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Pseudo-Jahn−Teller Effect as the Origin of the Exalted Frequency of the b_{2u} Kekulé Mode in the 1^1B_{2u} Excited State of Benzene

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In this paper we show that a pseudo-Jahn−Teller (PJT) coupling between the $^1A_{1g}$ ground state and the $^1B_{2u}$ excited states along the Kekulé mode of b_{2u} symmetry is responsible for the surprisingly low frequency of this mode in the ground state and its remarkable upward shift of 261 cm^{-1} upon excitation to the first $^1B_{2u}$ excited state.

I. Introduction

In 1961, Berry[1] noted that the frequency of the in-plane b_{2u} vibration in benzene, which has bond length alternation (BLA) nature and connects the symmetric D_{6h} benzene with a Kekulé-like D_{3h} symmetry structure, is surprisingly low as compared to that of other vibrational modes such as, for instance, the a_{1g} breathing mode, which elongates the C−C bonds simultaneously. Indeed, experimental gas-phase two-photon spectroscopy measurements[2] give a value of 1309 cm^{-1} for this vibrational mode, often referred to as the "Kekulé mode", while assuming that both the σ and π-electronic systems of benzene oppose resistance to this BLA distortion, one would predict a larger frequency of about 1600 cm^{-1}.[3−6]

In addition, there is a remarkable upshift of this low frequency upon excitation to the first $^1B_{2u}$ excited state from 1309 to 1570 cm^{-1}.[2,7,8] This result, which was confirmed theoretically through coupled cluster calculations,[9] is totally unexpected in the context of the $\pi^* \leftarrow \pi$ nature of the electronic transition involved in the transit from the $^1A_{1g}$ ground state to the 1^1B_{2u} excited state. Considering that the π-system is weakened in the 1^1B_{2u} excited state, one may expect a reduction in the frequency of this b_{2u} vibrational mode upon excitation.[10] This is observed for all vibrational modes with CC stretching contributions but this Kekulé mode. In an attempt to account for the observed increased frequency of this b_{2u} vibrational mode when going from the ground $^1A_{1g}$ to the first $^1B_{2u}$ excited state, Berry suggested that the π-electrons tend to distort the ground state of benzene to a D_{3h} structure.[1] Then, promotion of a π electron to an antibonding orbital reduces the π-distortivity power and, consequently, increases the frequency of this Kekulean vibrational mode as observed experimentally. This line of reasoning was reinforced later on by the work of Haas and Zilberg,[11] and, in fact, the theory about the distortive tendencies of π electronic systems has gained support over the years, especially thanks to the work of Hiberty, Shaik, and co-workers[6,12−17] among others.[18−22] As a result of these investigations, it is now widely accepted that the properties attributed to aromaticity derive from the π-delocalization, but that it is the σ-electrons which are responsible for the symmetric D_{6h} framework.[23−25]

In connection with these studies, Shaik, Shurki, Danovich, and Hiberty (SSDH) used a Kekulé-crossing model to provide yet another related explanation about the origin of the exalted b_{2u} BLA frequency in the first excited state of benzene as well as for its mode- and state-selectivity.[26] In the framework of the valence bond method, SSDH found that the two Kekulé structures undergo avoided crossing along the b_{2u} coordinate. As a result of the avoided crossing, the ground-state potential energy surface along this Kekulean model becomes flat and that of the excited-state turns out to be steeper, thus explaining the source of the upshift of the b_{2u} mode's frequency when going from the ground to the 1^1B_{2u} excited state. The Kekulé-crossing model successfully accounted not only for the origin of the b_{2u} exalted frequency but also for its state- and mode-selectivity, and it was generalized later on to other polyacenes.[27]

In the present work, we offer an alternative physical basis for the large increase in the b_{2u} mode's frequency when going from the 1^1A_{1g} to the 1^1B_{2u} states of benzene, based on the pseudo-Jahn−Teller (PJT) effect.[28−31] We show that the anomalous frequency upshift observed for this Kekulé mode is due to PJT effects or equivalently to the vibronic coupling between the ground and lowest-lying $^1B_{2u}$ excited state through the in-plane CC stretching modes. This explanation was first proposed by Mikami and Ito[7] and Metz and co-workers,[32] and it was supported by semiempirical calculations of Orlandi and Zerbetto, where the vibronic coupling contributions were determined using approximate electronic diabatic states.[33] Here we put this explanation in the framework of the PJT theory with the help of ab initio CASSCF calculations of the nuclear Hessian matrix. Thus, the Hessian is calculated by switching off the PJT coupling, and this allows us to show the effect directly on the calculated frequencies. Our calculations of the PJT effect for the Kekulé mode of benzene in the 1^1A_{1g} and 1^1B_{2u} states provide a firm physical explanation for the upshift of the b_{2u} frequency as well as for its state- and mode-selectivity. Moreover, the generality of the explanation is confirmed by calculations on naphthalene. As compared to the avoided crossing model of SSDH,[26] our explanation is not restricted to electronic states and vibrational modes showing avoided cross-

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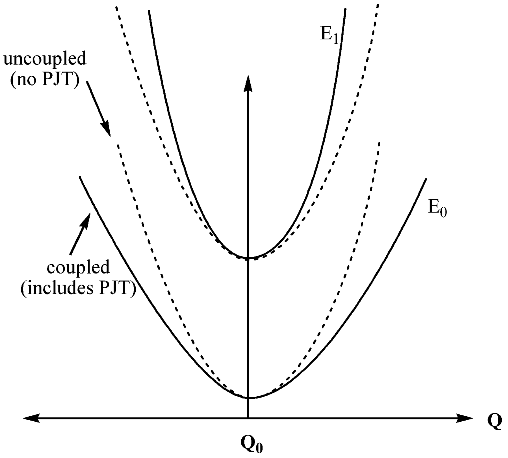

Figure 1. PJT effect between Ψ_0 and Ψ_1 along a vibrational mode Q. Dashed parabolas: "uncoupled" potential energy surfaces. Full-line parabolas: "coupled" potential energy surfaces.

ings along a given coordinate, and therefore it can be generalized to analyze frequency upshifts or downshifts of any vibrational mode in any electronic state of a given molecule.

II. Theoretical Considerations

The PJT effect is usually formulated using second-order perturbation theory,[28,30,31] where the energy is expanded about the point of minimum energy $Q_0 = 0$ as

$$E = E_0 + Q\left\langle \Psi_0 \left| \frac{\partial U}{\partial Q} \right| \Psi_0 \right\rangle + \frac{Q^2}{2}\left\langle \Psi_0 \left| \frac{\partial^2 U}{\partial Q^2} \right| \Psi_0 \right\rangle + \sum_k \frac{\left[Q\left\langle \Psi_0 \left| \frac{\partial U}{\partial Q} \right| \Psi_k \right\rangle \right]^2}{E_0 - E_k} + \ldots \quad (1)$$

where Q represents a nuclear displacement coordinate and U the nuclear-electronic and nuclear−nuclear parts of the potential energy. If the original wave function Ψ_0 is nondegenerate, the linear term is zero at the minimum geometry, and the sum of the two second-order terms gives the force constant of the vibration Q. At the minimum, the first second-order term is positive, because the electron density was optimized for the original nuclear configuration.[28] The last term corresponds to the PJT coupling. It only appears for vibrational modes with the same symmetry as the product $\Psi_0\Psi_k$. Its value is negative for the ground state of the molecule, because $E_0 < E_k$, and therefore it lowers the force constant of the ground state. In general the inverse effect can be expected for the excited state Ψ_k, leading in principle to an increase of the force constant. The effect of the coupling on the potential energy surface of the first two electronic states is shown in Figure 1, where the relevant excited state is Ψ_1. It is worth noting that couplings with higher lying states can affect the force constant of the excited state, and therefore Figure 1 is a simplification of the whole picture.

The present methodology to determine the PJT effect on nontotally symmetric vibrations has been explained in previous papers.[29,34] There it is shown that the expression for the second derivatives of the CASSCF energy with respect to nuclear displacements is a sum that includes, among others, orbital rotation terms that contain the $\langle \varphi_i | \partial \mathbf{H} / \partial Q | \varphi_k \rangle$ elements, and CI vector rotation contributions with the derivative coupling elements $\langle \Psi_0 | \partial \mathbf{H} / \partial Q | \Psi_k \rangle$. For comparison, in the Hartree−Fock (HF) formalism there are only orbital rotation terms, and they represent the PJT contributions to the second derivatives. In contrast to this, in the CASSCF formalism, the orbital rotation terms do not include coupling between pairs of active space orbitals. These terms appear as derivative coupling elements, and by restricting the symmetry of the excited states Ψ_k to the symmetry of the ground state ($^1A_{1g}$ for benzene) it is possible to eliminate the PJT contributions from a frequency calculation.

The present results are also related with the calculations of Gobbi, Yamaguchi, Frenking, and Schaefer on the second derivatives of the π and σ orbital energies in benzene, which show that the second derivatives of the π orbital energies along the b_{2u} BLA mode are negative.[22] Thus, the expressions for $\partial^2\epsilon_i/\partial Q^2$ contain the vibronic orbital coupling terms $\langle \varphi_i | \partial \mathbf{H} / \partial Q | \varphi_k \rangle$[35,36] (the $\epsilon_{ri}{}^a$ terms of eq 15 in ref 35), which are the HF equivalent of our PJT terms evaluated at the CASSCF level.

III. Computational Details

In this work, we have used the GAUSSIAN 03 package[37] to perform geometry optimizations and frequency calculations with the CASSCF method using the Pople standard 6-31G(d) basis set.[38] For benzene, we have used a (6,6) active space (6 electrons in 6 π orbitals). For naphthalene, the active space employed has been of 8 electrons in 8 π orbitals, which is the current maximum active space for frequency calculations with Gaussian03. Previous CASSCF and CASPT2 calculations[39,40] showed that the ground and the 1^1B_{2u} excited state can be treated in a satisfactory manner at the CASSCF level.

The "coupled" frequencies that contain the PJT contribution were calculated analytically at the optimized geometries, at the same level of theory, using the default procedure. The PJT contribution was calculated repeating the frequency calculation using a symmetry-restricted CASSCF wave function and subtracting the resulting "uncoupled" frequency from the "coupled" one.[29] This yields an approximate value of the PJT effect, as the "coupled" and "uncoupled" frequencies are not identical. Thus, to carry out the subtraction, the "coupled" and "uncoupled" modes were matched by projecting one set of normalized Cartesian displacements (without mass-weighting) on the other one, i.e., forming the scalar products between all displacements from one calculation with the displacements of the other calculation. For benzene and naphthalene, this has allowed us to match the "coupled" modes of 1186 and 1458 cm^{-1}, respectively, with the "uncoupled" ones of 1905 and 1889 cm^{-1}.

IV. Results and Discussion

The $1^1B_{2u} \leftarrow 1^1A_{1g}$ transition in benzene involves basically the excitation of an electron from the degenerate pair of HOMOs (e_{1g}) to the pair of LUMOs (e_{2u}). The resulting 0−0 transition energy is 4.78 eV in comparison with the 4.72 eV experimental value.[8] Due to the excitation, the ring expands from a CC bond length of 1.396 to 1.434 Å. For comparison, CCSD/TZ2P results are 1.392 and 1.425 Å, respectively, whereas experimental values range from 1.390 to 1.397 Å for the CC bond length in the 1^1A_{1g} electronic state and from 1.432 to 1.435 Å for the 1^1B_{2u} excited state.[9] As expected in the context of the $\pi^* \leftarrow \pi$ nature of the electronic transition involved in this transit, CC bonds are lengthened by about 0.03 Å. One may also expect a general lowering of all vibrational frequencies involving CC stretching after the transition and this is indeed the case except for the abnormal b_{2u} Kekulé mode.

Figure 2 depicts the calculated frequencies and vector displacement diagrams of the two b_{2u} modes of benzene in the

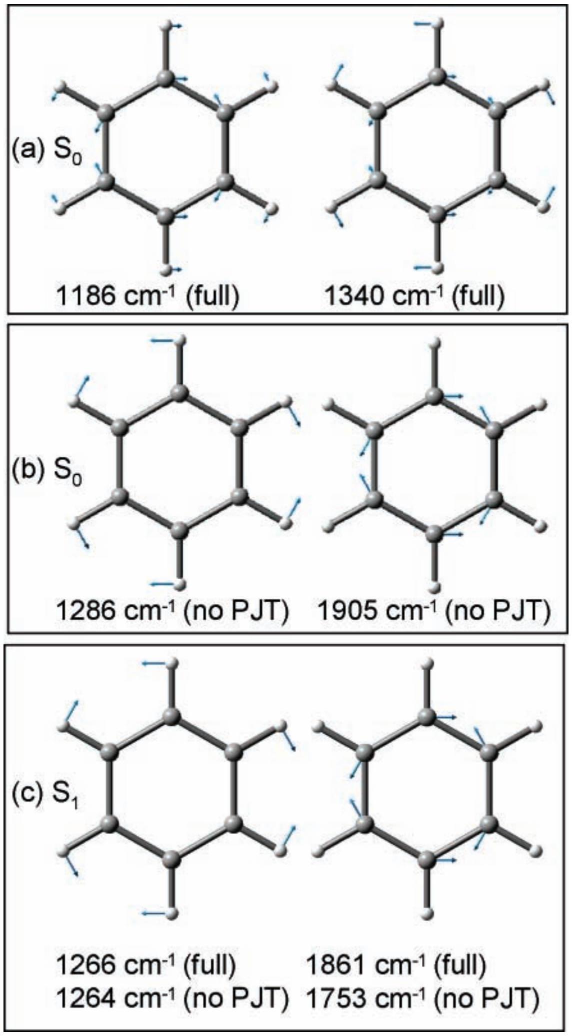

Figure 2. Calculated frequencies and vector displacements of the b_{2u} modes of benzene. Displacements are not mass-weighted for clarity. (a) S_0 ($^1A_{1g}$ ground state), full frequencies including PJT coupling (default procedure); (b) S_0, PJT "uncoupled" frequencies; (c) S_1 ($^1B_{2u}$ excited state), full and PJT "uncoupled" frequencies.

ground (S_0) and the 1^1B_{2u} (S_1) electronic states with and without including the PJT effect. In the excited state, the two b_{2u} modes corresponding to the BLA of the carbon skeleton and the hydrogen b_{2u} rocking vibration are almost totally separated. For the ground state, the two b_{2u} modes possess mixed Kekulé and H-rocking modes (the so-called Duschinsky mixing[10,32,41]) and this strong mixing occurs because the two modes are almost degenerate in the ground state.[26] Our CASSCF(6,6)/6-31G(d) results gives a frequency of 1186 cm^{-1} for the Kekulé mode of the ground state (experimental value is 1309 cm^{-1}), and the frequency in the 1^1B_{2u} excited state for the same mode is 1861 cm^{-1} (experimental value is 1570 cm^{-1}). Thus, according to our CASSCF(6,6)/6-31G(d) values, the frequency is upshifted by 675 cm^{-1}, a result that is overestimated in comparison with the experimental 261 cm^{-1}. More interesting is the analysis of the frequencies without the inclusion of the PJT effect. As can be seen in Figure 2, when the PJT effect is turned off in the ground state, the Kekulé and H-rocking modes become more separated and the frequency of the Kekulé mode increases by 719 cm^{-1}, and the frequency of the H-rocking modes remains almost unchanged. Conversely, for the 1^1B_{2u} excited state, the frequency of the Kekulé mode is reduced by 108 cm^{-1}. The excited-state frequency is reduced by a smaller amount than the ground-state one because couplings with higher excited states are also switched off in the calculation. As a whole, without the inclusion of the PJT effect, the frequency of the Kekulé mode becomes higher in the ground state than in the 1^1B_{2u} excited state as expected from the $\pi^* \leftarrow \pi$ nature of the electronic transition involved in the transit from the $^1A_{1g}$ ground state to the first $^1B_{2u}$ excited state. Thus, we can conclude that the PJT effect is responsible for the surprisingly low frequency of the Kekulé mode in the ground state and the remarkable upward shift of this vibrational mode upon excitation to the first $^1B_{2u}$ excited state. In addition, the important mixing of the two b_{2u} modes in benzene (Kekulé and H-rocking modes) is also due to the important reduction in the frequency of the Kekulé mode in the ground state due to the vibronic coupling between the $^1A_{1g}$ ground state and the $^1B_{2u}$ excited states. It is important to underline that our explanation based on the PJT effect readily explains the state- and mode-selectivity of the b_{2u} frequency upshift. It is clear from eq 1 that a b_{2u} vibrational model can only couple the 1^1A_{1g} ground state with excited states of $^1B_{2u}$ symmetry. In addition, eq 1 also indicates that the smaller the energy difference between the 1^1A_{1g} ground state and the $^1B_{2u}$ is, the larger the coupling will be.

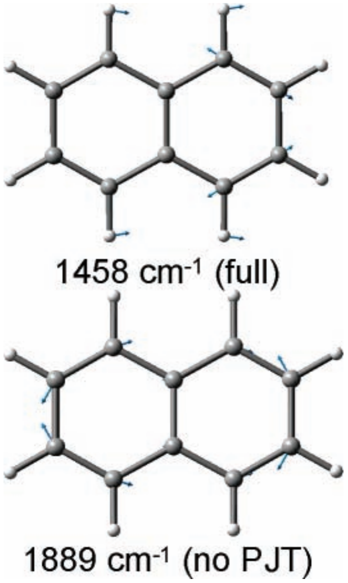

Figure 3. Calculated frequencies and vector displacements of the ground-state b_{2u} mode of naphthalene most affected by PJT coupling. Displacements are not mass-weighted for clarity.

The frequency upshift of the Kekulé mode is not exclusive of benzene and, in fact, it has been also observed in other polyacenes[42−46] and other conjugated species.[47] In the particular case of naphthalene, the Kekulé mode undergoes a frequency exaltation of 189 cm^{-1} in the 1^1B_{2u} state as compared to the ground state.[42] Our CASSCF(8,8) calculations confirm that the lowering of the ground-state frequency for the corresponding b_{2u} mode (Figure 3) is due to PJT coupling. Thus, the calculated frequency of 1458 cm^{-1} increases to 1889 cm^{-1} when the PJT effect is switched off.

From a more general point of view, the present calculations show that the π distortivity in planar aromatic hydrocarbons is caused by PJT coupling between the ground state and an excited state of suitable symmetry ($^1B_{2u}$ in benzene). In addition to that, it has been shown elsewhere that the PJT effect is related to the breakdown of the generalized maximum hardness and minimum polarizability principles (MHP and MPP, respectively) in pyridine and other nitrogen heterocycles.[48] Benzene and naphthalene, together with other organic aromatic compounds, also disobey the MHP and MPP principles along the Kekulé modes.[49−51] Overall this suggests that both phenomena, namely the frequency exaltation of the Kekulé modes in the excited state and the breakdown of the MHP and MPP principles, have a common origin in the PJT effect.

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