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LETTERS

Evaluation of the Analogy between Exceptions to the Generalized Maximum Hardness Principle for Non-Totally-Symmetric Vibrations and the Pseudo-Jahn−Teller Effect

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Exceptions to the generalized maximum hardness principle (MHP) for nitrogen heterocycles, along non-totally-symmetric vibrations (bond-length alternating modes), are caused by pseudo-Jahn−Teller (PJT) coupling between the ground and the excited state along those modes. Thus, the PJT effect causes an increase of the energy gap between the ground and the excited state, and this is reflected in an increase of hardness. This relationship is based on the assumption that the hardness (defined as difference between ionization potential and electron affinity) is approximately equal to the HOMO−LUMO gap (Koopmans' approximation), and this is in turn assumed to be approximately equal to the energy difference between the ground and excited state. The analogy is valid here because the excited state and the relevant vibration have the same symmetry, and the geometry and force constants of the optimized minima for the two coupled states are reasonably similar.

Introduction

Recent computations have shown the existence of exceptions to the generalized version of the maximum hardness principle (MHP) for non-totally-symmetric distortions.[1] The MHP[2] states that, at a given temperature and potential, molecular systems evolve toward maximum hardness, where the hardness is given by

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r}),T}$$

Here N is the number of electrons and $v(\vec{r})$ is the potential of the nuclei and any external potential. Calculations of hardness usually involve the following approximations:

$$\eta \cong \mathrm{IP} - \mathrm{EA} \cong \epsilon_L - \epsilon_H$$

That is, the hardness is approximated as the difference between ionization potential (IP) and electron affinity (EA) of the molecule, and these quantities are in turn calculated as the negative of the energies of the HOMO and LUMO, respectively, following Koopmans' theorem. Although the rigorous MHP has been proved by Parr and Chattaraj,[3] the generalized MHP relaxes the constraint of constant nuclear and external potential. One consequence of the generalized MHP is that hardness should be maximal at the minimum geometry of a molecule along the non-totally-symmetric vibrational modes. However, there is no proof for this principle, and some non-totally-symmetric distortions, namely bond length alternation (BLA), break this principle for several organic aromatic molecules.[1]

The observation of exceptions to the generalized MHP suggests a relationship with the pseudo Jahn−Teller (PJT) effect.[4,5] In the general case of a totally-symmetric electronic ground state, this effect couples the ground and excited states of a molecule along a non-totally-symmetric mode of the same symmetry as the excited state. It induces an increase of the energy gap between the two states along that displacement. Because the energy gap is related to the HOMO−LUMO gap, and this in turn is the approximate expression of the hardness, the PJT effect (increase of the energy gap between states) can provide an explanation for the behavior of the hardness along that mode (increase of the HOMO−LUMO gap).

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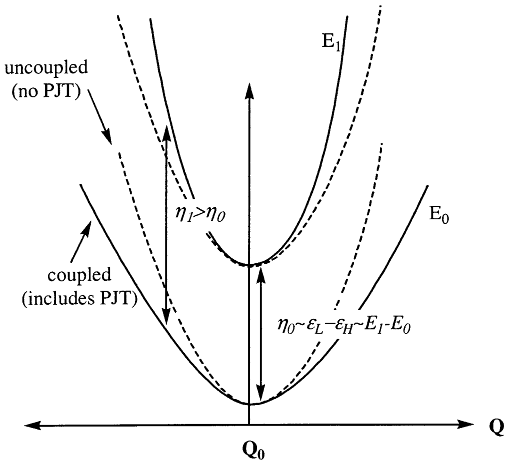


Figure 1. PJT effect between Ψ_0 and Ψ_1 along a non-totally-symmetric mode Q. Dashed parabolas: "uncoupled" potential energy surfaces. Full-line parabolas: coupled potential energy surfaces.

The relationship between the two phenomena was suggested earlier by Pearson,[6] but no calculations were carried out then to explore the analogy. In this paper we use a method that allows us to calculate the PJT effect, using a symmetry-constrained CASSCF wave function,[5] to test this relationship.

Theoretical Considerations

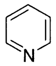
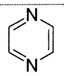
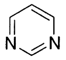
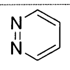
The PJT effect is usually formulated using second-order perturbation theory,[4] where the energy is expanded about the point of minimum energy Q_0.

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

Here Q represents a nuclear displacement coordinate and U is 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.[4,7] The last term corresponds to the PJT coupling. It only appears for non-totally-symmetric vibrations 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. There will be an inverse effect on the excited state Ψ_k, leading in principle to an increase of the force constant. The effect of the coupling on the energy gap between the two states is shown in Figure 1, where the relevant excited state is Ψ_1. However, Figure 1 is a simplification that only shows the coupling between the ground state Ψ_0 and Ψ_1. There will be further couplings between Ψ_0 and higher-lying excited states of the symmetry of Ψ_1, as well as between Ψ_1 and other excited states of the symmetry of Ψ_0. The overall effect on the surface of Ψ_0 will be a lowering of the force constant because all couplings have the same sign. On the other hand, the total effect on the surface of Ψ_1 will depend on the magnitude of the couplings, because the coupling of this state with higher-lying states will be opposite in sign to the coupling with the ground state. Thus, in general, there will be a widening of the energy gap along the non-totally-symmetric vibration, as shown in Figure 1, except for cases where the couplings between excited-states dominate over the Ψ_0/Ψ_1 one.

For the analogy between the PJT effect and the violation of the generalized MHP to be valid, using Koopmans' approximation to evaluate hardness, several other conditions have to be fulfilled: first, we assume that the energy gap between the ground and excited-state equals the HOMO−LUMO gap; second, the excited-state coupled to the ground state has to be dominated by the HOMO−LUMO excitation; and finally, the minimum geometry and "uncoupled" force constants of the two coupled states have to be similar. Because these assumptions are only approximate, only a substantial PJT effect will induce

TABLE 1: Calculated Frequencies for Modes with Relevant PJT Contribution and Characterization of the Excited-state Coupled to the Ground State

Compound	ν [cm^{-1}]^a	PJT [cm^{-1}]^b	HOMO->LUMO^c	Coefficient^d
 Pyridine (C_{2v})	1157.6 (b_2) 1725.8 (b_2)	777.5 120.2	a_2->b_1 (B_2)	0.70 (49%)
 Pyrazine (D_{2h})	1164.7 (b_{2u}) 1548.1 (b_{2u})	391.9 407.3	b_{1g}->b_{3u} (B_{2u}) “	0.70 (49%) “
 Pyrimidine (C_{2v})	1176.7 (b_2)	775.8	b_1->a_2 (B_2)	0.70 (49%)
 Pyridazine (C_{2v})	-^{e} 1727.7 (b_2)	-^{e} 125.1	a_2->a_2 (A_1) b_1->a_2 (B_2)^f	0.65 (42%) 0.61 (37%)^f

[a] Frequencies of "coupled" vibrational normal modes (symmetry in brackets). [b] PJT contribution. [c] Symmetries of HOMO, LUMO, and (in brackets) HOMO−LUMO excited state. [d] Coefficients of the HOMO−LUMO excitation in the first singlet excited state (percentage of squared value in brackets). [e] No PJT coupling, totally-symmetric excited state. [f] Symmetry labels and coefficients refer to (HOMO-2)−LUMO excitation, second singlet excited state.

the exception to the generalized MHP in non-totally-symmetric vibrations. For the compounds considered here, which have a totally-symmetric ground state, the relevant distortions will have the same symmetry as the excited state, so that $\langle \Psi_0 | \partial U / \partial Q | \Psi_k \rangle \neq 0$.

Computational Details. Geometries were optimized at the CASSCF/6-31G* level of theory, using a (6,6) active space (6 electrons in 6 π orbitals). 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 by repeating the frequency calculation using a symmetry-restricted CASSCF wave function and subtracting the resulting "uncoupled" frequency from the "coupled" one.[5] The uncoupled frequencies are not the normal modes, and to carry out the subtraction, the coupled and uncoupled modes were matched by projecting one set of modes on the other one. The violation of the generalized MHP by the normal modes listed in Table 1 was confirmed at the CASSCF/6-31G* level, by displacing the ground-state minimum geometry along those modes and calculating the hardness as the difference between ionization potential and electron affinity (see Supporting Information for details). Calculations were carried out with Gaussian98.[8]

Results and Discussion

The PJT contributions to the vibrational modes, calculated for a series of nitrogen heterocycles, are summarized in Table 1. The PJT contributions are the decrease in frequency of the ground-state normal modes, caused by the PJT effect. Only vibrations with a significant PJT contribution are reported.

Exceptions to the generalized MHP principle along the BLA modes were observed for pyridine, pyrazine, and pyrimidine.[1] For pyridine and pyrimidine, the first excited state has B_2 symmetry, and the PJT effect is observed along modes of the same symmetry: 777.5 and 120.2 cm^{-1} for two pyridine modes[9] and 775.8 for a pyrimidine mode. For pyrazine, the first excited state has B_{2u} symmetry, and the PJT effect is observed for two modes of the same symmetry, with a contribution of 391.9 and 407.3 cm^{-1}, respectively. In the three cases, the modes correspond to BLA modes of the carbon−carbon and carbon−nitrogen bonds, combined with C−H bending modes.

The b_2 symmetric BLA mode of pyridazine obeys the generalized MHP, in contrast to the previous examples. Our calculations show that here the first excited state (HOMO−LUMO excitation) has A_1 symmetry (see Table 1). The second excited state ((HOMO-2)−LUMO excitation) has the required symmetry (B_2), but the PJT effect along the corresponding BLA mode is substantially smaller (125.1 cm^{-1}) than for the previous cases, because the denominator of the PJT term ($E_0 - E_k$) is larger (E_k is the second excited state). Presumably, also the matrix element that appears in the numerator, $\langle \Psi_0 | \partial U / \partial Q | \Psi_k \rangle$, is smaller.

Conclusions

Our CASSCF calculations of the PJT effect for different non-totally-symmetric vibrational modes in some nitrogen heterocycles (pyridine, pyrazine, and pyrimidine) show that the PJT coupling is the reason behind the violation of the generalized MHP (increase of hardness) along those modes. At the same time, we find that pyridazine, for which the generalized MHP is kept, has only a small PJT coupling. The analogy between the PJT coupling and breaking of the generalized MHP is valid for these nitrogen heterocycles because the distortion that breaks the generalized MHP has the same symmetry as the excited state. At the same time, the minimum geometry and the uncoupled force constants along the relevant modes are approximately equal for the ground and the excited state. Calculations for pyridine reveal that the difference between the optimized bond lengths for the ground state and the first excited state ($^1B_2$ state) is less than 0.04 Å for all carbon−carbon and carbon−nitrogen bonds, whereas the variation in the ring angles is less than 2°. Moreover, the uncoupled frequencies for the two minima differ by less than 200 cm^{-1} (see Supporting Information for details). The reason for the small difference between geometry and uncoupled frequencies of the two states is that the excitation affects only the π system, but not the carbon−carbon σ framework of the molecule. Calculations on further systems are necessary to verify that the analogy between PJT and breaking the generalized MHP has a broader validity.

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Supporting Information Available: Details of hardness calculations along modes that break the generalized MHP. List of geometries, and frequencies for which PJT and violation of the generalized MHP is found. Ground- and excited-state frequencies of pyridine. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(9) Smaller PJT couplings (up to 110 cm^{-1}) are found for the excited-state S_1 of pyridine, presumably because of coupling with higher-lying states (see above). Thus, the second excited state at the CASSCF level has the same symmetry than S_0 and is coupled to S_1 along the vibrations of b_2 symmetry.