

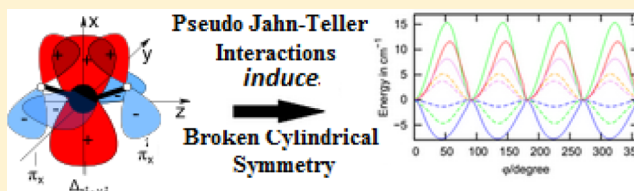
Novel Effect Induced by Pseudo-Jahn–Teller Interactions: Broken Cylindrical Symmetry in Linear Molecules

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ABSTRACT: It is shown that in linear molecules the pseudo-Jahn–Teller (PJT) interaction of a Σ or Π term with a Δ term induces a bending instability that is angular dependent, reducing the symmetry of the adiabatic potential energy surface from expected $D_{\infty h}$ to D_{4h} and $C_{\infty v}$ to C_{2v} or C_{4v} . This spontaneously broken cylindrical symmetry (BCS) emerges from the solution of the vibronic coupling equations of the PJT effect (PJTE) problems $(\Sigma+\Delta)\otimes w$, $(\Pi+\Delta)\otimes w$, $(\Pi+\Sigma+\Delta)\otimes w$, and $(\Delta+\Delta)\otimes w$, where w includes linear, quadratic, and fourth order vibronic coupling terms, and it is confirmed by ab initio calculations for a series of triatomic molecules with ground or excited Δ terms. The BCS is due to the angular symmetry of the electronic wave functions of the Δ term, $\sim\cos 2\varphi$, and $\sim\sin 2\varphi$, split by the fourth order vibronic coupling, which in overlap with the other symmetry wave functions of the Σ or Π term provides for the periodical symmetry of the added covalency that facilitates the bending. The mechanism of this PJT-induced BCS effect is discussed in detail; the numerical values of the vibronic coupling parameters for the molecules under consideration were estimated by means of combining separate ab initio calculations of some of them with a procedure fitting the analytical expressions to ab initio calculated energy profiles. It is also shown that the bending of linear molecules in Δ states, similar to Π states, is exclusively a PJT (not Renner–Teller) effect. The BCS revealed in this paper illustrates again the predicting power of the PJTE.



1. INTRODUCTION

It is well-known that the Jahn–Teller effect (JTE) and pseudo-JTE (PJTE) result in spontaneous distortions of high-symmetry configurations of molecules and solids, that is, spontaneous symmetry breakings (SSB), and it is proved that the JTE and PJTE are the only source of structural SSB in polyatomic systems (see refs 1–3 and references therein). Starting from the high-symmetry configuration, the SSB is caused by the vibronic coupling of the electronic states with linear, quadratic, and higher order terms of nuclear displacements. Employing the symmetry rules of group theory, the direction of distortions in such SSB can be determined from the type of degeneracy of the electronic term producing the JTE, or from the symmetries of the interacting (pseudodegenerate) electronic states in the PJTE, and the symmetry of the vibronic coupling. For the simplest linear molecules, triatomics, the SSB can be described by two bending normal displacements Q_x and Q_y , which form a 2-fold degenerate pair transforming as a Π type irreducible representation π_u in the group of $D_{\infty h}$ (or π in $C_{\infty v}$), and their higher order terms.

Distinguished from nonlinear molecules, linear triatomics in 2-fold degenerate state Π , Δ , Φ , ..., are not subjected to the JTE because the two electronic wave functions have the same parity, while the linear vibronic coupling displacements are odd, and hence, they do not split the degenerate state. However, the quadratic terms of the vibronic coupling do split the Π state, while the fourth order terms split Δ states, and these splittings are called the Renner–Teller effect (RTE).^{4–6} However, it was shown recently⁷ that the RTE just splits the degenerate term and softens

its lower branch without producing instability and SSB; the RTE softening is insufficient to overcome the basic rigidity of the linear configuration. This general conclusion was confirmed by ab initio calculations for a series of specific molecules.^{8,9} Moreover, there are SSB in linear molecules in nondegenerate Σ states with no RTE.¹ In all these cases the SSB is caused by the PJTE, which is thus the only source of bending of linear molecules.^{7–10}

Linear molecules possess cylindrical symmetry due to which one may expect that in cylindrical coordinates ρ , φ , z , with $Q_x = \rho \cos \varphi$ and $Q_y = \rho \sin \varphi$ the adiabatic potential energy surface (APES) of the bending along ρ will be independent of the angle φ . This understanding remained unchallenged until the present publication. We show here that, because of its PJTE origin, the SSB becomes strongly dependent on the properties of the mixing ground and excited states that produce the bending; if the PJTE is sufficiently strong and involves a Δ term, it violates the cylindrical symmetry in the higher order of the bending coordinates, making the bent configuration at $\rho > 0$ dependent on the angle φ . This new type of symmetry breaking induced by the PJT vibronic coupling between two or more terms in $(\Sigma+\Delta)\otimes w$, $(\Pi+\Delta)\otimes w$, $(\Pi+\Sigma+\Delta)\otimes w$, and $(\Delta+\Delta)\otimes w$ type problems (w includes all nonzero linear, quadratic, and fourth order terms) is confirmed by independent ab initio calculations of the APES of a series of triatomic molecules with ground or excited Δ terms, for which the vibronic coupling constants are also evaluated.

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2. BREAKING CYLINDRICAL SYMMETRY

To demonstrate this new type of SSB, the broken cylindrical symmetry (BCS), and to explain its origin, consider linear triatomic molecules in Σ , Π , Δ ground and/or excited states. The angular dependence of the wave functions of a linear molecule is determined by the quantum number $\Lambda = 0, 1, 2, \dots$ of the projection of the angular moment of the electrons on the molecular axis producing Σ , Π , Δ , ... terms, respectively. In cylindrical coordinates the wave function of a nondegenerate Σ term has no angular dependence. If the electronic term is 2-fold degenerate, the two wave functions have the angular dependence of $|1, \Lambda\rangle \sim \sin \Lambda\varphi$ and $|2, \Lambda\rangle \sim \cos \Lambda\varphi$. They can be presented as a sum of Slater determinants $|1, \Lambda\rangle = \sum_A c_A \Psi_A^{(1\Lambda)}$ and $|2, \Lambda\rangle = \sum_A c_A \Psi_A^{(2\Lambda)}$, where A identifies the set of orbitals in each determinant. Expanding these determinants to show explicitly the angular dependence of the wave function we get

$$\begin{aligned} |1, \Lambda\rangle &= \sum_A c_A \sum_i \phi_{1\Lambda}^A(r_i, z_i, \Lambda\varphi_i) C_{i\Lambda}^A(r_j, z_j, \Lambda\varphi_j; j \neq i) \\ &= \sum_A c_A \sum_i \phi_{1\Lambda}^A(r_i, z_i) \sin \Lambda\varphi_i C_{i\Lambda}^A(r_j, z_j, \Lambda\varphi_j; j \neq i) \\ |2, \Lambda\rangle &= \sum_A c_A \sum_i \phi_{2\Lambda}^A(r_i, z_i, \Lambda\varphi_i) C_{i\Lambda}^A(r_j, z_j, \Lambda\varphi_j; j \neq i) \\ &= \sum_A c_A \sum_i \phi_{2\Lambda}^A(r_i, z_i) \cos \Lambda\varphi_i C_{i\Lambda}^A(r_j, z_j, \Lambda\varphi_j; j \neq i) \end{aligned} \quad (1)$$

where (in conventional denotations) $C_{i\Lambda}^A$ is the cofactor of the orbital $\phi_{1\Lambda}^A(\mathbf{r}_i)$ in the Slater determinant, and $\phi_{1\Lambda}^A(r_i, z_i)$ is the radial part of this orbital, while $\cos \Lambda\varphi_i$ and $\sin \Lambda\varphi_i$ are the corresponding angular parts in the two functions of the degenerate term; they realize the transformation properties of the Λ term in the symmetry group of the linear molecule. Below we denote the nondegenerate function of the Σ term by $|\Sigma\rangle$, the two functions of the Π term by $|\pi_x\rangle$ and $|\pi_y\rangle$, and those of the Δ term by $|\Delta_{xy}\rangle$ and $|\Delta_{x^2-y^2}\rangle$.

The active (in the problems under consideration below) linear $W^{(1)}$, quadratic $W^{(2)}$, and fourth order $W^{(4)}$ vibronic coupling terms in the expansion of the Hamiltonian $W = \sum_i W^{(i)}$ are as follows:

$$W^{(1)} = \left(\frac{\partial V}{\partial Q_x} \right)_0 Q_x + \left(\frac{\partial V}{\partial Q_y} \right)_0 Q_y = \sum_i Z_i D_i r_i^{-2} [\cos \varphi_i Q_x + \sin \varphi_i Q_y] \quad (2)$$

$$\begin{aligned} W^{(2)} &= \frac{1}{2} \left[\left(\frac{\partial^2 V}{\partial Q_x^2} \right)_0 Q_x^2 + \left(\frac{\partial^2 V}{\partial Q_y^2} \right)_0 Q_y^2 + 2 \left(\frac{\partial^2 V}{\partial Q_x \partial Q_y} \right)_0 (Q_x Q_y) \right] \\ &= \frac{1}{2} \sum_i Z_i D_i^2 r_i^{-3} [(3 \cos^2 \varphi_i - 1) Q_x^2 + (3 \sin^2 \varphi_i - 1) Q_y^2 \\ &\quad + 3 \sin 2 \varphi_i Q_x Q_y] \end{aligned}$$

$$\begin{aligned} W^{(4)} &= \frac{1}{24} \left[\left(\frac{\partial^4 V}{\partial Q_x^4} \right)_0 Q_x^4 + \left(\frac{\partial^4 V}{\partial Q_y^4} \right)_0 Q_y^4 + 6 \left(\frac{\partial^4 V}{\partial Q_x^2 \partial Q_y^2} \right)_0 Q_x^2 Q_y^2 \right. \\ &\quad \left. + 4 \left(\frac{\partial^4 V}{\partial Q_x \partial Q_y^3} \right)_0 Q_x Q_y^3 + 4 \left(\frac{\partial^4 V}{\partial Q_x^3 \partial Q_y} \right)_0 Q_x^3 Q_y \right] \\ &= \frac{3}{8} \sum_{i \neq j} Z_i Z_j D_i^4 \frac{1}{l_{ij}^5} - \frac{1}{24} \sum_i Z_i D_i^4 \frac{1}{r_i^5} [(105 \cos^4 \varphi_i - 90 \cos^2 \varphi_i + 9) \\ &\quad \times Q_x^4 + (105 \sin^4 \varphi_i - 90 \sin^2 \varphi_i + 9) Q_y^4 + 6(105 \cos^2 \varphi_i \sin^2 \varphi_i - 12) \\ &\quad \times Q_x^2 Q_y^2 + 4(105 \cos^3 \varphi_i \sin \varphi_i - 45 \cos \varphi_i \sin \varphi_i) Q_x Q_y^3 \\ &\quad + 4(105 \sin^3 \varphi_i \cos \varphi_i - 45 \cos \varphi_i \sin \varphi_i) Q_x^3 Q_y] \end{aligned}$$

where $V = V_{\text{en}} + V_{\text{nn}}$, $V_{\text{en}} = \sum_{ij} Z_i Z_j |\mathbf{r}_i - \mathbf{R}_j|^{-1}$ and $V_{\text{nn}} = \sum_{i \neq j} Z_i Z_j |\mathbf{R}_i - \mathbf{R}_j|^{-1}$ are the operators of the electron–nuclear and nuclear–nuclear interactions, respectively (\mathbf{r}_i and \mathbf{R}_j are electronic and nuclear coordinates, respectively, while the electronic charge is taken as $e = 1$), and the transformation of the normal coordinates Q_x and Q_y into Cartesian ones, $(\partial/\partial Q) = \sum_i (\partial/\partial X_i) (\partial X_i/\partial Q) = \sum_i D_i (\partial/\partial X_i)$, is taken into account. The first term in the right-hand side of the expression for $W^{(4)}$ is a constant emerging from the nuclear–nuclear interaction V_{nn} and l_{ij} are interatomic distances in the linear geometry.

With the wave functions (eq 1) the matrix elements of the linear terms of vibronic coupling perturbation $W^{(1)}$ are zero by symmetry, and hence, the JTE in these degenerate states is inoperative. For the 2-fold degenerate Π states with $\Lambda = 1$ the matrix elements are nonzero for the quadratic coupling $W^{(2)}$. It splits the adiabatic potential energy surface (APES) of this term in two branches by lowering the curvature of one of them and increasing the curvature of the other one along the bending coordinate ρ ; this is the RTE.^{4–6} It can be easily checked that for Δ terms with $\Lambda = 2$ the matrix elements for both the linear and quadratic terms of vibronic coupling are zero, and only the fourth order terms $W^{(4)}$ produce the RTE splitting.^{5,6} All this is only true if the PJTE is neglected.

With the PJTE included these statements change essentially.^{1–3,7–10} First, since the number of excited states is infinite and they are of different symmetries; there is a nonzero mixing of any ground state with appropriate excited states by the linear perturbation $W^{(1)}$. Except for the low-lying (close in energy) states (see below), the interaction with the higher ones can be taken into account as a second order perturbation correction.⁸ For the Π term, the matrix elements of the latter are

$$w_{xx} = -2 \sum_n \frac{\left| \left\langle \pi_x \left| \left(\frac{\partial V}{\partial Q_x} \right)_0 \right| n \right\rangle \right|^2}{E_n - E_0} Q_x^2 = -p Q_x^2 \quad (3)$$

$$w_{yy} = -p Q_y^2$$

$$w_{xy} = -p Q_x Q_y$$

where the active excited states $|n\rangle$ are Σ states, and p is a positive constant. Similarly, in the second order perturbation corrections to the Δ term produced by the $W^{(1)}$ perturbation the active excited states are of Π symmetry and the interaction parameter is p_1 . With these corrections and the nonzero matrix elements of the quadratic perturbation $W^{(2)}$ the secular equation for a single standing Π term is⁸

$$\begin{vmatrix} \frac{1}{2}(K_0 - p)\rho^2 - \left(g + \frac{1}{2}p\right)\rho^2 \cos(2\varphi) - \varepsilon & -\left(g + \frac{1}{2}p\right)\rho^2 \sin(2\varphi) \\ -\left(g + \frac{1}{2}p\right)\rho^2 \sin(2\varphi) & \frac{1}{2}(K_0 - p)\rho^2 + \left(g + \frac{1}{2}p\right)\rho^2 \cos(2\varphi) - \varepsilon \end{vmatrix} = 0 \quad (4)$$

where

$$K_0 = \frac{1}{2} \left\langle \pi_x \left| \left(\frac{\partial^2 V}{\partial Q_x^2} + \frac{\partial^2 V}{\partial Q_y^2} \right) \right| \pi_x \right\rangle \quad (5)$$

and

$$g = \frac{1}{2} \left\langle \pi_x \left| \left(\frac{\partial^2 V}{\partial Q_x \partial Q_y} \right) \right| \pi_y \right\rangle \quad (6)$$

With the wave functions (1) this yields the following expressions:

$$K_0 = \sum_A c_A^2 \sum_i Z_i D_i^2 \int |\phi_i^A|^2 \frac{1}{r_i^3} dr_i dz_i \quad (7)$$

$$g = \frac{3}{8} \sum_A c_A^2 \sum_i Z_i D_i^2 \int |\phi_i^A|^2 \frac{1}{r_i^3} dr_i dz_i \quad (8)$$

where the denotations follow eqs 1 and 2, and in the off-diagonal expression for g the only contribution comes from the angular

dependence of the wave functions (the contribution of the unpaired electron in the doublet states) that realizes the 2-fold degeneracy.

The solution of eq 4 yields the following two branches of the APES near the linear configuration:

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

In this approximation, the detailed structure of the excited states contributing to the PJTE in the ground state and the back influence of the latter on the active excited states disappear, they are all represented in average by the parameter p in the APES of the ground state. There is no BCS in this approach; the solutions (eq 9) do not depend on the angle φ . The numerical value of p expressed by an infinite sum in eq 3 cannot be calculated separately, but it can be determined involving ab initio calculated energy profiles⁸ (see below).

For a separate Δ term, similarly, there is the mentioned above second order perturbation correction p_1 on the $W^{(1)}$ coupling terms, and the fourth order $W^{(4)}$ Renner–Teller splitting. The resulting 2×2 matrix of the vibronic coupling is

$$\begin{vmatrix} \frac{1}{2}(K_0 - p_1)\rho^2 + K'_0\rho^4 + g_4\rho^4 \cos(4\varphi) - \varepsilon & -g_4\rho^4 \sin(4\varphi) \\ -g_4\rho^4 \sin(4\varphi) & \frac{1}{2}(K_0 - p_1)\rho^2 + K'_0\rho^4 - g_4\rho^4 \cos(4\varphi) - \varepsilon \end{vmatrix} = 0 \quad (10)$$

where K_0 is the same matrix element (5) calculated with the Δ functions, while K'_0 and g_4 are the contributions of the $W^{(4)}$ perturbation to the curvature and the Renner–Teller splitting parameter, respectively,

$$K'_0 = \frac{3}{8} \sum_{i \neq j} Z_i Z_j D_i^4 \frac{1}{l_{ij}^5} - \frac{9}{32} \sum_A c_A^2 \sum_i Z_i D_i^4 \times \int |\phi_i^A|^2 \frac{1}{r_i^5} dr_i dz_i \quad (11)$$

$$g_4 = \frac{35}{128} \sum_A c_A^2 \sum_i Z_i D_i^4 \int |\phi_i^A|^2 \frac{1}{r_i^5} dr_i dz_i \quad (12)$$

The solution of eq 10 is straightforward:

$$\varepsilon_{1,2} = \frac{1}{2}(K_0 - p_1)\rho^2 + (K'_0 \pm g_4)\rho^4 \quad (13)$$

We see that, similar to the Π term, the solutions for a separate Δ term do not violate the cylindrical symmetry: the bending distortion does not depend on the angle φ . However, if the energy gap to some of the active excited states is not large enough, their contribution cannot be included in the sum (eq 3) as a second order perturbation correction; it should be taken into account as a PJT interaction of pseudodegenerate terms. If only a Σ ground term and Δ excited term (or a Δ ground state and Σ excited state) with the energy gap δ between them is taken into account, the secular equation of the vibronic coupling problem is as follows (the two constants of PJTE contributions of the higher excited states are here denoted as p_1 and p_2 , respectively):

$$\begin{vmatrix} \frac{1}{2}(K_1 - p_1)\rho^2 + K'_1\rho^4 + g_4\rho^4 \cos 4\varphi - \varepsilon & -g_4\rho^4 \sin 4\varphi & H\rho^2 \cos 2\varphi + H'\rho^4 \cos 2\varphi \\ -g_4\rho^4 \sin 4\varphi & \frac{1}{2}(K_1 - p_1)\rho^2 + K'_1\rho^4 - g_4\rho^4 \cos 4\varphi - \varepsilon & H\rho^2 \sin 2\varphi + H'\rho^4 \sin 2\varphi \\ H\rho^2 \cos 2\varphi + H'\rho^4 \cos 2\varphi & H\rho^2 \sin 2\varphi + H'\rho^4 \sin 2\varphi & \frac{1}{2}(K_3 - p_3)\rho^2 + K'_3\rho^4 + \delta - \varepsilon \end{vmatrix} = 0 \quad (14)$$

where in addition to the parameters for the separate terms, introduced above, the constants of interaction between them by the quadratic $W^{(2)}$ and fourth order $W^{(4)}$ vibronic coupling terms are denoted by H and H' , respectively:

$$H = \frac{3}{4\sqrt{2}} \sum_A c_A^2 \sum_i Z_i D_i^2 \int \phi_{r\sigma}^A \phi_{r\delta}^A \frac{1}{r_i^3} dr_i dz_i \quad (15)$$

$$H' = -\frac{5}{16\sqrt{2}} \sum_A c_A^2 \sum_i Z_i D_i^4 \int \phi_{r\sigma}^A \phi_{r\delta}^A \frac{1}{r_i^5} dr_i dz_i \quad (16)$$

Simplifying the denotations by introducing the a , b , c , and h constants, we get

$$\begin{vmatrix} a + b \cos 4\varphi - \varepsilon & -b \sin 4\varphi & h \cos 2\varphi \\ -b \sin 4\varphi & a - b \cos 4\varphi - \varepsilon & h \sin 2\varphi \\ h \cos 2\varphi & h \sin 2\varphi & c - \varepsilon \end{vmatrix} = 0 \quad (17)$$

with $a = \frac{1}{2}(K_1 - p_1)\rho^2 + K'_1\rho^4$, $b = g_4\rho^4$, $c = \frac{1}{2}(K_3 - p_3)\rho^2 + K'_3\rho^4 + \delta$, $h = H\rho^2 + H'\rho^4$, which is a cubic equation:

$$\varepsilon^3 - (2a + c)\varepsilon^2 - (-a^2 + b^2 - 2ac + h^2)\varepsilon - a^2c + b^2c + ah^2 - bh^2 \cos 8\varphi = 0 \quad (18)$$

We see that the roots of this equation are angular dependent, and the dependence on the angle φ is proportional to both the Σ - Δ interaction constant h and the Δ term splitting constant b , both of which are functions of ρ , while the relative value of this term as a whole should be taken in comparison with the other

terms that contain also the energy gap δ . This means that the APES of the system is periodical on φ , and hence, its symmetry is lower than the reference symmetry of the linear molecule, $C_{\infty v}$ or $D_{\infty h}$. Along the cross section $\varphi = 0$ we easily get the three roots of eq 17:

$$\begin{aligned} \varepsilon_1 &= \frac{1}{2}(K_1 - p_1)\rho^2 + (K'_1 - g_4)\rho^4 \\ \varepsilon_{2,3} &= \frac{1}{4}(K_1 - p_1 + K_3 - p_3)\rho^2 + \frac{1}{2}(K'_1 + K'_3 + g_4)\rho^4 \\ &\quad + \frac{\delta}{2} \pm \frac{1}{2} \left[\left(\frac{1}{2}(K_1 - p_1 - K_3 + p_3)\rho^2 + (K'_1 - K'_3 + g_4)\rho^4 - \delta \right)^2 \right. \\ &\quad \left. + 4(H\rho^2 + H'\rho^4)^2 \right]^{1/2} \end{aligned} \quad (19)$$

By fitting these equations to the corresponding cross sections of the APES calculated by ab initio methods (in combination with some additional ab initio calculations), we can estimate the parameters of the PJTE (section 4). Since

$$\begin{aligned} \varepsilon_1 + \varepsilon_2 + \varepsilon_3 &= 2a + c \\ \varepsilon_1\varepsilon_2 + \varepsilon_1\varepsilon_3 + \varepsilon_2\varepsilon_3 &= a^2 - b^2 + 2ac - h^2 \\ \varepsilon_1\varepsilon_2\varepsilon_3 &= a^2c - b^2c - ah^2 + bh^2 \cos 8\varphi \end{aligned} \quad (20)$$

the sum of the three energies does not depend on φ (as expected in perturbational splitting).

Similarly, for the PJT Δ - Π (or Π - Δ) interaction the secular equation is

$$\begin{vmatrix} \frac{1}{2}(K_1 - p_1)\rho^2 + K'_1\rho^4 + g_4\rho^4 \cos 4\varphi - \varepsilon & -g_4\rho^4 \sin 4\varphi & F\rho \cos \varphi & F\rho \sin \varphi \\ -g_4\rho^4 \sin 4\varphi & \frac{1}{2}(K_1 - p_1)\rho^2 + K'_1\rho^4 - g_4\rho^4 \cos 4\varphi - \varepsilon & F\rho \sin \varphi & F\rho \cos \varphi \\ F\rho \cos \varphi & F\rho \sin \varphi & \frac{1}{2}(K_2 - p_2)\rho^2 + \left(g_2 + \frac{1}{2}p_2\right)\rho^2 \cos 2\varphi + \delta - \varepsilon & \left(g_2 + \frac{1}{2}p_2\right)\rho^2 \sin 2\varphi \\ F\rho \sin \varphi & F\rho \cos \varphi & \left(g_2 + \frac{1}{2}p_2\right)\rho^2 \sin 2\varphi & \frac{1}{2}(K_2 - p_2)\rho^2 - \left(g_2 + \frac{1}{2}p_2\right)\rho^2 \cos 2\varphi + \delta - \varepsilon \end{vmatrix} = 0 \quad (21)$$

In this equation, in addition to the parameters inherent to the separate terms Π and Δ in eqs 4 and 10, we introduced the PJTE vibronic coupling constant between them F ,

$$F = \left\langle \pi_x \left| \left(\frac{\partial V_{en}}{\partial Q_y} \right)_0 \right| \Delta_{xy} \right\rangle \quad (22)$$

The explicit form of the fourth order algebraic eq 21 with respect to the four energy levels as a function of the bending coordinates ρ and φ describing the four branches of the APES is cumbersome, but its only term that depends on φ is proportional to $F^2 g_4 (g_2 + (1/2)p_2) \rho^8 \cos 8\varphi$. In other words, the solutions of eq 21, similar to eq 18, are angular dependent, their combinations acquiring periodical values. This result means that under the PJTE the cylindrical symmetry of the linear molecule $C_{\infty v}$ (or $D_{\infty h}$) is reduced to C_{nv} (or D_{nh}) with integer n , and this novel effect of spontaneously broken cylindrical symmetry (BCS) is induced exclusively by the PJTE involving a Δ term. Obviously, obtained for a Δ term interacting with a low-lying Π term the

effect remains also for a Π ground term interacting with a Δ excited one.

It follows from the angular dependent term $F^2 g_4 (g_2 + (1/2)p_2) \rho^8 \cos 8\varphi$, that the nonzero interaction between the two degenerate terms F and the splitting of each of them (g_4 and $g_2 + (1/2)p_2$, respectively) are the necessary conditions for the realization of this effect, while its numerical value is dependent on Δ and ρ . The resulting angular symmetry of the APES is due to the splitting of the Δ term by the fourth order vibronic coupling, which is proportional to $g_4 \rho^4 \sin 4\varphi$. We see also that the two kinds of PJT interactions, the second order perturbation represented by the p_1 and p_2 parameters and the direct vibronic coupling F in the PJT secular equation, yield qualitatively different results; only the latter one (direct coupling) leads to the cylindrical symmetry breaking. The presence of a strong PJTE in combination with high order vibronic-coupling perturbation of the Δ term is thus required for the novel SSB to take place. This result shows also that the term "second order JTE" sometimes used in the literature instead of PJTE may be misleading (see more in ref 3).

In the cross sections the APES in this case has four equivalent profiles with the following solutions of eq 21 at $\varphi = 0$:

$$\begin{aligned}\varepsilon_{1,2} &= \frac{1}{4}(K_1 + K_2 - p_1 - 2p_2 - 2g_2)\rho^2 + \frac{\delta}{2} + \frac{1}{2}K_1'\rho^4 - \frac{1}{2}g_4\rho^4 \\ &\pm \frac{1}{2}\left(\left[\frac{1}{2}(K_1 - K_2 - p_1 + 2g_2 + 2p_2)\rho^2 + K_1'\rho^4 - g_4\rho^4 - \delta\right]^2 + 4F^2\rho^2\right)^{1/2} \\ \varepsilon_{3,4} &= \frac{1}{4}(K_1 + K_2 - p_1 + 2g_2)\rho^2 + \frac{\delta}{2} + \frac{1}{2}K_1'\rho^4 + \frac{1}{2}g_4\rho^4 \\ &\pm \frac{1}{2}\left(\left[\frac{1}{2}(K_1 - K_2 - p_1 - 2g_2)\rho^2 + K_1'\rho^4 + g_4\rho^4 - \delta\right]^2 + 4F^2\rho^2\right)^{1/2}\end{aligned}\quad (23)$$

In the more complicated case of the PJT problem $(\Delta + \Sigma + \Pi) \otimes \omega$, the secular equation is

$$\begin{pmatrix} a + b'\cos 4\varphi - \varepsilon & -b'\sin 4\varphi & h\cos 2\varphi & f\cos \varphi & f\sin \varphi \\ -b'\sin 4\varphi & a - b'\cos 4\varphi - \varepsilon & h\sin 2\varphi & f\sin \varphi & f\cos \varphi \\ h\cos 2\varphi & h\sin 2\varphi & b - \varepsilon & g\cos \varphi & g\sin \varphi \\ f\cos \varphi & f\sin \varphi & g\cos \varphi & c + d\cos 2\varphi - \varepsilon & d\sin 2\varphi \\ f\sin \varphi & f\cos \varphi & g\sin \varphi & d\sin 2\varphi & c - d\cos 2\varphi - \varepsilon \end{pmatrix} = 0 \quad (24)$$

where $a = 1/2(K_1 - p_1)\rho^2 + K_1'\rho^4$, $b' = g_4\rho^4$, $b = 1/2(K_3 - p_3)\rho^2 + \delta_1$, $c = 1/2(K_2 - p_2)\rho^2 + \delta_2$, $d = (g_2 + 1/2p_2)\rho^2$, $f = F\rho$, $g = G\rho$, $h = H\rho^2$.

In this case, the angular dependence of the energies is more complicated, the fifth order equation with respect to ε contains terms proportional to $\cos 8\varphi$ in the coefficients to ε^2 , ε , and in the free term. At $\varphi = 0$, this equation decomposes into a second order and third order, respectively. This eases the estimation of the numerical values of the parameters by means of a procedure of fitting eq 24 to the corresponding cross sections of the ab initio calculated APES (section 4). Similar angular dependent solutions emerge from the PJTE mixing two Δ terms, mixing a Δ term with two Σ terms, etc., but there is no angular dependence in any single standing term or in $\Sigma - \Pi$ mixing problems.

Thus, in all PJTE problems for linear molecules involving a Δ term, considered above, we got a periodic angular dependence of the energies in the bent configuration, meaning a periodic angular dependent APES, a BCS. The period of this BCS depends on the number and kind of mixing electronic states involved in the PJTE, and on the constants of vibronic coupling between them. Therefore, it cannot be given in a general way. However, similar to all the other vibronic coupling problems, there are limitations on the possible symmetry of SSB:^{11,12} it should be a common subgroup of the symmetries of the reference charge distribution (electronic states in the linear configuration) and the vibronic perturbation. For electronic Δ terms the fourth order terms of the vibronic coupling are active, and the possible symmetries of BCS configurations are D_{4h} and D_{2h} for linear A-B-A molecules with $D_{\infty h}$ symmetry, and C_{4v} and C_{2v} for A-B-C or A-A-C molecules with $C_{\infty v}$ symmetry. The choice between the two possibilities is still dependent on the interacting terms and the vibronic coupling constants, but some prediction can be made based on general considerations (section 4): A-B-A molecules prefer BCS with D_{4h} configurations, while A-B-C or A-A-C molecules prefer C_{2v} broken symmetry, although in this case the C_{4v} symmetry is not excluded,

especially when the marginal A and C atoms are similar with respect to their PJT interaction with the central atom. In the single standing Δ term the BCS disappears because of the mutual compensation of the angular dependence in the two states of the degenerate term; the PJT interaction with other terms splits this term and fixes the angular dependence of the lower component (sections 3 and 4).

3. NOVEL EFFECT OF BCS IS CONFIRMED BY AB INITIO CALCULATIONS

The predicted cylindrical symmetry breaking induced by the PJTE creates a specific APES, which should be seen directly in ab initio calculations. We performed such calculations for a series of triatomic molecules with Σ and Π terms interacting with a Δ term, revealing their APES in the vicinity of the linear configurations. The multireference configuration interaction (MRCI) method¹³ is employed for the geometry optimization and frequency calculations of the $^3\Sigma_g^-$ or $^2\Pi_u$ ground state in the linear configurations of CH_2 , NH_2^+ , SiH_2 , PH_2^+ , CH_2^+ , NH_2 , SiH_2^+ , HCF , HCCl , HCB , HOF , and COS systems. Based on the $^3\Sigma_g^-$ or $^2\Pi_u$ ground state geometry, the vertical low-lying excited states are calculated by the MRCI+Q method including the Davidson correction.¹⁴ The amplitudes of the broken cylindrical symmetry are calculated by the complete active space self-consistent field (CASSCF)^{15,16} state-average CASSCF (SA-CASSCF),¹⁷ as well as MRCI,¹³ MRCI+Q,¹⁴ CCSD(T),¹⁸ and MP2¹⁹ methods, respectively. The mass-weighted normalized coordinates for the bending mode are used.

The equipotential lines in the (ρ, φ) space of the adiabatic potential energy profiles (APES) are obtained at the CASSCF, CCSD(T), and MP2 levels. For each molecule, the electrons (m) and orbitals (n) in the active space, denoted as CAS(m,n), are CAS(6,6) for CH_2 and NH_2^+ ; CAS(14,10) for SiH_2 and PH_2^+ ; CAS(5,6) for CH_2^+ ; CAS(7,6) for NH_2 ; CAS(13,10) for SiH_2^+ ; CAS(12,9) for HCF , HCCl , HCB ; CAS(14,9) for HOF ;

Table 1. Relative Energy Levels of the Ground and Excited States of Triatomics in the Linear Configuration Calculated by the MRCI+Q Method, the States Involved in SA-CASSCF Calculations, and the ρ Values with BCS Amplitudes in Parentheses for the Lowest State Calculated by the SA-CASSCF Method with Only One State of the Split Δ Term Included

molecule	relative energy levels of the ground and excited states (eV)	states involved in SA-CASSCF	ρ values (Å) and BCS amplitudes (cm^{-1})
CH ₂	$^3\Sigma_g^-[0.00]$, $^1\Delta_g[1.29]$, $^1\Sigma_g^+[2.34]$, $^3\Pi_u[6.46]$, $^1\Pi_u[7.11]$	$^1\Delta_g$, $^1\Pi_u$	0.03(0.19), 0.06(3.01), 0.09(15.33)
NH ₂ ⁺	$^3\Sigma_g^-[0.00]$, $^1\Delta_g[1.86]$, $^1\Sigma_g^+[3.31]$, $^3\Pi[10.86]$, $^1\Pi_u[11.67]$	$^1\Delta_g$, $^1\Pi_u$	0.03(0.91), 0.06(5.16), 0.09(7.74)
PH ₂ ⁺	$^3\Sigma_g^-[0.00]$, $^1\Delta_g[1.06]$, $^1\Sigma_g^+[2.10]$, $^3\Pi_u[2.96]$, $^1\Pi_u[3.73]$	$^1\Delta_g$, $^1\Pi_u$	0.03(1.48), 0.04(2.87), 0.06(7.93)
SiH ₂	$^3\Sigma_g^-[0.00]$, $^1\Delta_g[0.77]$, $^1\Sigma_g^+[1.47]$, $^3\Pi_u[1.64]$, $^1\Pi_u[2.47]$	$^1\Delta_g$, $^1\Pi_u$	0.03(0.00), 0.04(0.09), 0.06(10.51)
BH ₂	$^2\Pi_u[0.00]$, $^2\Sigma_g^+[4.65]$, $^2\Sigma_u^-[7.34]$, $^4\Sigma_u^+[7.53]$, $^2\Sigma_u^-[7.16]$, $^2\Delta_u[7.51]$, $^2\Sigma_g^+[8.26]$, $^2\Delta_g[9.76]$	$^2\Pi_u$, $^2\Sigma_g^+$, $^2\Delta_g$	0.03(1.29), 0.04(2.30), 0.06(5.17)
CH ₂ ⁺	$^2\Pi_u[0.00]$, $^4\Sigma_u^-[6.44]$, $^2\Sigma_u^-[7.53]$, $^2\Delta_u[8.11]$, $^2\Sigma_g^+[8.71]$, $^2\Sigma_u^+[9.31]$, $^2\Sigma_g^+[12.78]$, $^2\Delta_g[13.01]$	$^2\Pi_u$, $^2\Sigma_g^+$, $^2\Delta_g$	0.03(1.07), 0.04(2.15), 0.06(4.82)
NH ₂	$^2\Pi_u[0.00]$, $^4\Sigma_u^-[4.62]$, $^2\Sigma_g^-[5.58]$, $^2\Delta_g[6.68]$	$^2\Pi_u$, $^2\Sigma_g^+$, $^2\Delta_g$	0.03(0.38), 0.04(0.64), 0.06(1.33)
SiH ₂ ⁺	$^2\Pi_u[0.00]$, $^2\Sigma_g^+[1.83]$, $^4\Sigma_u^-[5.76]$, $^2\Sigma_u^-[6.38]$, $^2\Delta_u[6.77]$, $^2\Sigma_g^+[7.21]$, $^2\Delta_g[7.39]$	$^2\Pi_u$, $^2\Sigma_g^+$, $^2\Delta_g$	0.02(0.48), 0.03(1.51), 0.04(3.77)
HCF	$^3\Sigma^-[0.00]$, $^1\Delta[1.31]$, $^1\Sigma^+[2.13]$, $^3\Pi[3.74]$, $^1\Pi[4.89]$	$^1\Delta$, $^1\Sigma^+$, $^1\Pi$	0.03(0.07), 0.04(4.4), 0.06(15.82)
HCCl	$^3\Sigma^-[0.00]$, $^1\Delta[1.13]$, $^1\Sigma^+[1.93]$, $^3\Pi[3.95]$, $^1\Pi[4.92]$	$^1\Delta$, $^1\Sigma^+$, $^1\Pi$	0.03(0.61), 0.04(1.10), 0.06(1.82)
HCB _r	$^3\Sigma^-[0.00]$, $^1\Delta[1.16]$, $^1\Sigma^+[1.92]$, $^3\Pi[2.48]$, $^1\Pi[4.33]$	$^1\Delta$, $^1\Sigma^+$, $^1\Pi$	0.03(0.60), 0.04(1.42), 0.06(3.07)
HOF	$^1\Sigma^+[0.00]$, $^3\Pi[1.47]$, $^1\Pi[2.64]$, $^3\Sigma^-[5.14]$, $^1\Delta[5.93]$	$^1\Sigma^+$, $^1\Pi$, $^1\Delta$	0.03(0.07), 0.04(0.17), 0.06(0.94)
COS	$^1\Sigma^+[0.00]$, $^1\Sigma^-[2.67]$, $^1\Delta[2.69]$	$^1\Sigma^+$, $^1\Sigma^-$, $^1\Delta$	0.03(0.02), 0.04(2.52), 0.06(4.83)

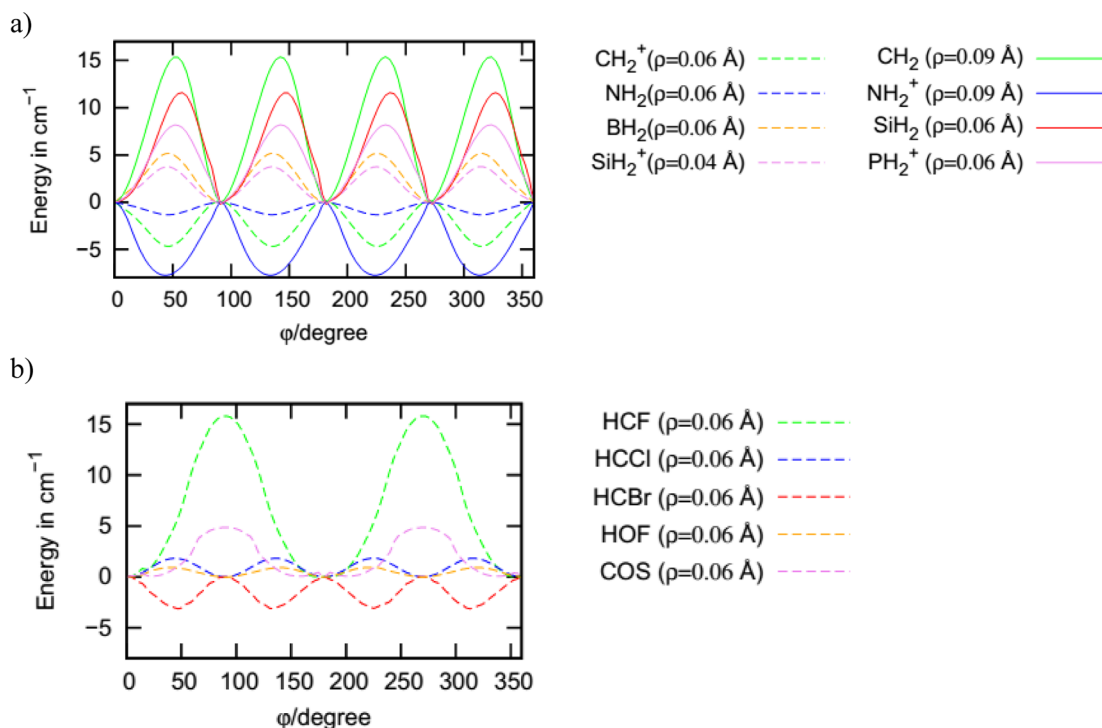


Figure 1. Potential energy profiles along the angle φ at a constant ρ value calculated by the CASSCF or SA-CASSCF method showing the amplitude of BCS in a series of linear triatomic molecules with D_{ohh} symmetry (a) and C_{ooV} symmetry (b) in the linear configuration.

CAS(16,12) for COS. The Dunning's correlation consistent triple- ζ basis set cc-pVTZ^{20–22} is used in the calculations. As an example, the CH₂ with additional cc-pVQZ²⁰ and aug-cc-pVTZ²⁰ basis sets are taken to show the influence of different basis sets for the BCS effect. All the calculations are performed by the MOLPRO 2010 quantum-chemistry program packages.²³ It is important that the calculations of the φ dependence of the energy starts at a bent configuration $\rho > 0$ where the degenerate term Δ is split; as seen from the PJTE equations above, the angular dependence of the APES branches are proportional to this splitting.

The molecules studied in this paper are divided into two classes, CH₂, NH₂⁺, SiH₂, PH₂⁺, CH₂⁺, NH₂, SiH₂⁺, with D_{ohh}

symmetry in the linear configuration, and HCF, HCCl, HCB_r, HOF, and COS with C_{ooV} symmetry. Table 1 shows the energy levels of low-lying electronic states of these molecules at the linear configurations. According to the general Jahn–Teller effect theory, the combined PJTE of ($^1\Delta_g + ^1\Pi_u$) \otimes w and RTE of $^1\Delta_g$ state result in the formations of 1A_1 stable bent structures of CH₂, NH₂⁺, SiH₂, and PH₂⁺. Based on our previous finding,^{7–9} however, the RTE just splits the degenerate term and softens its lower component, so the main contribution to the bending instability is the PJTE. For the triplet 3B_1 bent structures of CH₂, NH₂⁺, SiH₂, and PH₂⁺, the wave functions with two spin-parallel electrons are not angular dependent, so there is no BCS effect in these states. The PJTE of the ($^2\Pi_u + ^2\Sigma_g^+ + ^2\Delta_g$) \otimes w kind leads to

the bent 2A_1 states of CH_2^+ , NH_2 , SiH_2^+ , and the PJTE of the $(^1\Pi+^1\Sigma+^1\Delta)\otimes w$ type produces the bending instability of HCF, HCCl, HCBBr, HOF, and COS.

Figure 1 illustrates the angular dependence of the BCS calculated along circular cross sections of the APES at constant ρ values of 0.04–0.09 Å, which correspond to several degrees of bending. More BCS amplitudes obtained for different ρ values are shown in Table 1. The contour (equipotential) lines in the (ρ, φ) space of the APES of CH_2 and CH_2^+ are shown in Figure 2. The table and pictures show a clear periodic dependence of the energies with a period of $\pi/2$ or π . As

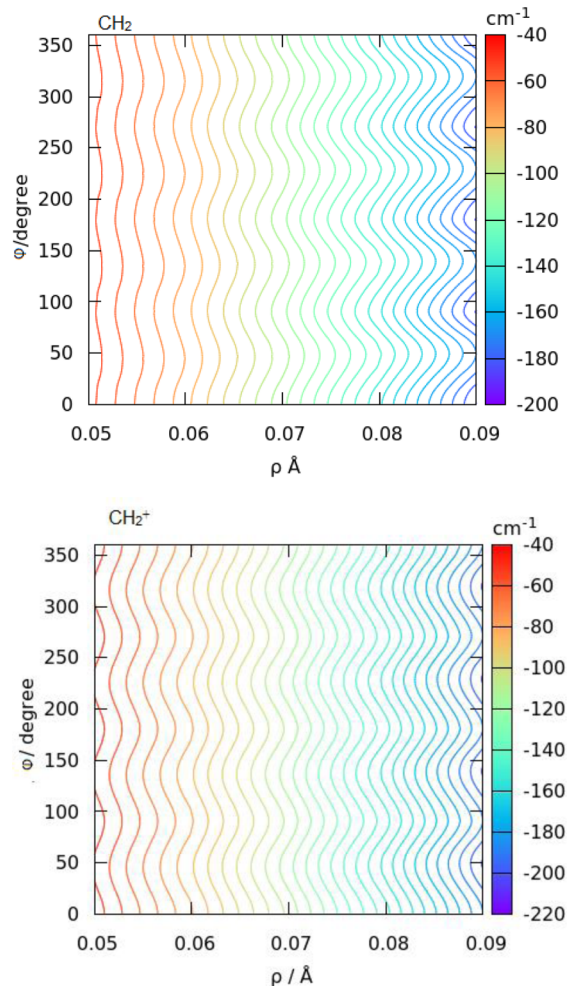


Figure 2. Equipotential lines in the (ρ, φ) space of the APES of CH_2 (a) and CH_2^+ (b) at the CASSCF level of calculation.

predicted by the general theory (section 3) the APES of linear molecules of the A-B-A type and some of A-B-C type have 4-fold symmetry with four equivalent lower waleys at $\varphi = 0, \pi/2, \pi$, and $3\pi/2$, and equivalent barriers between them, while some of the A-B-C molecules have 2-fold symmetry (see Section 4). The amplitude of BCS at the chosen ρ values varies up to 16 cm^{-1} . Even though these values are small, the BCS effect as such is confirmed by the ab initio calculations convincingly.

Table 2. BCS Amplitude and the Change of the CI Coefficients in the Wavefunctions of Two Electronic Configurations with the Orbital Occupations of $\sigma_{\text{C-H}}^2 \sigma_{\text{C-H}}^2 \text{C}_{2\text{px}}^0 \text{C}_{2\text{py}}^0 \sigma_{\text{C-H}}^0 \sigma_{\text{C-H}}^0$ (Denoted 222000) and $\sigma_{\text{C-H}}^2 \sigma_{\text{C-H}}^2 \text{C}_{2\text{px}}^0 \text{C}_{2\text{py}}^2 \sigma_{\text{C-H}}^0 \sigma_{\text{C-H}}^0$ (Denoted 220200) along the Angle φ for CH_2 at $\rho = 0.09 \text{ Å}$

angle φ (deg)	BCS amplitude (cm^{-1})	electronic configuration and CI coefficient
0	0.00	222000, 0.7338082 220200, -0.6677459
10	1.44	222000, 0.7322889 220200, -0.6694120
20	4.85	222000, 0.7283445 220200, -0.6737022
30	9.03	222000, 0.7224462 220200, -0.6800239
45	14.42	222000, 0.7097437 220200, -0.6932680
60	14.30	222000, 0.7102322 220200, -0.6927679
70	9.83	222000, 0.7210965 220200, -0.6814549
80	3.71	222000, 0.7297293 220200, -0.6722018
90	0.00	222000, 0.7337948 220200, -0.6677608

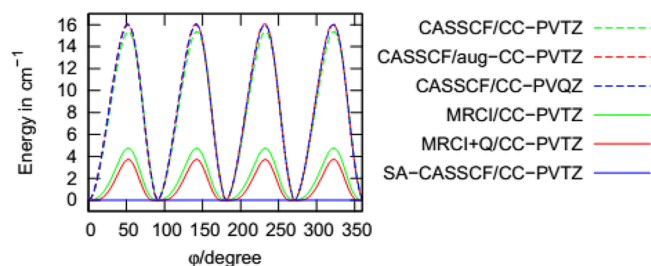


Figure 4. Amplitude of BCS in CH_2 at a constant ρ value of 0.09 Å calculated with different methods and basis sets.

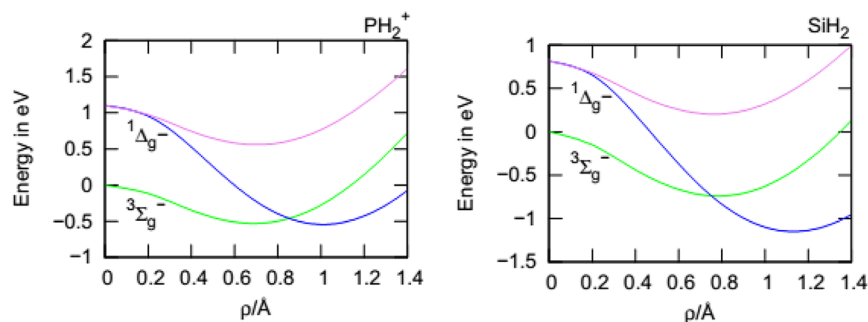


Figure 3. Energy profile of two lowest states of PH_2^+ and SiH_2 along the bending coordinate ρ at $\varphi = 0$ calculated by the MRCI+Q method.

Table 3. Comparison of Angular Dependent Adiabatic Potential Energies of Bent Triatomics ($\rho = 0.06 \text{ \AA}$) Obtained by Including Only One State of the Split Δ Term (in a CASSCF Calculation) Denoted as $\Delta(1)$, and Both Components (in a SA-CASSCF calculation) Denoted as $\Delta(2)$ ^a

φ	CH_2		NH_2^+		PH_2^+		SiH_2	
	$\Delta(1)$	$\Delta(2)$	$\Delta(1)$	$\Delta(2)$	$\Delta(1)$	$\Delta(2)$	$\Delta(1)$	$\Delta(2)$
0	-38.894973	-38.892959	-55.186196	-55.183872	-341.483242	-341.478730	-289.965487	-289.959637
22.5	-38.894967	-38.892959	-55.186210	-55.183872	-341.483229	-341.478730	-289.965474	-289.959637
45	-38.894960	-38.892959	-55.186220	-55.183872	-341.483207	-341.478730	-289.965440	-289.959637
67.5	-38.894966	-38.892959	-55.186211	-55.183872	-341.483216	-341.478730	-289.965446	-289.959637
90	-38.894973	-38.892959	-55.186196	-55.183872	-341.483242	-341.478730	-289.965487	-289.959637
112.5	-38.894967	-38.892959	-55.186210	-55.183872	-341.483229	-341.478730	-289.965474	-289.959637
135	-38.894960	-38.892959	-55.186220	-55.183872	-341.483207	-341.478730	-289.965440	-289.959637
157.5	-38.894966	-38.892959	-55.186211	-55.183872	-341.483216	-341.478730	-289.965446	-289.959637
180	-38.894973	-38.892959	-55.186196	-55.183872	-341.483242	-341.478730	-289.965487	-289.959637
202.5	-38.894967	-38.892959	-55.186210	-55.183872	-341.483229	-341.478730	-289.965474	-289.959637
225	-38.894960	-38.892959	-55.186220	-55.183872	-341.483207	-341.478730	-289.965440	-289.959637
247.5	-38.894966	-38.892959	-55.186211	-55.183872	-341.483216	-341.478730	-289.965446	-289.959637
270	-38.894973	-38.892959	-55.186196	-55.183872	-341.483242	-341.478730	-289.965487	-289.959637
292.5	-38.894967	-38.892959	-55.186210	-55.183872	-341.483229	-341.478730	-289.965474	-289.959637
315	-38.894960	-38.892959	-55.186220	-55.183872	-341.483207	-341.478730	-289.965440	-289.959637
337.5	-38.894966	-38.892959	-55.186211	-55.183872	-341.483216	-341.478730	-289.965446	-289.959637
360	-38.894973	-38.892959	-55.186196	-55.183872	-341.483242	-341.478730	-289.965487	-289.959637

^a $\Delta(1)$ is lower in energy and angular dependent, whereas $\Delta(2)$ is higher in energy and has no angular dependence.

In several molecules of Table 1 the singlet $^1\Delta$ state, for which the calculations were carried out, is not the ground state in the linear approximation, but it is a very low lying excited state, which becomes the ground state upon bending. Figure 3 shows the calculated ground $^3\Sigma_g$ and first excited $^1\Delta_g$ states as a function of the bending angle (in ρ coordinates) for two molecules. We see that at approximately $\rho \cong 0.8 \text{ \AA}$ or less the two levels cross over and the $^1\Delta_g$ term becomes the ground one.

To follow the change in charge distribution and overlap of the wave functions of the PJT interacting terms along the path of BCS we extracted some configuration interaction coefficients in the singlet ground state of CH_2 , taken as an example. Table 2 shows the changes of the electronic wave functions along the angle φ at a constant ρ value of 0.09 \AA . At $\varphi = 0$, the electronic distribution has larger occupation on the $\text{C}_{2\text{px}}$ atomic orbitals than $\text{C}_{2\text{py}}$. With increasing angle φ , the CI coefficients of each electronic configuration change. It means that along the angle φ at $\rho > 0$ the electronic population transfers from $\text{C}_{2\text{px}}$ to $\text{C}_{2\text{py}}$ and vice versa. Hence, the orbital wave functions are angular dependent, and the changes follow the PJTE overlap.

To check the influence of the method of calculation and basis sets on the amplitude of BCS, we calculated the APES cross section of CH_2 at a constant ρ value of 0.09 \AA shown in Figure 4. We see that the dependence of the BCS effect on the basis set is not significant, but the amplitude of BCS depends on the method, decreasing from CASSCF to MRCI to MRCI+Q and from CCSD(T) to MP2 (see below). In the SA-CASSCF calculations, the BCS effect disappears when both states of the split Δ term are included in the state average of this method. To illustrate this situation, we present in Table 3 some more details of the CASSCF calculations for the split Δ states in the bent configuration of several systems. It shows that when only one state of the split Δ term is included in the SA-CASSCF calculations, we get both BCS and lower energy, whereas with both states included the BCS disappears and the energy is higher. The lower energy with the BCS effect and higher energy when

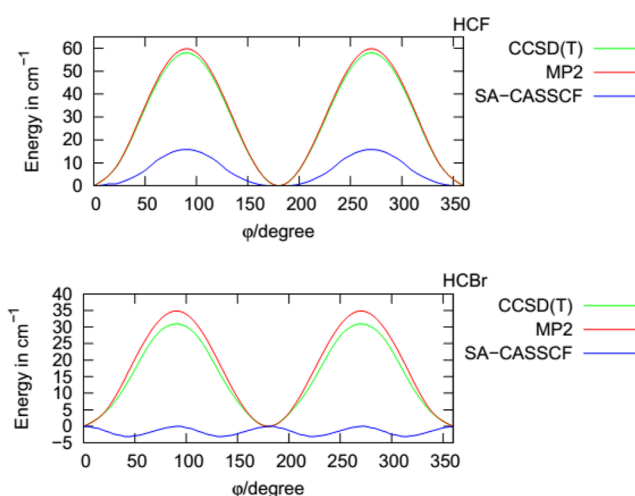


Figure 5. Potential energy profiles along the angle φ at $\rho = 0.06 \text{ \AA}$ showing the amplitude of BCS in HCF and HBr calculated by CCSD(T) and MP2 methods, as well as by SA-CASSCF for comparison.

both Δ states are included in the SA-CASSCF calculations indicates that in the latter case the two states of the Δ term compensate each other in the angular dependence diminishing the angular dependent part of the PJT additional covalency (note that in the split Δ state, for which the BCS is observed, the angular dependent wave function of the lower component is fixed by the PJT overlap with the state of another term, see also section 4).

Figure 5 shows the BCS in two linear triatomic molecules with $\text{C}_{\infty\text{v}}$ symmetry, HCF and HBr, calculated by CCSD(T) and MP2 methods, as well as by SA-CASSCF for comparison. In both cases, the amplitude of BCS is smaller in the SA-CASSCF approximation, while for HBr the latter predicts a small $\text{C}_{4\text{v}}$ effect instead of the $\text{C}_{2\text{v}}$ obtained by other method. We relate this discrepancy to the quenching symmetries in the state average method, which in averaging states of different symmetry may

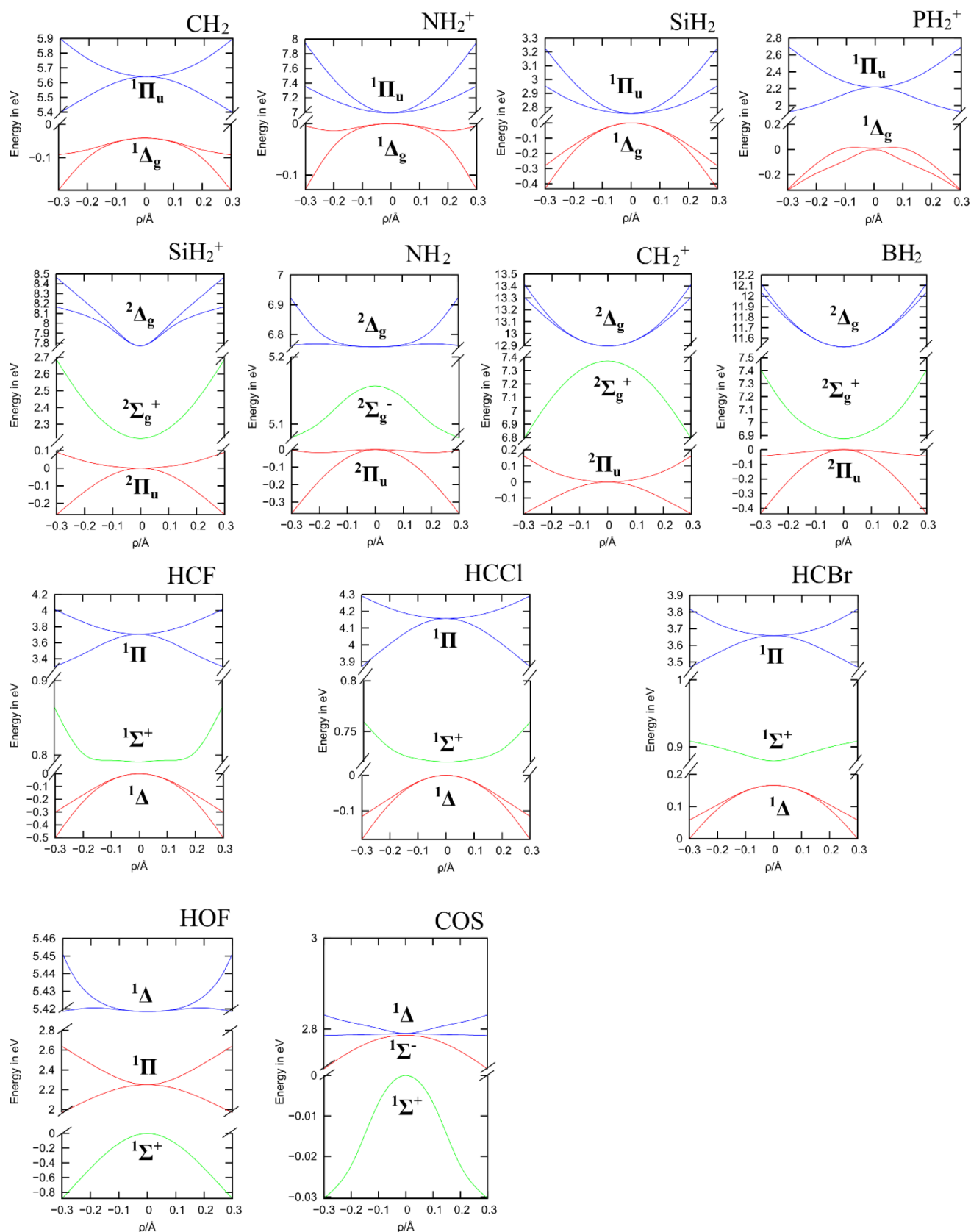


Figure 6. Cross sections of the APES of a series of linear molecules along the bending coordinate ρ at $\varphi = 0$ (energy profiles) calculated by the SA-CASSCF method.

complicate the BCS effect (as with the two components of the Δ term discussed above). These results show also that one has to be

careful when employing SA-CASSCF calculations with many roots in fine-tuned symmetry problems.

Table 4. Vibronic Coupling Constants and Energy Gaps δ_1 and δ_2 between PJT Coupled Σ - Δ , Δ - Π , Δ - Σ - Π , and Δ - Σ - Σ Terms Obtained by Independent Ab Initio Calculations (δ_1 , δ_2 , K_1 , K_2 , K_3 , and g_2) and Fitting the Analytical Solutions to Ab Initio Obtained Energy Profiles (for p_1 , p_2 , p_3 , H , H' , F , G , K'_1 , K'_3 , and g_4)^a

molecule	Δ term params.				Π term (first Σ term for COS)			Σ term (second Σ term for COS)			interaction constants					
	K_1	K'_1	g_4	p_1	K_2	g_2	p_2	K_3	p_3	K'_3	H	H'	F	G	δ_1	δ_2
CH ₂	17.35	3.24	1.94	28.32	41.04	23.24	54.94						16.36		5.82	
NH ₂ ⁺	17.79	4.37	1.46	34.12	9.34	1.65	16.76						12.44		9.81	
PH ₂ ⁺	7.09	6.42	2.73	28.43	10.77	2.51	12.35						10.62		2.67	
SiH ₂	12.29	4.32	2.62	26.52	17.71	5.42	24.94						8.47		1.70	
BH ₂	7.15	2.02	1.50	10.42	6.15	12.15	23.20	8.16	13.15		8.42		9.12	5.23	5.11	9.76
CH ₂ ⁺	13.22	5.02	4.01	28.25	48.45	26.06	64.21	16.21	22.12		12.32		17.16	12.26	4.30	13.01
NH ₂	14.34	6.01	3.02	26.51	7.97	7.89	12.05	13.23	25.33		14.15		15.41	11.42	1.10	6.68
SiH ₂ ⁺	11.93	4.01	2.01	23.45	12.68	13.52	23.25	14.42	26.12		15.12		14.32	13.13	5.56	7.39
HCF	17.74	8.42	3.45	26.42				14.15	27.35	1.06	17.35	8.23			1.31	
HCCl	22.47	9.26	4.56	28.63				21.21	42.21	2.13	19.52	9.16			1.13	
HCBBr	26.73	9.46	4.23	29.56				24.54	49.31	2.61	20.64	9.42			1.16	
HOBr	23.45	8.52	3.56	31.20	7.52	13.13	26.21	25.61	52.26		10.24		9.53	6.41	2.64	5.93
COS	24.56	5.26	3.64	32.51	26.32		35.21	23.56	28.62		7.52	5.21			2.67	2.69

^a δ_1 , δ_2 in eV; F and G in eV/Å; K_1 , K_2 , K_3 , p_1 , p_2 , p_3 , g_2 , and H , in eV/Å²; K'_1 , K'_3 , H' , and g_4 in eV/Å⁴.

4. DISCUSSION OF THE RESULTS: TWO-STATE PARADIGM IN APPLICATION TO LINEAR MOLECULES

As stated above and elsewhere,^{1,3} the PJTE is the only source of structural symmetry breaking in molecular systems and solids in nondegenerate states, and it essentially contributes to the instability of degenerate states, for which the JTE is also operative. With regard to linear molecules, there is no JTE in their degenerate states, nor is there symmetry breaking induced by the RTE in these states.⁷ It remains that the only source of SSB in linear molecules is the PJTE. The latter requires the presence of at least two interacting electronic states, leading thus to the *two-state paradigm* in formation, deformation, and transformation of molecular systems and solids.³ The results obtained in this paper for linear molecules illustrate well the two-state paradigm, and complement it with an additional specification: in the novel SSB revealed in this paper, the BCS in linear molecules, at least two electronic terms are involved, one of them being necessarily a Δ term.

Following the previous papers^{8,9} and using the computer program reported there, we calculated ab initio the parameters K_1 , K_2 , K_3 , and g_2 of eqs 19, 23, and 24, and estimated the values of p_1 , p_2 , p_3 , F , G , H , H' , K'_1 , K'_3 , and g_4 by fitting the expressions of the energies at $\varphi = 0$ to the calculated energy profiles of the molecules under consideration shown in Figure 6, as collected in Table 4.

In addition to the exclusive role of the PJTE in the origin of bending of linear molecules in Π states, proved earlier,⁷⁻⁹ we got here similar conclusions for Δ states. For molecules with Δ ground states in Figure 6, we see that in vicinity of the point of linear symmetry $\rho = 0$ the curvature of the APES is negative for both branches of the degenerate term, and only at larger ρ values, it begins to increase in one of the branches due to the RTE splitting in the fourth order of ρ . The negative curvature of both branches of the APES with respect to bending cannot be explained without involving the PJTE. Indeed, as seen from the solutions (eq 13) for a Δ term, the curvature of the APES at $\rho = 0$ equals $1/2(K_0 - p_1)$, and since $K_0 > 0$,^{1,3} only the negative PJTE contribution p_1 may provide for the negative curvature.

It is important to give also a more visual explanation of the origin of the symmetry breakings in linear molecules including

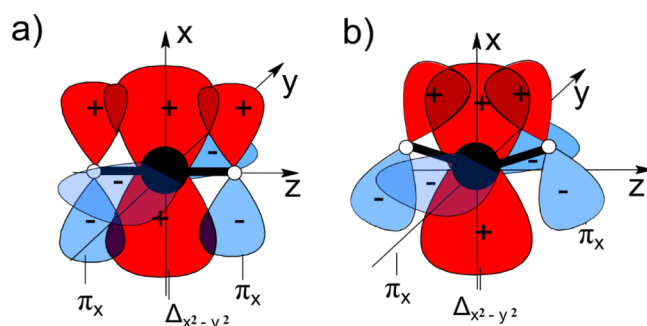


Figure 7. Illustration to the Δ - Π PJT interaction in a linear triatomic molecule producing added covalency by bending and its 4-fold symmetry. (a) In the linear configuration, the Δ_{xy} and π_x orbitals are orthogonal (their total overlap is zero), and they do not participate in the bonding. (b) By bending, their overlap becomes nonzero resulting in additional covalence bonding that facilitates the bending. The angular dependence of the wave functions of the 2-fold degenerate terms in the linear configuration (π_x , π_y and Δ_{xy} , $\Delta_{x^2-y^2}$, respectively) becomes definitive after their splitting in the bent configuration, making their overlap periodical with a fourth-fold (for same marginal atoms) or 2-fold symmetry.

the one revealed in this paper for the first time. As stated repeatedly (see, e.g., ref 3), the energy gain beyond the PJTE resulting in SSB is due to the atomic rearrangements that produce better covalence bonding between the atoms. The PJTE is thus an instrument of search for better covalency by means of atomic displacements from the high-symmetry configuration (symmetry breaking). From this point of view, we should explain how the effect of BCS produces better covalence bonding. In general, this happens because of the PJT splitting of the degenerate terms making their overlap angular dependent.

Roughly speaking, the two Δ functions are similar to two d orbitals, d_{xy} and $d_{x^2-y^2}$, of the central atom oriented perpendicular to the molecular axis, while in a A-B-A system the Π ones can be viewed as appropriate combinations of the two π orbitals, π_x and π_y , of the marginal atoms (Figure 7). In the linear configuration these orbitals are orthogonal (they have different parity). Upon bending their orthogonality is destroyed, and the two sets of functions overlap, resulting in additional covalency in the corresponding interatomic bonding. Since the terms are split, the

better (minimum-energy) overlap producing extra covalency becomes angular dependent resulting in BCS. The effect occurs only after some significant bending when, due to the splitting of the Δ term by the fourth order vibronic coupling (proportional to $\rho^4 \sin 4\varphi$), the two Δ wave function with orthogonal angular dependence do not compensate each other in their overlap with the Π functions. This explains also why the BCS is not seen when both states of the split Δ term are included in the SA-CASSCF calculations (Table 3).

As mentioned above, the 4-fold symmetry of the APES produced by the SSB in linear molecules with active Δ terms is conceptually similar to the other SSB in polyatomic systems. Indeed $C_{4v}(D_{4h})$ and $C_{2v}(D_{2h})$ are common subgroups of $C_{\infty v}(D_{\infty h})$ and the symmetry of the fourth order terms of the vibronic coupling. The choice between the two symmetries of BCS depends on the parameters of the specific system. As seen from Figure 7, in the case of a linear A-B-A molecule the best overlap between the two states involving one component of the Δ term has a 4-fold symmetry making the D_{4h} BCS preferable. If the marginal atoms are different (as in A-B-C or A-A-C molecules), the overlap with only one of them becomes advantageous, and the symmetry of the better overlap (added covalency) is reduced to C_{2v} . In this case, however, there is a possibility that the marginal atoms are approximately similar in their PJT interaction with the central atom, and then, the BCS may become of C_{4v} symmetry.

As for the possible experimental observation of the effect of BCS, it is subjected to the general rules of observation of SSB:²⁴ multim minima APES demonstrate specific properties in their interaction with external perturbations. In view of possible misunderstanding that we encountered even from experts in this field, arguing that an isolated bent molecule cannot change its energy by rotation, we emphasize that *APES by themselves are not observable, they are just operators of potential energy*, which together with the operator of kinetic energy may produce the observable energy as a solution of the Schrödinger equation. In the BCS under consideration, as in any other multim minimum system, the total energy is definitely conserved: in the minima the lower potential energy is compensated by higher kinetic energy. In linear molecules with BCS, one may expect that, if the bending is not very large, the complicated APES plays a primary role in vibration–rotation interactions resulting in specific effects in the *rovibronic spectrum*. Among other interactions with external perturbations, if the molecule with BCS is placed in a field with cylindrical symmetry its interaction with the external field follows the symmetry of its APES, and its rotation becomes non-cylindrical, hindered by four or two energy barriers. Another example, if the molecule is weakly coordinated by its marginal atom that does not violate the linearity, its reactivity may become angular dependent.

5. CONCLUSIONS

We report the effect of spontaneously broken cylindrical symmetry (BCS) in linear molecules with any terms interacting with Δ terms via the pseudo Jahn–Teller effect (PJTE), revealed in this paper for the first time. The BCS effect follows directly from the PJTE problems $(\Sigma+\Delta)\otimes w$, $(\Pi+\Delta)\otimes w$, $(\Delta+\Sigma+\Pi)\otimes w$, $(\Delta+\Sigma+\Sigma)\otimes w$, $(\Delta+\Delta)\otimes w$ (where w includes nonzero first, second, and fourth order terms of vibronic coupling), for which the adiabatic potential energy surfaces (APES) in the space of the bending coordinates emerges angular dependent. A detailed analysis shows that the BCS is due to the angular dependence of the wave functions of the Δ term split in the bent configuration

and fixed by the PJT interaction. Independent ab initio calculations of the APES of a series of triatomic molecules around the linear configuration fully confirm the BCS effect: in A-B-A molecules with Δ terms the symmetry of the APES is D_{4h} , while in A-B-C or A-A-C molecules the cylindrical symmetry is reduced to either C_{2v} or C_{4v} . The vibronic coupling constants for the molecules under consideration are estimated using a combined approach of ab initio calculations with a procedure of fitting of the PJTE equations to the ab initio calculated energy profiles. We confirm also that the bending of the molecules in a Δ state is exclusively of PJTE (not RTE) origin, similar to the previously proved PJTE origin of the molecular bending in a Π state. The revealed effect of BCS induced by the PJT interactions confirms again the predicting power of the PJTE.

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Notes

The authors declare no competing financial interest.

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