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Jahn-Teller Configurational Instability in Square-Planar Complexes*

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The static and the dynamic Jahn-Teller vibronic couplings found in square planar molecules are investigated. Without spin-orbit coupling and considering only one distorting vibration, the problem can be solved exactly within the adiabatic Born-Oppenheimer approximation. In this case the vibrational pattern is that expected for a harmonic oscillator. If on the other hand spin-orbit coupling is included the vibrational pattern becomes highly irregular. Finally, in the limit of large spin-orbit coupling the Jahn-Teller coupling is completely quenched and the potential surfaces are again harmonic.

Statische und dynamische Jahn-Teller-Verzerrung quadratischer Komplexe wurden untersucht. Vernachlässigt man Spin-Bahn-Kopplung und betrachtet nur eine verzerrende Normalkoordinate, so ist das Problem in Born-Oppenheimer-Näherung lösbar. Das Schwingungsspektrum ist das eines harmonischen Oszillators. Bei Berücksichtigung der Spin-Bahn-Kopplung wird es jedoch sehr unregelmäßig. Im Grenzfall großer Spin-Bahn-Kopplung schließlich wird die Jahn-Teller-Kopplung völlig unterdrückt; die Potentialflächen sind wieder harmonisch.

Les distorsions statiques et dynamiques d'après Jahn-Teller sont étudiées au cas des molécules quadratiques. Sans couplage spin-orbite et avec une seule distorsion normale, le problème se résout au cadre de l'approximation de Born-Oppenheimer; les vibrations sont celles d'un oscillateur harmonieux. L'inclusion du couplage spin-orbite conduit à des spectres très irréguliers. Finalement, pour les grands couplages spin-orbite, le couplage de Jahn-Teller est complètement supprimé, et les surfaces d'énergie potentielle sont de nouveau harmonieuses.

Introduction

It might naively be supposed that atoms in polyatomic molecules normally would tend to seek positions such that the molecule would achieve the greatest "symmetry". However, experience has shown that such vague idealized arguments rarely form a sound basis for structural predictions. Furthermore, many factors such as crystal packing considerations, anharmonic forces between the atoms etc. are difficult to visualize in advance, and may destroy all our preconceived ideas.

Quite apart from the above it has been shown by Jahn and Teller [2] that on completely general grounds a molecule cannot assume a shape which would lead to the molecule possessing a degenerate electronic ground state. If, therefore, in a calculation we start out assuming a geometry which gives rise to degeneracy in the ground state, and if we want to find the equilibrium conformation of the molecule, we must consider the couplings of the vibrational and electronic properties of the molecule. In such a "vibronic" coupling the nuclei are displaced, the degeneracy is done away with and the molecule moves towards its equilibrium conformation.

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In this note we want to investigate the Jahn-Teller coupling in square-planar molecules. A similar investigation has recently been published by HOUGEN [*1*]. However, our treatment differs somewhat from his, among other things in the inclusion of the spin-orbit coupling. As to the general theory and treatment of Jahn-Teller effects we refer to the brilliant research and review papers of LIEHR [*3*] and LONGUET-HIGGINS [*4*].

The Static Jahn-Teller Problem

We want to investigate the influence of nuclear displacements upon the degenerate electronic levels of a 5 atom molecule possessing D_{4h} symmetry. Using the notation of WILSON, DECIUS and CROSS [*5*] we find for a square-planar molecule (Fig. 1) the vibrational symmetry coordinates α_{1g}, β_{1g}, β_{2g}, α_{2u}, β_{2u}, $2\,\varepsilon_u$. In a D_{4h} point group we can have at most two-fold electronic degeneracy. An E_g or E_u level is thus the only level which can experience a configurational instability of the Jahn-Teller type. Furthermore an E level may exhibit a first-order spin-orbit coupling.

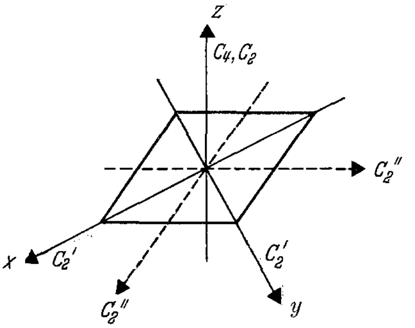

Fig. 1

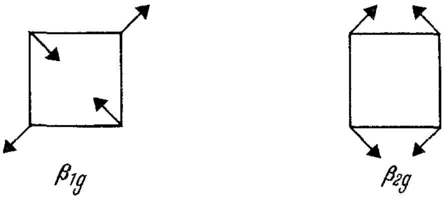

Fig. 2

Fig. 1. Symmetry elements in a square planar molecule

Fig. 2. The Jahn-Teller active β_{1g} and β_{2g} vibrations

The Hamiltonian for the system, including spin-orbit coupling, is to the first order in the nuclear displacement coordinates

$$\mathcal{H} = \mathcal{H}_0 + \sum_i \left(\frac{\partial \mathcal{H}}{\partial q_i}\right)_0 q_i + \lambda\, \vec{L}.\vec{S}\ .$$

Here $\mathcal{H}_0$ is the Hamiltonian for the fixed D_{4h} nuclear geometry without spin-orbit coupling included and the expansion in the vibrational symmetry coordinates q_i runs over all the nine normal vibrations.

Let us investigate the behaviour of an ${}^2E_g$ state. As our zero order wavefunctions we take $e_g^a\alpha$, $e_g^a\beta$, $e_g^b\alpha$ and $e_g^b\beta$ where e_g^a and e_g^b together span an e_g orbital in D_{4h} and α and β are the two spin-functions.

Neglecting for the moment the spin-orbit coupling term, which to good approximation is independent of nuclear displacements, and because q_i is a function of the nuclear displacements only, then the "active" vibrations are found by demanding that the matrix elements $\left(e_g^{a,b}\middle|\sum_i\left(\frac{\partial\mathcal{H}}{\partial q_i}\right)_0\middle|e_g^{a,b}\right)$ should be different from zero. The symmetric product of the e_g wavefunctions transforms as a_{1g}, b_{1g} and b_{2g}, and consequently the β_{1g} and β_{2g} vibrations are Jahn-Teller active. These vibrations will take the molecule to a D_{2h} symmetry (Fig. 2).

We now characterize our wavefunctions in D_{2h} symmetry and get e_g $(D_{4h}) \rightarrow$ $(b_{3g} + b_{2g})$ (D_{2h}), β_{1g} $(D_{4h}) \rightarrow \alpha_{1g}$ (D_{2h}) and β_{2g} $(D_{4h}) \rightarrow \beta_{1g}$ (D_{2h}). With $\mathscr{H}^{(1)}$ equal to $\mathscr{H} - \mathscr{H}_0$ transforming as $a_{1g} q_1 + b_{1g} q_2 + \lambda\ (b_{3g}\, s_x + b_{2g}\, s_y + b_{1g}\, s_z)$ and remembering that $b_{1g}\, s_z$ is a complex operator, we get the secular equation,

$$\begin{array}{c} e_g^a \alpha \\ e_g^a \beta \\ e_g^b \alpha \\ e_g^b \beta \end{array} \left| \begin{array}{cccc} -c_1 q_1 - W^{(1)} & 0 & c_2 q_2 + \frac{1}{2} i \lambda & 0 \\ 0 & -c_1 q_1 - W^{(1)} & 0 & c_2 q_2 - \frac{1}{2} i \lambda \\ c_2 q_2 - \frac{1}{2} i \lambda & 0 & c_1 q_1 - W^{(1)} & 0 \\ 0 & c_2 q_2 + \frac{1}{2} i \lambda & 0 & c_1 q_1 - W^{(1)} \end{array} \right| = 0 \ .$$

Here

$$- c_1 = \int e_g^a \left(\frac{\partial \mathscr{H}}{\partial q_1} \right)_0 e_g^a \, d\tau$$

and

$$c_2 = \int e_g^a \left(\frac{\partial \mathscr{H}}{\partial q_2} \right)_0 e_g^b \, d\tau$$

and we have furthermore utilized the following relation derived by a symmetry operation in D_{4h}:

$$\int e_g^a \, (b_{1g}) \, e_g^a \, d\tau = - \int e_g^b \, (b_{1g}) \, e_g^b \, d\tau \ .$$

The solutions are

$$W^{(1)} = \pm \sqrt{c_1^2 q_1^2 + c_2^2 q_2^2 + \frac{\lambda^2}{4}}$$

each solution being two fold degenerate (KRAMER's degeneracy).

The potential surfaces are now obtained by adding to the above expression the quasiharmonic potentials $\frac{1}{2} k_1 q_1^2$ and $\frac{1}{2} k_2 q_2^2$ where k_1 and k_2 are the force constants for the harmonic vibrations in q_1 and q_2. The two potential surfaces are thus

$$\tfrac{1}{2} k_1 q_1^2 + \tfrac{1}{2} k_2 q_2^2 \pm \tfrac{1}{2} \sqrt{\lambda^2 + 4 c_1^2 q_1^2 + 4 c_2^2 q_2^2}$$

and the original four-fold degenerate potential surface is seen to be split into an upper (plus sign) and a lower (minus sign) potential surface. The minimum value of the energy can now be found by minimizing the lowest surface with respect to q_1 and q_2.

Apart from $q_1^0 = q_2^0 = 0$ the following solutions are obtained:

$$q_1^0 = 0 \qquad q_2^0 = \pm \sqrt{\frac{c_2^2}{k_2^2} - \frac{\lambda^2}{4 c_2^2}} \tag{1}$$

$$q_2^0 = 0 \qquad q_1^0 = \pm \sqrt{\frac{c_1^2}{k_1^2} - \frac{\lambda^2}{4 c_1^2}} \ . \tag{2}$$

Besides the above solutions, we have in the special case where

$$\frac{c_1^2}{k_1} = \frac{c_2^2}{k_2}$$

a solution set which satisfy

$$\frac{(q_1^0)^2}{\dfrac{c_1^2}{k_1^2} - \dfrac{\lambda^2}{4 c_1^2}} + \frac{(q_2^0)^2}{\dfrac{c_2^2}{k_2^2} - \dfrac{\lambda^2}{4 c_2^2}} = 1 \ .$$

Hence

$$q_1^0 = \sqrt{\frac{c_1^2}{k_1^2} - \frac{\lambda^2}{4\,c_1^2}}\cos\varphi \qquad q_2^0 = \sqrt{\frac{c_2^2}{k_2^2} - \frac{\lambda^2}{4\,c_2^2}}\sin\varphi \tag{3}$$

where φ is a cyclic coordinate. This means that, in this last very special situation, the molecule can "rotate" freely between an "elongated" and a "rhombic" configuration. Specifically we must demand that the square roots appearing in (1), (2) and (3) have a positive argument. For instance in case (2) we must have

$$\frac{c_1^2}{k_1^2} > \frac{\lambda^2}{4\,c_1^2} \text{ or } \left|\frac{\lambda}{2}\right| < \frac{c_1^2}{k_1}$$

if the complex is to be stabilized due to a Jahn-Teller effect.

We find for $W_{\min}$:

$$W_{\min} = -\frac{c_1^2}{2\,k_1} - \frac{\lambda^2\,k_1}{8\,c_1^2}$$

or for the Jahn-Teller stabilization energy (Table)

$$W_{\text{stab}} = \frac{c_1^2}{2\,k_1} + \frac{\lambda^2\,k_1}{8\,c_1^2} - \frac{\lambda}{2}\,.$$

Table

λ	W_{stab}	ν_1^*/ν_1
0	500 cm^{-1}	1.000
100 cm^{-1}	451 cm^{-1}	0.999
1000 cm^{-1}	125 cm^{-1}	0.866
2000 cm^{-1}	0 cm^{-1}	

With $\frac{c_1^2}{2\,k_1} = 500\ \text{cm}^{-1}$, a very reasonable order of magnitude, W_{stab} is given as a function of λ.

Notice, that in all our results we have not once used the actual form of the orbitals, only their angular transformation properties. Hence our results are completely general.

The Dynamic Jahn-Teller Problem

So far we have treated the vibrational coordinates as parameters that we could use to minimize the electronic energy. However, for the simultaneous treatment of the electronic and vibrational properties we have that the Jahn-Teller Hamiltonian is

$$\mathscr{H} = \mathscr{H}_{\text{el}}^0 + \mathscr{H}_{\text{vib}}(q_1) + \mathscr{H}_{\text{vib}}(q_2) + q_1\left(\frac{\partial\mathscr{H}}{\partial q_1}\right)_0 + q_2\left(\frac{\partial\mathscr{H}}{\partial q_2}\right)_0 + \lambda\,\vec{L}.\vec{S}\,.$$

The "complete" wavefuction is in the "crude adiabatic" approximation [*4*] given as

$$\Psi(r, q) = e_g^a\alpha\,\varphi_1(q_1, q_2) + e_g^a\beta\,\varphi_2(q_1, q_2) + e_g^b\alpha\,\varphi_3(q_1, q_2) + e_g^b\beta\,\varphi_4(q_1, q_2)\,.$$

We have further that

$$\left(\frac{\partial\mathscr{H}}{\partial q_1}\right)_0 e_g^a = -c_1\,e_g^a$$

$$\left(\frac{\partial\mathscr{H}}{\partial q_1}\right)_0 e_g^b = c_1\,e_g^b$$

$$\left(\frac{\partial \mathscr{H}}{\partial q_2}\right)_0 e_g^a = c_2\, e_g^b \,.$$

Operating with $\mathscr{H}$ on $\Psi\,(r, q)$, multiplying with the four electronic wavefunctions and integrating over the electronic and spin coordinates we get the following coupled equation for φ_1 and φ_3

$$\begin{pmatrix} \mathscr{H}_{\text{vib}}\,(q_1) + \mathscr{H}_{\text{vib}}\,(q_2) - c_1\, q_1 & c_2\, q_2 + \frac{1}{2}\, i\, \lambda \\ c_2\, q_2 - \frac{1}{2}\, i\, \lambda & \mathscr{H}_{\text{vib}}\,(q_1) + \mathscr{H}_{\text{vib}}\,(q_2) + c_1\, q_1 \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_3 \end{pmatrix} = W \begin{pmatrix} \varphi_1 \\ \varphi_3 \end{pmatrix}$$

and a completely analogous one for φ_2 and φ_4. The "diagonal Hamiltonian" is then

$$\mathscr{H} = \mathscr{H}_{\text{vib}}\,(q_1) + \mathscr{H}_{\text{vib}}\,(q_2) \pm \sqrt{c_1^2\, q_1^2 + c_2^2\, q_2^2 + \tfrac{1}{4}\, \lambda^2} \,.$$

First we assume $c_2 = \lambda = 0$. Then

$$\mathscr{H} = -\frac{\hbar^2}{2\,\mu_1}\,\frac{\partial^2}{\partial q_1^2} - \frac{\hbar^2}{2\,\mu_2}\,\frac{\partial^2}{\partial q_2^2} + \tfrac{1}{2}\, k_1\, q_1^2 + \tfrac{1}{2}\, k_2\, q_2^2 \pm c_1\, q_1$$

or closing the square

$$\mathscr{H} = -\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial q_1^2} + \tfrac{1}{2} k_1 \left(q_1 \pm \frac{c_1}{k_1}\right)^2 - \frac{c_1^2}{2 k_1} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial q_2^2} + \tfrac{1}{2} k_2\, q_2^2 \,.$$

It follows therefore that the energy is given as

$$W = W_{el}^0 - \frac{c_1^2}{2\, k_1} + (n_1 + \tfrac{1}{2})\, h\nu_1 + (n_2 + \tfrac{1}{2})\, h\nu_2 \,.$$

All that has happened is evidently that the equilibrium of the harmonic oscillation in q_1 has been shifted an amount $\left|\frac{c_1}{k_1}\right|$. A transition from a non degenerate state terminating in the Jahn-Teller distorted state will therefore show a vibrational progression in ν_1.

Next we consider only $c_2 = 0$. Expanding the lower potential surface $\frac{1}{2}\, k_1\, q_1^2 - \frac{1}{2}\, \sqrt{4\, c_1^2\, q_1^2 + \lambda^2}$ around the minimum point $q_1^0 = \sqrt{\frac{c_1^2}{k_1^2} - \frac{\lambda^2}{4\, c_2^2}}$ of the potential surface we get to the second order in q_1

$$\begin{aligned} \mathscr{H} \simeq & -\frac{\hbar^2}{2\,\mu_1}\,\frac{\partial^2}{\partial q_1^2} + \tfrac{1}{2} k_1 \left(1 - \frac{k_1^2\, \lambda^2}{4\, c_1^4}\right) q_1^2 - \frac{\lambda^2\, k_1}{8\, c_1^2} - \tfrac{1}{2}\,\frac{c_1^2}{k_1} \\ & - \frac{\hbar^2}{2\,\mu_2}\,\frac{\partial^2}{\partial q_2^2} + \tfrac{1}{2}\, k_2\, q_2^2 \end{aligned}$$

and for the vibrational levels, well below the cusp

$$W \simeq W_{\text{el}}^0 - \frac{c_1^2}{2\, k_1} - \frac{\lambda^2\, k_1}{8\, c_1^2} + (n_1 + \tfrac{1}{2})\, h\nu_1^* + (n_2 + \tfrac{1}{2})\, h\nu_2$$

with

$$\nu_1^* = \nu_1 \sqrt{1 - \frac{k_1^2\, \lambda^2}{4\, c_1^4}} \,.$$

For an electronic transition, terminating on the lower potential surface, the first members of the vibrational progression in ν_1 should therefore be separated by $h\nu_1^*$. In the table ν_1^*/ν_1 is tabulated as a function of λ.

The complete energy pattern in say the vibrational coordinate q_1 can be obtained as follows. The electronic wavefunctions are taken as

$$\omega_1\,\alpha = \frac{1}{\sqrt{2}}\,(e_g^a + i e_g^b)\,\alpha \qquad \omega_1\,\beta = \frac{1}{\sqrt{2}}\,(e_g^a + i e_g^b)\,\beta$$

$$\omega_2\,\alpha = \frac{1}{\sqrt{2}}\,(e_g^a - i e_g^b)\,\alpha \qquad \omega_2\,\beta = \frac{1}{\sqrt{2}}\,(e_g^a - i e_g^b)\,\beta\,.$$

The coupled differential equations which give the solutions to the vibrational functions $\chi_1\,(q_1)$ and $\chi_2\,(q_1)$ associated with the interacting potential surfaces are then

$$(\mathscr{H}_{\text{vib}} + \tfrac{1}{2}\lambda)\,\chi_1 + c_1\,q_1\,\chi_2 = W\,\chi_1$$

$$c_1\,q_1\,\chi_1 + (\mathscr{H}_{\text{vib}} - \tfrac{1}{2}\lambda)\,\chi_2 = W\,\chi_2\,.$$

Expanding $\chi_1 = \sum\limits_{n=0}^{\infty} a_n\,\psi_n$ and $\chi_2 = \sum\limits_{n=0}^{\infty} b_n\,\psi_n$ where ψ_n is a solution to the harmonic equation $\mathscr{H}_{\text{vib}}\,\psi_n = W_n\,\psi_n$ with $W_n = (n + \frac{1}{2})\,h\nu_1$ we get two infinite determinants, which can be written in compact form

$$\begin{vmatrix} \frac{1}{2}h\nu_1 \pm \frac{\lambda}{2} - W & \Delta\sqrt{1} & 0 & 0 & \cdot \\ \Delta\sqrt{1} & \frac{3}{2}h\nu_1 \mp \frac{\lambda}{2} - W & \Delta\sqrt{2} & 0 & \cdot \\ 0 & \Delta\sqrt{2} & \frac{5}{2}h\nu_1 \pm \frac{\lambda}{2} - W & \Delta\sqrt{3} & \cdot \\ 0 & 0 & \Delta\sqrt{3} & \frac{7}{2}h\nu_1 \mp \frac{\lambda}{2} - W & \cdot \\ \cdot & \cdot & \cdot & \cdot & \end{vmatrix} = 0\,.$$

In the diagonal terms the signs of λ must be taken both as $+ - + \ldots$ and $- + - \ldots$ and $\Delta = \sqrt{\frac{c_1^2}{2k_1}\,h\nu_1}\,.$

The solutions can of course only be obtained by numerical methods, and in order to see the general pattern of vibrational levels, we have solved 10×10

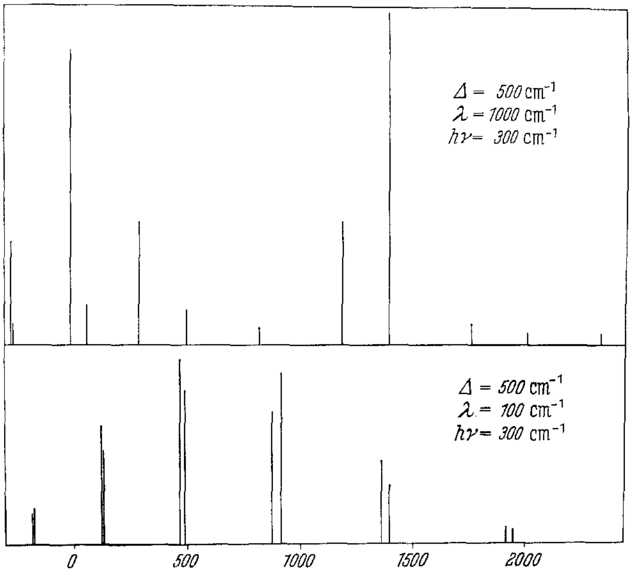

Fig. 3. Vibrational pattern in an electronic transition $^2A \rightarrow {}^2E$ with varying amount of LS coupling

determinants with $\Delta = 500\ \text{cm}^{-1}$, $h\nu_1 = 300\ \text{cm}^{-1}$ and $\lambda = 100\ \text{cm}^{-1}$ and $1000\ \text{cm}^{-1}$. This value of Δ corresponds to a Jahn-Teller stabilization energy W_{stab} equal to respectively some $784\ \text{cm}^{-1}$ and $408\ \text{cm}^{-1}$. The results are given in Fig. 3, where we have pictured the appearance of the vibrational pattern of a Jahn-Teller active vibration in a ${}^2A \rightarrow {}^2E$ transition. The pictured vibrational pattern is that expected at 0 °K with no hot bands present. In that case the line intensity is given proportional to a_0^2, where a_0 is the first coefficient in the expansion of χ. Using the Franck-Condon principle it is not difficult to understand that a large spin-orbit coupling will lead to two well separated potential surfaces and therefore to two intensity maxima. It is, however, important to realize that the convergence of our numerical calculation is rather slow, and therefore it is only the general shape of the vibrational patterns, not the finer details, that is significant.

Conclusions

A square planar molecule which in its ground state is expected to have a doubly degenerate electronic state will evidently undergo a stabilization by means of a nuclear distortion, thereby assuming a D_{2h} symmetry. On the other hand, in a doubly degenerate excited state, the Jahn-Teller effect will manifest itself dynamically: that is the vibrational pattern will reflect the vibronic coupling. With no spin-orbit coupling present we will observe a regular progression in single quanta of the Jahn-Teller active vibration. In that case the appearance of such a progression is a certain sign of a Jahn-Teller effect. This is of course exactly what we should expect, since this vibration has taken the role of a totally symmetric vibration in the distorted molecule. However, if there is spin-orbit coupling present the vibrational pattern will show irregularities. For a small spin-orbit coupling the lines in the progression will appear double. Then with increasing spin-orbit coupling the line spacing and intensity will be completely redistributed until finally, when the spin-orbit coupling has wiped out the Jahn-Teller effect, the intensity will be concentrated in two $0-0$ lines associated with the two separated potential surfaces.

Finally we notice that in the special case $c_2 = \lambda = 0$, we will have no "inversion" doubling of the vibrational levels. The reason is quite straightforward; there is no torque which will take the molecule from one of the distorted configurations to its "mirror" image. Once the molecule has "chosen" which half of the potential surface it wants to be in, it will have to stay there.

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