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Pseudo Jahn–Teller origin of bending instability of triatomic molecules

Hakan Kayi, Isaac B. Bersuker, James E. Boggs *

Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712-0165, USA

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ABSTRACT

For several decades the bending of linear molecules in degenerate states has been assumed to be due to the Renner–Teller effect (RTE), whereas the pseudo Jahn–Teller effect (PJTE) has been completely ignored. But in a recent publication of *ab initio* calculations performed on a series of triatomics it was shown that the contribution of the PJTE to their bending instability is much larger than that of the RTE. This raised the question of whether the finding of the essential role of the PJTE in the instability is a particular case for the molecules studied or a general trend. The problem is important not only for rationalizing the experimental observations and *ab initio* calculations of such systems, but also for a correct interpretation of their spectra, as the PJTE, by admixing excited states of different symmetry (opposite parity) to the ground one, influences significantly their spectroscopic properties. To contribute to the solution of this problem we performed *ab initio* calculations of electronic structure and energy profiles of a group of triatomic systems including CH_2^+, H_2O^+, SiH_2^+, PH_2, and HNF which have a Π twofold degenerate state in the linear configuration, but are bent in the equilibrium geometry. For them we formulated the combined RTE and PJTE problem and, by calculating *ab initio* the Renner–Teller vibronic coupling constant g and estimating the other parameters by fitting the PJTE equations to the *ab initio* calculated energy profiles, we show that in all the cases under consideration the PJTE contribution is significantly larger than that of the RTE. The parameters of the equilibrium geometry and electronic structure of these systems obtained in our calculations are in good agreement with those reported in other publications.

1. Introduction

The study of the origin of equilibrium geometry of triatomic molecules and radicals has a long history, and the continuing interest in this subject is supported by their widespread applications. Among many other fields of active interest, small triatomic species are most important in combustion, photochemistry, atmospheric chemistry, interstellar medium astrophysics, and they often serve as intermediate products of chemical reactions [1–10]. Note that the whole spectroscopy of these systems is essentially based on the correct presentation of their equilibrium configuration.

In spite of the seeming simplicity of triatomics and a massive number of relevant publications, the origin of their equilibrium geometry is not fully clarified as yet. *Ab initio* calculations provide essential information about the optimized configurations of specific molecular systems, but they do not explain directly their origin, especially, the origin of their differences. In particular, electronic structure calculations alone do not explain why many of the triatomic systems (e.g., HBF, HNF, HNO^+, CH_2^+, H_2O^+, SiH_2^+) are bent in the ground state equilibrium geometry and linear in the first excited state (see e.g., references in [11]). Walsh diagrams and orbital theories, the valence shell electron pair repulsion (VSEPR) model, polarized ion models, as well as softness–hardness-based models employed in many papers devoted to this subject cannot explain this either [12–17].

On the other hand, the vibronic coupling theory explains many features in the formation of molecular shapes [11,18]. Based on these ideas, it has been assumed for a long time that linear molecular systems in degenerate states may be unstable due to the Renner–Teller effect (RTE) (see [19–32] and references therein). Then it was rigorously proved that for any polyatomic system in a nondegenerate state the instability of the high-symmetry configuration is due to, and only to the pseudo Jahn–Teller effect (PJTE) [11]. Together with the proper Jahn–Teller effect (JTE) for nonlinear systems in degenerate states we come to the formulation that all the instabilities of polyatomic systems are due to these three (jointly called) Jahn–Teller effects. In general, the role of excited states in softening the ground state in certain directions of distortions was understood earlier [33–35] and the first application of the PJTE to solving structural problems can be related to the early 60s [36].

For linear molecules there are thus two sources of instability, RTE and PJTE. As mentioned above, until recently the bent configurations of all the triatomics studied were attributed to the RTE, but in a recent paper [37] it was shown that the contribution of

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* Corresponding author.
E-mail address: james.boggs@mail.utexas.edu (J.E. Boggs).

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the PJTE to the instability in a series of triatomics is significantly larger than that of the RTE. This result is of essential importance to the spectroscopy of such systems as the PJTE admixes excited electronic states of lower symmetry (opposite parity) to the ground state, and this changes significantly the spectroscopic matrix elements. Therefore it is important to find out whether the overwhelming contribution of the PJTE to the bending instability of triatomics is unique for the molecules studied in Ref. [37], or it takes place in other triatomics as well, thus suggesting an important pattern.

In this paper we explore the problem in more detail by studying a series of triatomics, CH_2^+, H_2O^+, SiH_2^+, PH_2, and HNF with regard to the contribution of the PJTE to their instability in the linear configuration. As in the previous paper [37], the PJTE interaction is added to the RTE by means of a second order perturbation correction in the Hamiltonian, and the parameters of the latter are obtained by *ab initio* calculation of some of them and comparison with *ab initio* calculated energy profiles as a function of the bending of the linear configuration. The problem is solved in combination with a detailed analysis of their electronic structure based on the *ab initio* calculations in comparison with the results obtained earlier by other authors where available. For all the molecular systems studied we found that, similar to the previous paper [37], the PJTE contribution to the instability of their linear configuration is significantly larger than that of the RTE. This means that many spectroscopic studies of such systems should be reviewed with respect to this implication.

2. Procedure

The equilibrium geometries of the molecular systems under consideration are defined as corresponding to the minimum point of the adiabatic potential energy surface (APES) determined by all the intermolecular interactions including vibronic coupling. For a linear system in a twofold degenerate Π state the Hamiltonian was introduced in previous publications [37,38]. Starting with the linear configuration of the molecule, denote the two wavefunctions of the Π term by $|\pi_x\rangle$ and $|\pi_y\rangle$ and the twofold degenerate bending nuclear displacements by Q_x and Q_y, respectively. Then by including the quadratic terms of vibronic coupling (linear terms do not mix the $|\pi_x\rangle$ and $|\pi_y\rangle$ functions) the Π term splits, and this is the Renner–Teller effect (RTE) [19]. The Hamiltonian of the potential energy of this system with the RTE is a 2 × 2 matrix [38];

$$U = \frac{1}{2}K_0(Q_x^2 + Q_y^2)\sigma_0 + g[(Q_x^2 + Q_y^2)\sigma_z + 2Q_xQ_y\sigma_x] \tag{1}$$

where K_0 denotes the primary force constant of bending without the vibronic coupling, g is the quadratic coupling constant [11],

$$g = \frac{1}{2}\left\langle \pi_x \left| \left(\frac{\partial^2 H}{\partial Q_x \partial Q_y}\right)_0 \right| \pi_y \right\rangle \tag{2}$$

and σ_0, σ_x, σ_z are the Pauli matrices,

$$\sigma_0 = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}, \quad \sigma_z = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}, \quad \sigma_x = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix} \tag{3}$$

If the nuclear displacements are given in terms of polar coordinates,

$$Q_x = \rho\cos\phi \quad \text{and} \quad Q_y = \rho\sin\phi \tag{4}$$

then the solution of the secular equation

$$U - \varepsilon\sigma_0 = 0 \tag{5}$$

with the vibronic interaction operator (1) is:

$$\varepsilon_{1,2}(\rho) = \left(\frac{1}{2}K_0 \pm |g|\right)\rho^2 \tag{6}$$

where $\varepsilon_{1,2}$ denotes the two branches of the APES including the RTE. The many dozens of papers exploring the origin of structure and spectra of linear molecules with a degenerate Π term are limited to this approximation (see, e.g., [11]).

Meanwhile, as indicated earlier [39], the Hamiltonian (1) does not include all the effective vibronic coupling interactions. Indeed, it does not include the PJTE interaction of the ground state with the appropriate excited states via the linear terms of the vibronic coupling. The PJTE for a Π term including only one excited state and without the RTE was considered first in Ref. [40]. As mentioned above, the combined RTE plus PJTE in linear molecules was explored first in [37]. Although the PJTE, in general, cannot be reduced to second order perturbations of the ground state [11], in some particular cases when there are no crossovers and avoided crossings (when the excited states are well separated from the ground one) the PJTE contribution can be estimated by such second order corrections W. Its matrix elements W_{xx}, W_{yy} and W_{xy} are:

$$\begin{aligned} W_{xx} &= -\sum_n \frac{|\langle \pi_x|(\partial H/\partial Q_x)_0|n\rangle|^2}{E_n - E_0} Q_x^2 = -pQ_x^2 \\ W_{yy} &= -pQ_y^2 \\ W_{xy} &= -pQ_xQ_y \end{aligned} \tag{7}$$

where E_n denotes the energies of the corresponding excited states, $|n\rangle$. Note that in these expressions the PJT vibronic coupling constant p is positive and the excited states are those for which $\langle \pi_x|(\partial H/\partial Q_x)_0|n\rangle = \langle \pi_y|(\partial H/\partial Q_y)_0|n\rangle \neq 0$.

With these PJT interactions included the Hamiltonian contains two perturbations, the RTE and PJTE, represented by the constants g and p, respectively, and in the same procedure that led to Eq. (1) we get the operator of the potential energy for a linear molecule with the combined RTE and PJTE as follows:

$$U = \frac{1}{2}(K_0 - p)(Q_x^2 + Q_y^2)\sigma_0 + \left(g - \frac{1}{2}p\right)[(Q_x^2 - Q_y^2)\sigma_z + 2Q_xQ_y\sigma_x] \tag{8}$$

The solution of Eq. (5) with this operator is straightforward; the two branches of the APES are:

$$\varepsilon_{1,2}(\rho) = \left[\frac{1}{2}(K_0 - p) \pm \left|g - \frac{1}{2}p\right|\right]\rho^2 \tag{9}$$

We see that the PJTE presented by the parameter p influences essentially both the primary curvature K_0 reducing it by p, and the RTE splitting parameter g reducing it by $(1/2)p$. A typical energy level diagram for a degenerate ground state term Π of a linear triatomic molecule along its bending coordinate ρ demonstrating the relative contributions of the different vibronic coupling terms is given in Fig. 1.

For a comparison of the contributions of the RTE and PJTE to the instability of the linear configuration, the numerical values of the three constants, K_0, g and p in Eq. (9) should be estimated. Direct *ab initio* calculation of all of them is hardly possible, especially the p value, as it requires the knowledge of all relevant excited states in Eq. (7). Another way for their estimation is to calculate some of them and to extract the others from comparison with the *ab initio* calculated energy profiles as explained below. Employing a technique worked out earlier [41] we can calculate numerically the RTE parameter g in Eq. (2) using the wavefunctions $|\pi_x\rangle$ and $|\pi_y\rangle$ determined from the *ab initio* calculations

$$g = \frac{1}{2}\sum_m^{N_{MO}} OCC_m^{eff} \sum_{i,j} c_{ix}^m c_{jy}^m \sum_\gamma k_\gamma^2 \left\langle \chi_i \left| \left(\frac{\partial^2 h}{\partial x_\gamma \partial y_\gamma}\right)_0 \right| \chi_j \right\rangle \tag{10}$$

In this expression c stands for the coefficients of the linear combination of atomic orbitals (LCAO's), k represents the Cartesian to normal coordinate transformation coefficients, h is the one-elec-