-active* intra-site distortions, $q_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}}$, will be non-zero as well. Indeed, using for them the same Van Vleck expansion, with the coefficients $a_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}}(\mathbf{k}j)$, and the equilibrium values of phonon coordinates (6), we obtain

$$q_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}(0)} = \sum_{\mathbf{n}''\mu''\tilde{\Gamma}''\tilde{\gamma}''} \zeta_{\mathbf{n}''\mu''\tilde{\Gamma}''\tilde{\gamma}''}^{\mathbf{n}\mu\tilde{\Gamma}\tilde{\gamma}} \sum_{\mathbf{n}'\mu'\tilde{\Gamma}'\tilde{\gamma}'} K_{\mathbf{n}'\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mathbf{n}''\mu''\tilde{\Gamma}''\tilde{\gamma}''} q_{\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mathbf{n}'(0)} \quad (8)$$

where the matrix elements of ζ connect now the non-active local distortion on one centre ($\mathbf{n}$) with active (Jahn–Teller) distortions on other centres.

The advantage of the effective Hamiltonian (7), beside the reduced space of nuclear coordinates, is that it involves effective force constants (elements of the matrix K) which rapidly decrease with the distance between centres. This allows for efficient models involving only few force constants. Furthermore, the force constants can be calculated. For this purpose the local nuclear coordinates, at the centre $\mathbf{n}$, are expanded in Cartesian displacements, $u_{\kappa\alpha}(\mathbf{n}')$, of surrounding atoms:

$$q_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}} = \sum_{\Delta\mathbf{n}\kappa\alpha} c_{\mu\tilde{\Gamma}\tilde{\gamma}}(\Delta\mathbf{n}\kappa\alpha) u_{\kappa\alpha}(\mathbf{n} - \Delta\mathbf{n}) \quad (9)$$

where $\Delta\mathbf{n} = \mathbf{n} - \mathbf{n}'$, κ denotes different atoms in a unit cell, and α is the Cartesian axis. The expansion coefficients c are known for different basic geometries of the centres [1]. Expanding $u_{\kappa\alpha}$ in phonon modes [7], we arrive at a relation from which Van Vleck coefficients can be identified [6]. Inserting them into the second equation in equation (5) we finally obtain

$$\zeta_{\mathbf{n}'\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mathbf{n}\mu\tilde{\Gamma}\tilde{\gamma}} = \sum_{\mathbf{1}\kappa'\alpha} \sum_{\mathbf{m}\kappa\beta} c_{\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mathbf{n}'\mu'\tilde{\Gamma}'\tilde{\gamma}'} (\mathbf{n}' - \mathbf{1}\kappa'\alpha) G_{\kappa'\alpha,\kappa\beta}(\mathbf{m} - \mathbf{1}) c_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}\mu\tilde{\Gamma}\tilde{\gamma}} (\mathbf{n} - \mathbf{m}\kappa\beta) \quad (10)$$

where $G_{\kappa'\alpha,\kappa\beta}(\mathbf{n})$ are static lattice Green's functions [7,8], found for a number of crystals both from calculations [8] and neutron scattering measurements [9]. The matrix elements of G (and therefore of ζ also) are generally expected to decrease fast with the distance between the centres, as $\Delta\mathbf{n}^{-3}$ [10].

The above derivation of the effective Hamiltonian is only complete when, for some reasons, the uniform strains of the crystal are not relevant. This is clearly the case for crystals with low concentration of Jahn–Teller impurities. Contrary to that, bulk deformations often arise in its low-symmetry structural phases of Jahn–Teller crystals [2,11]. The uniform strains describing the bulk deformations of the crystal cannot be reduced to a combination of phonon modes, as it was first pointed out by

Born and Huang [12]. In the following we generalize the approach by taking into account the effects of uniform strains.

2.2. Contributions from uniform strains

The uniform strains are independent degrees of freedom of the lattice, therefore they give an additional, elastic contribution to the potential energy (1):

$$U_{\text{us}} = \frac{1}{2} NV_0 \sum_{\Gamma\gamma} C_{\Gamma\gamma}^0 e_{\Gamma\gamma}^2 \quad (11)$$

where N denotes the number of sites, V_0 is the volume of unit cell, $e_{\Gamma\gamma}$ and $C_{\Gamma\gamma}^0$ are symmetrized strains and zeroth-order elastic constants, respectively, which transform after the irreducible representation Γ of the corresponding crystalline class [13]. The symmetrized strains can be written in the form:

$$e_{\Gamma\gamma} = \sum_{\alpha\beta} \eta_{\alpha\beta}^{\Gamma\gamma} e_{\alpha\beta} \quad (12)$$

where $\eta_{\alpha\beta}^{\Gamma\gamma}$ are matrix elements of an orthogonal transformation and the components of the strain tensor are defined as usual [13]:

$$e_{\alpha\beta} = \frac{1}{2} \left[\frac{\partial u_{\alpha}(\mathbf{R})}{\partial R_{\beta}} + \frac{\partial u_{\beta}(\mathbf{R})}{\partial R_{\alpha}} \right] \quad (13)$$

where $\mathbf{R}$ is an arbitrary point in the crystal and $\mathbf{u}$ is the displacement field. For uniform strains the components $e_{\alpha\beta}$ have constant values throughout the crystal. We have supposed for simplicity that the symmetrized components of the uniform strains transform after non-repeated irreducible representations Γ , which is not an essential constraint for the subsequent treatment.

It is generally accepted in the theory of the cooperative Jahn–Teller effect to include the interaction with uniform strains in the way proposed by Kanamori [14], i.e., as additional terms of vibronic interaction at each Jahn–Teller ion. On the other hand, within one-centre-coordinate approach used here the vibronic interaction is fully described by means of one-centre active nuclear displacements $\{q_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}}\}$. Therefore the interaction with uniform strains can be included implicitly as additional terms in the Van Vleck expansion (3). Since phonons and uniform strains are independent degrees of freedom this new expansion is written as follows:

$$q_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}} = \sum_{\mu\tilde{\Gamma}\tilde{\gamma}} a_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}}(\mathbf{k}j) Q_{\mathbf{k}j} + \sum_{\Gamma\gamma} a_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}}(\Gamma\gamma) e_{\Gamma\gamma} \quad (14)$$

To find the coefficients $a_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}}(\Gamma\gamma)$, we present the atomic displacements as a superposition of two contributions:

$$u_{\kappa\alpha}(\mathbf{n}) = u_{\kappa\alpha}(\mathbf{n}) + u'_{\kappa\alpha}(\mathbf{n}) \quad (15)$$

corresponding to phonons (u) and uniform strains (u'). The second contribution

has the form:

$$u'_{\kappa\alpha}(\mathbf{n}) = \sum_{\beta} \xi_{\alpha\beta} R_{\alpha}(\mathbf{n}\kappa) \quad (16)$$

where $\mathbf{R}(\mathbf{n}\kappa)$ is the position of the atom ($\mathbf{n}\kappa$) in a common coordinate system and the coefficients

$$\xi_{\alpha\beta} = \frac{\partial u'_{\alpha}(\mathbf{R})}{\partial R_{\beta}} \quad (17)$$

are constant in the case of uniform strains. The nine coefficients $\xi_{\alpha\beta}$ cannot be generally expressed through six components of the symmetric tensor $e_{\alpha\beta}$. There are also three components of an antisymmetric tensor,

$$\omega_{\alpha\beta} = \frac{1}{2} \left[\frac{\partial u'_{\alpha}(\mathbf{R})}{\partial R_{\beta}} - \frac{\partial u'_{\beta}(\mathbf{R})}{\partial R_{\alpha}} \right] \quad (18)$$

which describe uniform bulk rotation of the crystal around three Cartesian axes [11] and are obviously unimportant for cooperative Jahn–Teller effect. Quenching these degrees of freedom ($\omega_{\alpha\beta} = 0$) and using equations (13) and (18) we obtain $\xi_{\alpha\beta} = e_{\alpha\beta}$. Thus equation (16) can be rewritten:

$$u'_{\kappa\alpha}(\mathbf{n}) = \sum_{\beta} e_{\alpha\beta} R_{\alpha}(\mathbf{n}\kappa) \quad (19)$$

Substituting equation (19) into equation (9), the uniform strains contribution to $q_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}}$ in equation (14) becomes

$$q_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}} = \sum_{\alpha\beta} \left[\sum_{\Delta\mathbf{n}\kappa\alpha} c_{\mu\bar{\Gamma}\bar{\gamma}}(\Delta\mathbf{n}\kappa\alpha) R_{\beta}(\mathbf{n} - \Delta\mathbf{n}\kappa) \right] e_{\alpha\beta} \quad (20)$$

Unlike Van Vleck coefficients, the expression within the brackets in the above equation, i.e., the expansion coefficient corresponding to uniform strains, is independent from $\mathbf{n}$. This results from translational invariance of the coefficients $c_{\mu\bar{\Gamma}\bar{\gamma}}(\Delta\mathbf{n}\kappa\alpha)$ and the obvious relations:

$$\sum_{\Delta\mathbf{n}\kappa\alpha} c_{\mu\bar{\Gamma}\bar{\gamma}}(\Delta\mathbf{n}\kappa\alpha) = 0 \quad (21)$$

which are valid for all active nuclear displacements $q_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}}$. Passing in equation (20) to $e_{\Gamma\gamma}$, making use of the transformation (12), we obtain the coefficients $a_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}}(\Gamma\gamma)$ in equation (14):

$$a_{\mu\bar{\Gamma}\bar{\gamma}}^{\mathbf{n}}(\Gamma\gamma) = \sum_{\alpha\beta} \left[\sum_{\Delta\mathbf{n}\kappa\alpha} c_{\mu\bar{\Gamma}\bar{\gamma}}(\Delta\mathbf{n}\kappa\alpha) R_{\beta}(\mathbf{n} - \Delta\mathbf{n}\kappa) \right] (\eta^{-1})_{\alpha\beta}^{\Gamma\gamma} \quad (22)$$

which are independent from $\mathbf{n}$ as well (in the following we drop the site index). All quantities in right-hand side of this equation are generally known.

It follows from equation (5) that the matrix elements of ζ are additive with respect to different nuclear modes if the zero-order deformation energy is diagonal after corresponding degrees of freedom. The same is expected when the contribution from uniform strains, equation (11), is taken into account. Using equations (5) and (11) we obtain

$$\tilde{\zeta} = \zeta + \frac{1}{N} \zeta' \quad (23)$$

where the matrix elements of the additional contribution from uniform strains (ζ') are the same for arbitrary pairs of sites:

$$\zeta'_{\mu' \bar{\Gamma}' \bar{\gamma}'} = \sum_{\Gamma \gamma} \frac{a_{\mu' \bar{\Gamma}' \bar{\gamma}'}(\Gamma \gamma) a_{\mu \bar{\Gamma} \bar{\gamma}}(\Gamma \gamma)}{V_0 C_{\Gamma \gamma}^0} \quad (24)$$

Replacing in equation (5) ζ by $\tilde{\zeta}$, defined in equations (23) and (24), we obtain the general form of the effective Hamiltonian (7) for the static cooperative Jahn–Teller effect. Note that this has been obtained without any approximations.

It is possible to distinguish the contributions from phonons and uniform strains in the effective force constants. After some transformations (see Appendix A) we obtain

$$\tilde{K} = K + \frac{1}{N} K' \quad (25)$$

where the phonon contribution (K) is given by equation (5) and the contribution from uniform strains (K') is described by the matrix elements:

$$K'_{\mu' \bar{\Gamma}' \bar{\gamma}'}^{\mu \bar{\Gamma} \bar{\gamma}} = [(\zeta(0) + \zeta')^{-1}]_{\mu' \bar{\Gamma}' \bar{\gamma}'}^{\mu \bar{\Gamma} \bar{\gamma}} - (\zeta(0)^{-1})_{\mu' \bar{\Gamma}' \bar{\gamma}'}^{\mu \bar{\Gamma} \bar{\gamma}} \quad (26)$$

again equal for all pairs of sites ($\mathbf{n}, \mathbf{n}'$). The matrix $\zeta(0)$ is the Fourier transform of ζ , corresponding to $\mathbf{k} = 0$, with the matrix elements:

$$\zeta(0)_{\mu' \bar{\Gamma}' \bar{\gamma}'}^{\mu \bar{\Gamma} \bar{\gamma}} = \sum_{\Delta \mathbf{n}} \zeta_{\mathbf{n}' \mu' \bar{\Gamma}' \bar{\gamma}'}^{\mathbf{n} \mu \bar{\Gamma} \bar{\gamma}} \quad (27)$$

where $\Delta \mathbf{n} = \mathbf{n} - \mathbf{n}'$. It follows from equation (A.6) that only $\mathbf{k} = \mathbf{0}$ optical phonons contribute to the above matrix elements since $a_{\mu \bar{\Gamma} \bar{\gamma}}^{\mathbf{n}}(\mathbf{0}j) = 0$ for acoustic phonons. However the Van Vleck coefficients do vanish with $\mathbf{k} \rightarrow \mathbf{0}$ for optical branches too if the Jahn–Teller ions are placed at centres of inversion of the crystal [15]. In this case we have $\zeta(0) = 0$ and equation (26) becomes

$$K_{\mu' \bar{\Gamma}' \bar{\gamma}'}^{\mu \bar{\Gamma} \bar{\gamma}} = (\zeta' - 1)_{\mu' \bar{\Gamma}' \bar{\gamma}'}^{\mu \bar{\Gamma} \bar{\gamma}} \quad (28)$$

The matrix elements of K and K' between neighbour centres are of the same order of magnitude, in which case the second contribution in equation (25) is negligible compared to the first one. However, while the first contribution decreases rapidly with the distance between centres, the second one remains constant. Therefore the

interaction energy of a given centre with all other centres of the crystal has comparable contributions from both phonons and uniform strains.

3. LOW-TEMPERATURE STRUCTURAL PHASES OF JAHN–TELLER HEXAGONAL PEROVSKITES

The structure of hexagonal perovskites AMX_3 with Jahn–Teller ions $M = Cu^{2+}$, Cr^{2+} , halogens $X = Cl^-$, Br^- , I^- and counterions $A = Rb^+$, Cs^+ , $N(CH_3)_4$, $(CH_3)_2CHNH_3$, contains one-dimensional chains of face-sharing octahedra MX_6 aligned to the crystalline axis c (Fig. 1). At high temperatures all these compounds have a common structure of a $CsNiCl_3$ type, belonging to the $P6_3/mmc$ space group with two formula units per unit cell. The low-temperature structure of AMX_3 is characterized by strong tetragonal elongations of MX_6 octahedra. The ordering of these tetragonal distortions within the chains can be of two basic types [16–18].

In the compounds $CsCuCl_3$ and $CsCuBr_3$ the sequence of long axes of elongated octahedra form a helix along the c axis, so that the unit cell becomes tripled in this direction (Fig. 1a). With local coordinate axes as in Fig. 3, this sequence is described by the motif $xy'zx'yz'$. Similar but more complex helical ordering of distortions within one chain is realized in $N(CH_3)_4CuCl_3$. Other compounds display the

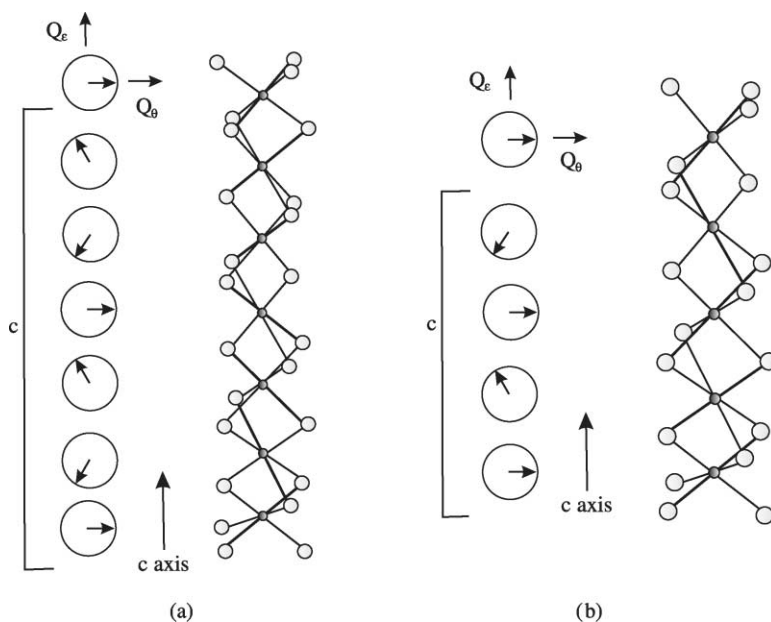


Fig. 1. Ordering of Jahn–Teller distortions along the MX_6 chains in the low-temperature structural phases of (a) $CsCuCl_3$ and $CsCuBr_3$ and (b) $RbCuCl_3$, $CsCrCl_3$, $RbCrCl_3$.

ordering of elongated axes of the type $\cdots zx'zy'zx'zy'\cdots$ (Fig. 1b). The unit cell becomes doubled in the c direction in this case. There are two common features in both low-temperature structures. First, the long axes of adjacent octahedra never meet at the same anion X. Second, the interchain structure is always of ferro type, i.e., the distortions of all octahedra lying in one ab plane are translationally equivalent.

Many investigations have been devoted to the understanding of the structure of these compounds [16–23]. The tetragonal distortions of octahedra in low-temperature phases are easily understood as a result of vibronic interaction of $E \otimes e$ type at each centre MX_6 [1]. In these crystals, the stabilization energy of Jahn–Teller distortions of individual octahedra is $E_{JT} = 2500 \text{ cm}^{-1}$ [23], while the barrier separating the minima on the lowest energy surface is $\Delta = 400 \text{ cm}^{-1}$ [21]. In the following we try to get more insight to the problem of low-temperature structure of hexagonal perovskites by applying the microscopic approach outlined in the previous section and taking into account all essential interactions contributing to the ordering of distortions. Our particular goal is the explanation of the fact that only two patterns of ordering of Jahn–Teller distortions (Fig. 1) are achieved out of many other possibilities.

3.1. Microscopic Hamiltonian and the basic model

The ground electronic state of each centre MX_6 corresponds to a double degenerate term E_g for both types of metal ions, $M = \text{Cu}^{2+}$, Cr^{2+} , also in the presence of trigonal crystal field (Fig. 2). This field is much weaker than 10Dq, the octahedral splitting of the ionic shell D into double degenerate e_g and triple degenerate t_g orbitals shells (Fig. 2). Excited terms lie relatively high in energy and are not expected to contribute significantly to vibronic interaction in the ground state (but see Ref. [24]).

The Jahn–Teller effect within the ground term E_g at each centre $\mathbf{n}$ is reduced to vibronic mixing of the one-electron functions $\psi_\theta^\mathbf{n}$ and $\psi_\epsilon^\mathbf{n}$ of the orbital doublet e_g , Fig. 3, by two symmetrized components of the deformation of octahedra, also belonging to a twofold degenerate manifold E_g , $q_{E\theta}^\mathbf{n}$ and $q_{E\epsilon}^\mathbf{n}$ [1]. This is described by vibronic operator:

$$\hat{U}_{\text{vib}}^\mathbf{n} = V_E(\sigma_z^\mathbf{n} q_{E\theta}^\mathbf{n} + \sigma_x^\mathbf{n} q_{E\epsilon}^\mathbf{n}) + W_E[(q_{E\theta}^\mathbf{n})^2 - (q_{E\epsilon}^\mathbf{n})^2]\sigma_z^\mathbf{n} - 2q_{E\theta}^\mathbf{n} q_{E\epsilon}^\mathbf{n} \sigma_x^\mathbf{n} \quad (29)$$

where σ_z and σ_x are Pauli matrices written in the basis of orbital doublet states of the corresponding centre ($\mathbf{n}$ distinguishes both different unit cells and the two Jahn–Teller ions within one cell) and V_E and W_E are linear and quadratic orbital vibronic constants, respectively [1].

Due to ferro-ordering of distortions in the ab planes and the lack of uniform strains [16–18], the problem of equilibrium structural phases of hexagonal perovskites is reduced to a single chain [25]. Passing to polar coordinates for

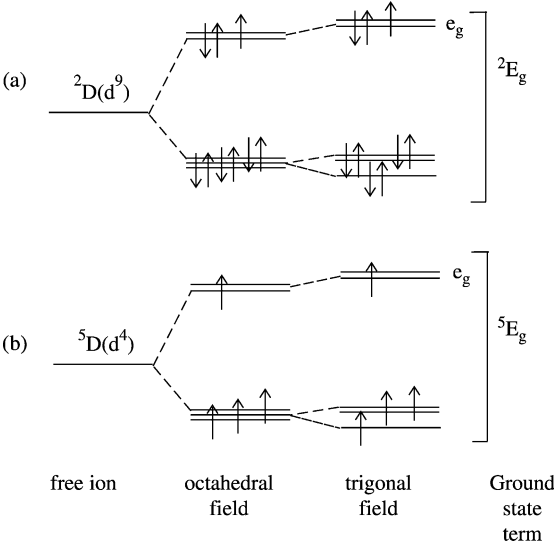


Fig. 2. Ligand-field orbitals of Cu^{2+} (a) and Cr^{2+} (b).

one-centre distortions,

$$q_{E\theta}^n = \rho_n \cos \varphi_n, \quad q_{E\epsilon}^n = \rho_n \sin \varphi_n \quad (30)$$

and then to adiabatic wave functions,

$$\phi_+^n(\varphi_n) = \cos \frac{\varphi_n}{2} \psi_\theta^n + \sin \frac{\varphi_n}{2} \psi_\epsilon^n, \quad \phi_-^n(\varphi_n) = -\sin \frac{\varphi_n}{2} \psi_\theta^n + \cos \frac{\varphi_n}{2} \psi_\epsilon^n \quad (31)$$

which diagonalize the vibronic operator at each centre [1], and having in mind that the interaction of local active distortions within one chain is diagonal after the

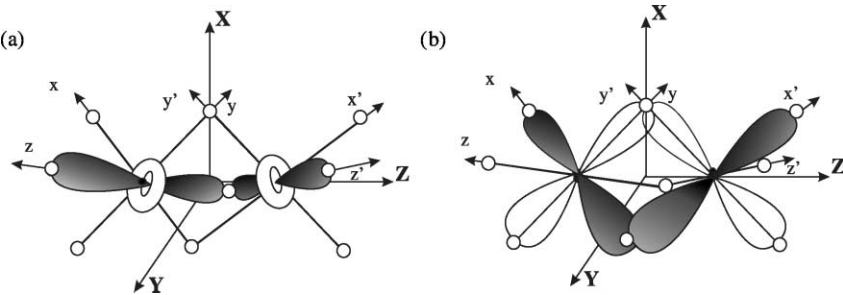


Fig. 3. Local coordinate frames and wave functions corresponding to the orbitals doublet e_g at neighbour centres: (a) $\psi_{E\theta} \equiv d_{z^2}$ and (b) $\psi_{E\epsilon} \equiv d_{x^2-y^2}$.

indices θ and ϵ , we arrive at a simple single-chain expression for the ground energy surface of equation (7), in which all centres are in the lowest adiabatic states ϕ^n :

$$U(\{\rho_n, \varphi_n\}) = \frac{1}{2} \sum_{n=-\infty}^{\infty} \sum_{m=0}^3 [K_m \rho_n \rho_{n+m} \cos(\varphi_n - \varphi_{n+m}) - |V_E| \rho_n - |W_E| \rho_n^2 \times \cos 3\varphi_n] \quad (32)$$

In this equation, the interaction between active local distortions up to three next nearest neighbour octahedra along the chain was taken into account, while the force constants K_m include the effects of interchain interactions. If the interchain contribution is confined by nearest neighbours then only the elastic constant corresponding to the interaction between nearest neighbour octahedra within the chain is renormalized:

$$K_1 = K_{n,E\gamma}^{n+1,E\gamma} + 3(K_{n,E\theta}^{n',E\theta} + K_{n,E\epsilon}^{n',E\epsilon}) \quad (33)$$

The first term in right-hand side is the intrinsic intra-chain force constant given by equation (5), while the two terms within the brackets describe the contributions from interchain interactions between octahedra shifted by $c/2$ and a (parallel to Y in Fig. 3) along the corresponding crystal axes [25].

The second-order Jahn–Teller effect at a single centre, equation (29), leads to three equivalent minima on the lowest surface of the adiabatic potential, with equilibrium distortions (V_E and W_E are of the same sign),

$$\rho^{(0)} = \frac{V_E^2}{K_0 - 2|W_E|}, \quad \varphi^{(0)} = 0, \frac{2\pi}{3}, -\frac{2\pi}{3} \quad (34)$$

corresponding to the elongation of the octahedron along one of three tetragonal axes [1]. If the intercentre elastic constants in equation (32) are significantly smaller than K_0 and $9W_E$ then the equilibrium values $\{\rho_n^{(0)}\}$, $\{\varphi_n^{(0)}\}$ in the crystal are expected to deviate only slightly from equation (34):

$$\rho_n^{(0)} = \rho^{(0)} + \Delta\rho_n, \quad \varphi_n^{(0)} = p_n \frac{2\pi}{3} + \Delta\varphi_n \quad (35)$$

where $p_n = 0, 1, -1$. This seems indeed to be the case in hexagonal perovskites. For instance, the X-ray structure data for RbCrCl_3 give the angular deviation $\Delta\varphi_n = \pm 8^\circ$ [26].

In a previous investigation of face-sharing bioctahedral fragments Cu_2X_9 [27] based on a model vibrational force field, a distorted configuration with elongated tetragonal axes of octahedra pointing to different halogen atoms on the common face was found to be the most stable one. The ultimate reason for that is the relatively low energy of induced non-Jahn–Teller distortions in two bioctahedra [27], which explains also the correlation of Jahn–Teller distortions for nearest neighbour octahedra in Fig. 1. This means that K_1 in equation (33) is positive, while $\{p_n\}$ in equation (35) always differ by unity for neighbour centres, which can be described

by an integer variable:

$$\sigma_n = p_{n-1} - p_n \quad (36)$$

taking only two values, 1 and -1 . The two distorted structures in Figs 1a and b correspond to the sequences of this variable along the chain $\cdots + + + + + \cdots$ and $\cdots + + - - \cdots$, respectively.

Further the minimization of the potential energy (32) is performed after $\{\Delta\rho_n\}$ and $\{\Delta\varphi_n\}$ considering them as small variables. The details of this calculation will be given elsewhere [25], here we quote the final result:

$$\begin{aligned} U(\{\sigma_n\}) &= A_1 \sum_n \sigma_n \sigma_{n+1} + A_2 \sum_n \sigma_n \sigma_{n+2}, \\ A_1 &= -K_2 \left(1 + \frac{K_1}{K_0}\right) + \frac{K_1^2}{9W_E} \left(\frac{1}{2} \frac{K_1}{K_0} - \frac{1}{2} \frac{K_1^2}{9W_E}\right) + K_3, \\ A_2 &= \frac{1}{2} K_2 \left(\frac{K_1}{9W_E}\right) + \frac{1}{8} K_1 \left(\frac{K_1}{9W_E}\right)^2 + \frac{1}{2} K_3 \end{aligned} \quad (37)$$

where only the main contributions from effective force constants, not smaller than K_3 , are included. The above equation was obtained in the assumption of a fast decrease of K_n s with distance between the centres. On the other hand, the relationship between W_E and K_0 is obtained [1] by using the experimental values for E_{JT} and Δ : $9|W_E|/K_0 \approx 0.4$.

Before investigating of long-range correlations of Jahn–Teller distortion using equation (37), we analyse in addition the effect of the exchange interaction between localized spins on the ordering of these distortions.

3.2. Orbital-dependent exchange interaction

The exchange interaction between localized electrons in orbitally degenerate states at neighbour sites can lead on its own to orbital ordering in crystals [28]. This results from a strong dependence of the exchange parameters on the orbitals occupation, which actually become operators defined in the orbital space of corresponding exchange pairs (the Kugel–Khomskii model [28]). In hexagonal perovskites the Jahn–Teller splitting of degenerate orbitals at each centre is $4E_{JT} = 10\,000\text{ cm}^{-1}$ [23], i.e., is by two orders of magnitude higher than the expected strength of exchange interactions between neighbour centres. In such a situation the exchange interaction takes place between orbitally non-degenerate states, with unpaired electrons occupying the adiabatic orbitals ϕ_+^n for $M = \text{Cu(II)}$ or ϕ_-^n for $M = \text{Cr(II)}$. Both these orbitals are strongly dependent on the nuclear coordinate φ_n , equation (31), the same is expected for the exchange parameters.

The exchange interaction between two centres in orbitally non-degenerate ground states with spins S_1 and S_2 is described by the Heisenberg Hamiltonian:

$$H_{\text{ex}} = -2JS_1S_2 \quad (38)$$

The kinetic contribution to the exchange parameter J contains antiferromagnetic and ferromagnetic parts, $J = J_a + J_f$, which in the Anderson's theory of superexchange [29] have the form:

$$J_a = -\frac{1}{n_1n_2} \sum_{ij} \frac{t_{ij}^2}{E_{i \rightarrow j}}, \quad J_f = \frac{1}{n_1n_2} \sum_{ij} \frac{t_{ij}^2}{E_{i \rightarrow j}} \frac{J_{ij}^H}{E_{i \rightarrow j}} \quad (39)$$

where i and j denote orbitals at different centres, n_1 and n_2 are the numbers of unpaired electrons on centres, t_{ij} is the transfer parameter, and $E_{i \rightarrow j}$ the electron promotion energy between centres. The sum in the first contribution runs over pairs of orbitals occupied by single electrons. In the second contribution it includes pairs of singly occupied and doubly occupied or empty orbitals. This second contribution is ferromagnetic due to the intra-atomic exchange interaction (Hund's rule coupling) between the transferred electron (or hole) and the spin of the metal ion, described by the parameter J_{ij}^H [30].

In the case of copper ions, the single unpaired electron occupies the upper adiabatic orbital at each centre, equation (31). Therefore the antiferromagnetic contribution in equation (39) includes only one term corresponding to electron delocalization between such orbitals on two neighbour centres in a chain. On the other hand, the main terms in the ferromagnetic contribution correspond to electron transfer between a doubly occupied lowest adiabatic orbital on one centre and a singly occupied highest adiabatic orbital on another centre. These processes involve virtual electron transfer between e_g orbital components of two centres, Fig. 3. It follows from this figure that only electron transfer between similar orbital components (θ or ϵ) is allowed by symmetry. Moreover, the trigonal symmetry of the pairs requires $t_{E\theta E\theta} = t_{E\epsilon E\epsilon} \equiv t_E$ [31]. Using equation (31) we obtain the transfer parameters (matrix elements of electronic Hamiltonian) between adiabatic orbitals:

$$\begin{aligned} \langle \phi_+^1 | H_{\text{el}} | \phi_+^2 \rangle &= \langle \phi_-^1 | H_{\text{el}} | \phi_-^2 \rangle = t_E \cos \frac{\varphi_1 - \varphi_2}{2} \\ \langle \phi_+^1 | H_{\text{el}} | \phi_-^2 \rangle &= -\langle \phi_-^1 | H_{\text{el}} | \phi_+^2 \rangle = t_E \sin \frac{\varphi_1 - \varphi_2}{2} \end{aligned} \quad (40)$$

Substituting them in equation (39) yields for the main part of the exchange interaction:

$$J(\varphi_1, \varphi_2) = -t_E^2 \left[\left(\frac{1}{U} - \frac{J_H}{U'2} \right) + \left(\frac{1}{U} + \frac{J_H}{U'2} \right) \cos(\varphi_1 - \varphi_2) \right] \quad (41)$$

where U is the electron repulsion of two electrons on one centre (Hubbard's energy), U' includes the additional gap between lower and higher adiabatic orbitals at

equilibrium point, $U' = U + 4E_{JT}$, and J_H is the intra-centre exchange (Hund's rule coupling) parameter.

The obtained exchange parameter shows indeed strong dependence on angular nuclear distortions. In the case of similar distortions at both centres, $\varphi_1 = \varphi_2$, the resulting adiabatic orbitals have mirror symmetry (e.g. as in Fig. 3) and the electron transfer between lower and higher adiabatic orbitals at different centres is forbidden. Then we recover Anderson's expression for antiferromagnetic kinetic exchange between singly occupied orbitals, $J = -2t_E^2/U$ [29]. In the case of opposite distortions at the centres, $\varphi_1 = \varphi_2 \pm \pi$, the unpaired electrons occupy the adiabatic orbitals of different symmetry. Then electron transfer between lower and higher adiabatic orbitals at different centres is only allowed, equation (40), leading to ferromagnetism, $J = (2t_E^2/U')(J_H/U')$ [30].

Due to the dependence of J on active nuclear distortions, the Heisenberg exchange interaction, equation (38), summed up over all nearest neighbour centres in a chain, should be added from the start to the energy functional in equation (32). Equation (41) shows, however, that this addition merely leads to the renormalization of the effective force constant K_1 in equation (32) by

$$\Delta K_1 = 2t_E^2 \left[\frac{1}{U} + \frac{J_H}{U'^2} \right] \langle \mathbf{S}_1 \mathbf{S}_2 \rangle_s \quad (42)$$

where $\langle \cdots \rangle_s$ means average over the ground spin state of the chain. The prefactor in this expression can be estimated following Ref. [29]. Considering the main contributions to the transfer parameter as arising *via* metal–ligand σ bonds involving valence p orbitals of halogen bridges, we obtain after simple calculations $t_E = -e_\sigma \cos 2\alpha$, where e_σ is a ligand field parameter of σ type [32] and α is the angle between the metal–ligand bond and the axis of the pair (Z in Fig. 3). Taking the estimation $e_\sigma = 10Dq/3$, with $10Dq \approx 10\,000\text{ cm}^{-1}$ for copper(II) in an octahedral field of six chlorines, and the cubic angle for α ($\cos \alpha = 1/\sqrt{3}$), we obtain $t_E \approx -1000\text{ cm}^{-1}$. Using then the value $U \approx 6\text{ eV}$ estimated for Cu^{2+} [29] and neglecting the second terms in brackets in equation (42) (several times smaller than the first one) we obtain:

$$\Delta K_1 \approx 40 \langle \mathbf{S}_1 \mathbf{S}_2 \rangle_s \text{ cm}^{-1} \quad (43)$$

The spin average entering this formula depends on the ground spin state of the chain. In the case of antiferromagnetic coupling ($J < 0$) between spins $S = 1/2$, it equals $-\ln 2$ ($= -0.69$) according to the exact solution for an infinite isolated chain [33], while it is $-1/4$ for the case of antiferromagnetic ordering (broken symmetry solution) which is stabilized by additional interchain exchange interactions. In the case of ferromagnetic coupling ($J > 0$) this average is $1/4$. Hence for magnetically ordered structures ΔK_1 is $\sim 10\text{ cm}^{-1}$. Being of different sign for ferromagnetic and antiferromagnetic coupling, ΔK_1 will respectively increase and decrease K_1 in equation (32). The latter is expected however to be one order of magnitude larger since the negative correlation of Jahn–Teller distortions of nearest neighbour octahedra is observed up to hundreds of kelvins.

In the case of chromium ions, the high lying unpaired electron occupies the lower adiabatic orbital, ϕ_{-}^n . Nevertheless the contribution of e_g orbitals to the exchange parameter is found to be the same, equation (41), as in the case of copper ions, which is the consequence of electron–hole complementarity (of course the entering parameters, especially J_H are quite different for the two ions). In chromium(II) we have another three unpaired electrons occupying the t_{2g} shell (Fig. 2b) which contribute independently to the exchange interaction between centres, mainly *via* the antiferromagnetic part, J_a , in equation (39). Since these unpaired electrons form a totally symmetric orbital configuration they are not sensitive to nuclear distortions of E type. Then the corresponding additional contribution to the exchange parameter will be independent from these distortions. Therefore, as in the case of copper ions, the only part of the exchange interaction relevant for orbital ordering is the second term in right-hand side of equation (41), leading to the correction (42) to K_1 .

We can conclude that orbital-dependent exchange interaction in hexagonal perovskites does not contribute essentially to the ordering of orbitals and Jahn–Teller distortions on sites but only results in a slight renormalization of the force constant K_1 and, therefore, of A_1 and A_2 parameters of the basic model in equation (37).

3.3. Equilibrium distortions: comparison with experiment

Figure 4 shows the dependence of the total energy (37), calculated for one Jahn–Teller centre, on the parameters A_1 and A_2 ($A_1 < 0$) for the following types of ordering of active distortions (coded as sequences of variables $\sigma_n = +1, -1$, equation (36)) along the chains:

$$\begin{array}{ll}
 \text{A} & \cdots + + + + + + + \text{CsCuCl}_3, \text{CsCuBr}_3 \\
 \text{B} & \cdots + - + - + - + - \\
 \text{C} & \cdots + + - - + + - - \text{RbCuCl}_3, \text{CsCrCl}_3, \text{RbCrCl}_3, \dots \\
 \text{D} & \cdots + + + - - + + + \\
 \text{E} & \cdots + + - + + - + + - \\
 \text{F} & \cdots + + + - + + + - \\
 \text{G} & \cdots + + + - - + + + - - \\
 \text{H} & \cdots + + + + - + + + + - \\
 \text{I} & \cdots + + + + - - + + + + - - \\
 \text{J} & \cdots + + + + - - - + + + + - - -
 \end{array} \tag{44}$$

We can see that only two types of ordering can become equilibrium configurations. Moreover, these are precisely the two low-temperature structural phases found in hexagonal perovskites (Fig. 1). The parameters A_1 and A_2 are expected to have different signs, which is in agreement with their definition in equation (37). According to the theory, the helical ordering (Fig. 1a) is achieved at $A_2/|A_1| < 1/2$.

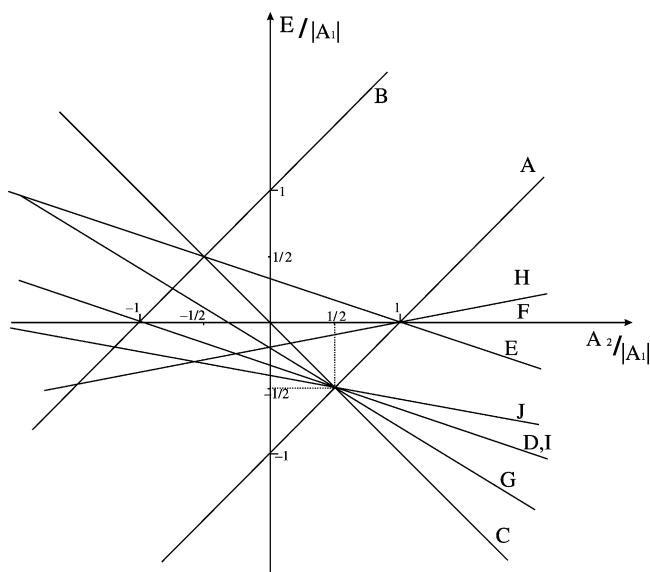


Fig. 4. Energies for different types of ordering of Jahn–Teller distortions specified in equation (44).

It corresponds to equal amplitudes ρ_n and angular shifts $\varphi_n - \varphi_{n-1} = -2\pi/3$ of Jahn–Teller distortions along the chains. Another type of ordering (Fig. 1b) is realized at $A_2/|A_1| > 1/2$ and is characterized by slight deviations of angular shifts from $\pm 2\pi/3$ [25]. These details are also supported by structural data [18,26].

The active one-site distortions induce distortions of non-active type on neighbour centres, described by equation (8). In the case of helical ordering of distortions as in CsCuCl_3 (Fig. 1a) this leads, in accord with experiment [18], to dipolar shifts of Cu^{2+} ions from the centres of octahedra and to shifts of the whole octahedra from the axis of the chain [25], following the helix of Jahn–Teller distortions [25]. Similar distortions have been found in separate biocahedral fragments as well [27] which however turned out to be weaker. Note that an intra-centre mechanism leading to dipole moments of individual octahedra would require a strong pseudo-Jahn–Teller admixing of an excited electronic state of odd parity [24].

Inserting the equilibrium distortions in equation (39) or (41), the exchange parameters can be obtained. For instance, substituting $\varphi_n - \varphi_{n-1} = 2\pi/3$ and $U' \approx U$ in equation (41) we obtain an approximate condition for ferromagnetism of copper perovskites: $J_H/U > 1/3$. Using typical Racah parameters for copper complexes, $B \approx 800 \text{ cm}^{-1}$, $C \approx 3600 \text{ cm}^{-1}$, we obtain for Hund's rule coupling parameter [32]: $J_H = 2C + 6B = 1.5 \text{ eV}$. This gives $J_H/U \approx 1/4$, i.e., already quite close to the critical value for ferromagnetic interaction. Actually all other terms from equation (39), not included in the approximate treatment by equation (41),

are ferromagnetic. The main contributions of this type come from electron transfer between double occupied t_{2g} orbitals of one centre to the single occupied e_g orbital of another centre (Fig. 2). These additional contributions are the reason for a weak ferromagnetism observed in copper perovskites. On the contrary in chromium compounds the strong through-space σ overlap of single occupied t_{2g} orbitals [31] leads alone to strong antiferromagnetism which overwhelms all ferromagnetic contributions.

4. CONCLUSIONS

The proposed approach to static cooperative Jahn–Teller effect is based on the exact effective Hamiltonian (7), acting in the reduced space of active one-centre distortions only. It involves effective force constants, which are analytically related to the parameters of the full microscopic Hamiltonian. Direct electronic interactions between sites, such as orbital-dependent electrostatic and exchange interactions [28], can be added to the effective Hamiltonian without modifying it. This approach proves to be especially efficient in the case of strong Jahn–Teller distortions, when the effects of second-order Jahn–Teller coupling become important.

In hexagonal perovskites it leads to a simple microscopic model (37) reproducing exactly the two types of long range ordering of Jahn–Teller distortions which have been observed in compounds with monoatomic counterions. An important conclusion is that the theory predicts only these two types of ordering for any reasonable values of effective force constants and vibronic constants, defining the two parameters of the model in equation (37). Therefore the fact that a number of different compounds are found at low temperatures in one of these two structural phases appears not to be accidental. The one-centre deformations of non-Jahn–Teller type, in particular, the dipolar distortions of octahedra in CsCuCl_3 , are naturally described as induced by Jahn–Teller distortions of surrounding centres. The orbital-dependent exchange interaction is not playing a key role in the ordering of distortions in hexagonal perovskites, which is mainly determined by phonon-mediated interaction of Jahn–Teller distortions at different centres. An entirely different situation occurs in the uranium dioxide crystal, where the orbital-dependent exchange interaction is of primary importance for the ordering of orbitals at uranium sites, while the intra-site Jahn–Teller distortions merely adjust them [34].

ACKNOWLEDGEMENTS

I would like to dedicate this chapter to Professor Isaac Bersuker on the occasion of his 75th birthday as an acknowledgement of his pioneering contributions to the field of vibronic crystal chemistry and structural phase transitions, and to the science of vibronic interactions in general. I had the advantage to work in the Laboratory

of Quantum Chemistry in Kishinev led by him, learning his approach to science and enjoying the creative atmosphere in his laboratory.

A part of the work related to hexagonal perovskites was done in collaboration with Michail Korotkov.

APPENDIX A: DERIVATION OF THE EFFECTIVE FORCE CONSTANTS

To obtain the matrix $\tilde{K} = \tilde{\zeta}^{-1}$, we first make a unitary transformation,

$$S_{\mathbf{k}\mathbf{n}} = \frac{1}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} \quad (\text{A.1})$$

corresponding to Fourier transform of the matrix $\tilde{\zeta}$:

$$(S\tilde{\zeta}S^\dagger)_{\mathbf{k}\mathbf{k}'} = \delta_{\mathbf{k}\mathbf{k}'} \sum_{\Delta\mathbf{n}} e^{i\mathbf{k}\Delta\mathbf{n}} \tilde{\zeta}_{\mathbf{n}'\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mathbf{n}\mu\tilde{\Gamma}\tilde{\gamma}} \equiv \delta_{\mathbf{k}\mathbf{k}'} \tilde{\zeta}_{\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mu\tilde{\Gamma}\tilde{\gamma}}(\mathbf{k}) \quad (\text{A.2})$$

where $\Delta\mathbf{n} = \mathbf{n} - \mathbf{n}'$. It was used in equation (A.2) that the matrix elements of $\tilde{\zeta}$ depend only on $\Delta\mathbf{n}$, i.e., are invariant under translations. Each matrix block $\tilde{\zeta}(\mathbf{k})$ in equation (A.2) has the dimension of the number of active nuclear displacements on one centre. The corresponding matrix elements are of the form:

$$\tilde{\zeta}_{\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mu\tilde{\Gamma}\tilde{\gamma}}(\mathbf{k}) = \sum_{\Delta\mathbf{n}} e^{i\mathbf{k}\Delta\mathbf{n}} \tilde{\zeta}_{\mathbf{n}'\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mathbf{n}\mu\tilde{\Gamma}\tilde{\gamma}} + \delta_{\mathbf{k},\mathbf{0}} \tilde{\zeta}_{\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mu\tilde{\Gamma}\tilde{\gamma}} \quad (\text{A.3})$$

The inverse of the matrix $\tilde{\zeta}(\mathbf{k})$ can be found analytically given its low dimension. Then the inverse of the whole matrix $\tilde{\zeta}$ is obtained analytically as well:

$$\tilde{\zeta}^{-1} = S^\dagger Z S \quad (\text{A.4})$$

where the matrix Z contains the matrix blocks $\tilde{\zeta}(\mathbf{k})^{-1}$ on the main diagonal. Substituting equations (A.1) and (A.3) in equation (A.4) we obtain:

$$\left(\tilde{\zeta}^{-1}\right)_{\mathbf{n}'\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mathbf{n}\mu\tilde{\Gamma}\tilde{\gamma}} = \frac{1}{N} \left[\left(\tilde{\zeta}(0)^{-1}\right)_{\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mu\tilde{\Gamma}\tilde{\gamma}} - \left(\tilde{\zeta}(0)^{-1}\right)_{\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mu\tilde{\Gamma}\tilde{\gamma}} \right] + \left(\tilde{\zeta}^{-1}\right)_{\mathbf{n}'\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mathbf{n}\mu\tilde{\Gamma}\tilde{\gamma}} \quad (\text{A.5})$$

where the expression within square brackets is independent from $\mathbf{n}$ and $\mathbf{n}'$. It corresponds to the uniform strains contribution into $\tilde{K}$. Substituting the second equation from equation (5) in equation (27) yields for $\zeta(0)$:

$$\zeta(0)_{\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mu\tilde{\Gamma}\tilde{\gamma}} = N \sum_j \frac{a_{\mu'\tilde{\Gamma}'\tilde{\gamma}'}^{\mathbf{n}'}(\mathbf{0}j)^* a_{\mu\tilde{\Gamma}\tilde{\gamma}}^{\mathbf{n}}(\mathbf{0}j)}{\omega_{0j}^2} \quad (\text{A.6})$$

In this equation only Van Vleck coefficients corresponding to the point $\mathbf{k} = \mathbf{0}$ are involved, for which they have the same values at all unit cells.

REFERENCES

- [1] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, Berlin, 1989.
- [2] G. A. Gehring and A. Gehring, *Rep. Prog. Phys.*, 1975, **38**, 1.
- [3] M. D. Kaplan and B. G. Vekhter, *Cooperative Phenomena in Jahn–Teller Crystals*, Plenum Press, New York, 1995.
- [4] R. J. Elliot, R. T. Harley, W. Hayes and S. R. P. Smith, *Proc. R. Soc. Lond. Ser. A*, 1972, **328**, 217.
- [5] L. F. Chibotaru, *J. Phys. A: Math. Gen.*, 1994, **27**, 6919.
- [6] J. H. Van Vleck, *Phys. Rev.*, 1940, **57**, 426.
- [7] A. A. Maradudin, E. W. Montroll and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation*, Academic Press, New York, 1963.
- [8] P. A. Flinn and A. Maradudin, *Ann. Phys.*, 1962, **18**, 81.
- [9] V. K. Tewary, *Adv. Phys.*, 1973, **3**, 1515.
- [10] R. Orbach and M. Tachiki, *Phys. Rev.*, 1967, **158**, 524.
- [11] R. L. Melcher, *Phys. Acoust.*, 1976, **12**, 1.
- [12] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Clarendon Press, Oxford, 1954.
- [13] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, Pergamon Press, London, 1959.
- [14] J. Kanamori, *J. Appl. Phys.*, 1960, **31**, 14S.
- [15] P. M. Levy, *J. Phys. C: Solid State Phys.*, 1973, **6**, 3545.
- [16] C. J. Kroese and J. A. Maaskant, *Chem. Phys.*, 1974, **5**, 224.
- [17] S. Hirotsu, *J. Phys. C: Solid State Phys.*, 1977, **10**, 967.
- [18] W. J. A. Maaskant and W. G. Haije, *J. Phys. C: Solid State Phys.*, 1986, **19**, 5295.
- [19] B. S. Lee, *J. Phys. C: Solid State Phys.*, 1979, **12**, 855.
- [20] M. Harada, *J. Phys. Soc. Jpn*, 1983, **52**, 1646.
- [21] U. Schotte, H. A. Graff and H. Dachs, *J. Phys.: Condens. Matter*, 1989, **1**, 3765.
- [22] D. I. Khomskii, *Pis'ma Zh. Eksp. Teor. Fiz.*, 1977, **25**, 579.
- [23] H. Tanaka, H. Dachs, K. Iio and K. Nagata, *J. Phys. C: Solid State Phys.*, 1986, **19**, 4861, 4879.
- [24] W. G. Haije and W. J. A. Maaskant, *J. Phys. C: Solid State Phys.*, 1987, **20**, 2089.
- [25] L. F. Chibotaru and M. M. Korotkov, *Adv. Quant. Chem.*, 2003, 599, present issue.
- [26] W. J. Crama, M. Bakker, L. C. Verschoor and W. J. A. Maaskant, *Acta Cryst. B*, 1979, **35**, 1875.
- [27] L. F. Chibotaru, *Mol. Phys.*, 1994, **81**, 891.
- [28] K. I. Kugel and D. I. Khomskii, *Sov. Phys. Usp.*, 1982, **136**, 231.
- [29] P. W. Anderson, *Phys. Rev.*, 1959, **115**, 2.
- [30] J. B. Goodenough, *Magnetism and the Chemical Bond*, Interscience, New York, 1963.
- [31] A. Ceulemans, L. F. Chibotaru, G. A. Heylen, K. Pierloot and L. G. Vanquickenborne, *Chem. Rev.*, 2000, **100**, 787.
- [32] I. B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory*, Wiley, New York, 1996.
- [33] P. Fulde, *Electron Correlations in Molecules and Solids*, Springer, Heidelberg, 1995.
- [34] V. S. Mironov, L. F. Chibotaru and A. Ceulemans, *Adv. Quant. Chem.*, 2003, 667, present issue.

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