Spin-orbit vibronic coupling in $^3\text{II}$ states of linear triatomic molecules

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The Renner-Teller vibronic-coupling problem of a $^3\text{II}$ electronic state of a linear molecule is analyzed with the inclusion of the spin-orbit coupling of the $^3\text{II}$ electronic state, employing the microscopic (Breit-Pauli) spin-orbit coupling operator for the two unpaired electrons. The $6 \times 6$ Hamiltonian matrix in a diabatic spin-electronic basis is obtained by an expansion of the molecular Hamiltonian in powers of the bending amplitude. The symmetry properties of the Hamiltonian with respect to the time-reversal operator and the relativistic vibronic angular momentum operator are analyzed. It is shown that there exists a linear vibronic-coupling term of spin-orbit origin, which has not been considered so far in the Renner-Teller theory of $^3\text{II}$ electronic states. While two of the six adiabatic electronic wave functions do not exhibit a geometric phase, the other four carry nontrivial topological phases which depend on the radius of the integration contour. The spectroscopic effects of the linear spin-orbit vibronic-coupling mechanism have been analyzed by numerical calculations of the vibronic spectrum for selected model examples. © 2007 American Institute of Physics.

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I. INTRODUCTION

Vibronic coupling in degenerate electronic states of linear molecules has been discussed in the pioneering work of Renner\textsuperscript{1} and later been termed Renner-Teller (RT) effect. After the first experimental detection of the RT effect in the NH$_2$ radical,\textsuperscript{2,3} Pople and Longuet-Higgins revisited the original work of Renner with a model Hamiltonian approach.\textsuperscript{4} Since then, significant progress has been made in the understanding of the RT effect both in theory as well as in experiment, see Refs. 5–12 and references therein.

Most of the above cited works ignore the spin-orbit (SO) coupling. Pople was the first to consider the SO coupling in $^2\text{II}$ electronic states of linear triatomic molecules.\textsuperscript{13} He provided a perturbative analysis of the vibronic energy levels of a $^2\text{II}$ electronic state with the inclusion of both RT and SO interactions, resulting in a clear picture of the perturbations caused by SO coupling in RT spectra. Pople assumed the simplified phenomenological form of the SO operator,

$$H_{SO} = A L_x S_z,$$

based on the argument that the $x$ and $y$ components of the electronic orbital angular momentum operator are effectively quenched for linear molecules.\textsuperscript{13} Since then, most of the investigations on the RT effect with SO coupling have been based on this approximation.\textsuperscript{5,9,14–18}

While there has been extensive research on the RT effect with SO coupling in the degenerate electronic states of linear triatomic molecules of doublet spin multiplicity (i.e., with one unpaired electron), studies on $\Pi$ or $\Delta$ electronic states with higher spin multiplicities are rather limited. This is partly due to the fact that high spin multiplicities are rather infrequent in nature (with the exception of transition-metal and rare-earth compounds) and partly due to the difficulties associated with the theoretical analysis of many-electron systems. Hougen performed the first systematic perturbative analysis of the vibronic and rotational energy levels of linear triatomic molecules in a $^3\text{II}$ electronic state, taking both RT and SO interactions into account.\textsuperscript{19} This analysis, which can be considered as an extension of Pople’s work on the RT-SO problem of $^2\text{II}$ states,\textsuperscript{13} was based on the analogous phenomenological form of the SO operator. An essential conclusion of Hougen’s work was that the vibronic energy levels of a $^3\text{II}$ electronic state can be divided into two sets: the energies of one set are like those of a $^1\text{II}$ electronic state, whereas the energies of the other set are like those of a $^2\text{II}$ electronic state.\textsuperscript{19} The same phenomenological form of SO coupling has been employed in subsequent studies of the spectra of specific systems. Perić et al. have investigated the RT effect in the $^3\text{II}$ electronic state of NCN with high-level quantum chemical methods, employing Hougen’s SO operator.\textsuperscript{20} In recent work by Carter et al., a variational calculation of spin-vibronic energy levels has been performed for the $^3\text{II}$ state of CCO.\textsuperscript{21} Other examples of vibronic and SO coupling in $^3\text{II}$ states are SiCO, CSiO, CCO,$^{22,23}$ CNN,$^{24}$ and InOH.$^{25}$ The purpose of the present work is a systematic study of the RT effect in $^3\text{II}$ electronic states of linear triatomic molecules by employing the microscopic expression for the SO operator (the Breit-Pauli operator$^{26–29}$). We determine the vi-
brane Hamiltonian by expanding the matrix elements of the electrostatic potential and the SO operator in a diabatic electronic basis in powers of the bending coordinate, taking into account the symmetry selection rules. This results in a 6 × 6 vibronic matrix which, unlike the Hamiltonian in Ref. 19, cannot be block-diagonalized. In particular, this Hamiltonian exhibits a linear (that is, of first order in the bending mode) vibronic-coupling term of SO origin which is absent when the phenomenological form of SO coupling is assumed. We derive the vibronic Hamiltonian in the adiabatic representation and discuss the geometric phases of the adiabatic electronic wave functions. The spectroscopic effects of RT and SO couplings in 3II states are investigated by variational calculations of the vibronic energy levels for selected models. It will be shown that the effects of linear relativistic vibronic coupling are particularly interesting when the bending vibrational frequency and the SO splitting of the 3II state are in resonance.

II. VIBRONIC HAMILTONIAN IN THE DIABATIC REPRESENTATION

Let us consider two electrons moving in the field of three linearly arranged nuclei of electric charges Q1, Q2, and Q3. Let us focus on the situation where the components of a 3II state are coupled by the degenerate bending vibrational mode. The Hamiltonian of this two-electron system, in atomic units, can be written as

\[ H = H_{el} + T_N = H_{el} + H_{SO} + T_N, \]

where

\[ H_{el} = \sum_{k=1}^{2} \left( -\frac{1}{2} \nabla_r^2 + 3 \sum_{n=1}^{3} \frac{Q_n}{r_{kn}} \right) + \frac{1}{r_{12}}, \]

\[ H_{SO} = \sum_{k=1}^{2} (H_{SO}^{(k)} + H_{SO}^{(12)}), \]

\[ T_N = -\frac{a}{2} \left[ \frac{\partial}{\partial \rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{1}{\rho} \frac{\partial^2}{\partial \phi^2} \right]. \]

Here \( H_{el} \) is the electrostatic part of the electronic Hamiltonian that includes the kinetic energy of the two electrons, the electron-nuclear interaction term, as well as the electron-electron repulsion term. \( H_{SO} \) represents the SO interaction and consists of two parts, the one-electron SO operator \( H_{SO}^{(k)} \), \( k=1 \) and 2, and the two-electron contribution \( H_{SO}^{(12)} \). These are given by

\[ H_{SO}^{(k)} = -\frac{2.023i}{4e^2} S_k \sum_{n=1}^{3} \frac{Q_n}{r_{kn}} (r_{kn} \times \nabla_k), \quad k = 1, 2, \]

\[ H_{SO}^{(12)} = \frac{2.023i}{4e^2 r_{12}^3} \left[ S_{12} (r_{12} \times (\nabla_1 - 2 \nabla_2)) + S_{21} (r_{21} \times (\nabla_2 - 2 \nabla_1)) \right]. \]

Denoting by \( r_1 \) and \( r_2 \) the radius vectors of electrons 1 and 2, respectively, and by \( R_n \) (\( n = 1, 2, 3 \)) the nuclear radius vectors, the vectors in Eqs. (6) and (7) are defined as

\[ r_{kn} = r_k - R_n, \quad k = 1, 2, \]

\[ r_{12} = r_1 - r_2 = -r_{21}, \]

\[ S_k = i\hat{\sigma}^{(k)}_z + j\hat{\sigma}^{(k)}_y + k\hat{\sigma}^{(k)}_x, \quad k = 1, 2. \]

Here \( \hat{\sigma}^{(k)}_z, \hat{\sigma}^{(k)}_y, \) and \( \hat{\sigma}^{(k)}_x \) are the Pauli spin matrices acting on the spin eigenstates of the first (\( k=1 \)) or second (\( k=2 \)) electron. \( c \) is the speed of light, \( r_{kn} = |r_{kn}| \), and \( r_{12} = |r_{12}| \). \( T_N \) is the nuclear kinetic-energy operator in polar coordinates (\( \rho, \phi, \chi \)), which are defined as

\[ r_{kn} = |r_{kn}| \]

\[ r_{12} = |r_{12}| \]

\[ T_N = \frac{a}{2} \left[ \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right]. \]

The eigenvalues (\( \mu \)) of \( \hat{J}_z \) are integers (\( \mu = 0, \pm 1, \pm 2, \ldots \)).

The full Hamiltonian \( H \) of Eq. (2) also possesses the time-reversal symmetry and commutes with the total (electronic+nuclear) angular momentum operator

\[ \hat{J}_z = \hat{J}_z - i \frac{\partial}{\partial \chi}, \]

The eigenvalues (\( \mu \)) of \( \hat{J}_z \) are integers (\( \mu = 0, \pm 1, \pm 2, \ldots \)).

Let us consider electronic diabatic basis functions associated with the two components of the degenerate 3II electronic state with electronic orbital angular momentum quantum numbers \( \Lambda = \pm 1 \) and spin angular momentum quantum numbers \( S_z = 0, \pm 1 \). These basis functions refer to the linear geometry of the triatomic system in the absence of the inter-electronic interactions and SO effects. We introduce two molecular orbitals, one of \( \sigma \) type \([Q(r, z)]\) and the other of \( \pi \) type \([P(r, z)\exp(\pm i\phi)]\), where \( r, \phi, \) and \( z \) are cylindrical elec-
tronic coordinates. The molecular orbitals $Q(r,z)$ and $P(r,z)$ are solutions of a one-electron Schrödinger equation. Two-electron basis functions $(\psi_l^j)_l$, where $J_z = \Lambda + S_z$), which are orthonormal, antisymmetric with respect to electron exchange and simultaneous eigenfunctions of $S^2$, $S_z$, and $L_z$ are defined as follows:

$$\psi_{+2} = \frac{1}{\sqrt{2}}[Q(2)P(1)\exp(i\varphi_1) - Q(1)P(2)\exp(i\varphi_2)]\alpha_{1}\alpha_2,$$

$$\psi_{+1} = \frac{1}{2}[Q(2)P(1)\exp(i\varphi_1) - Q(1)P(2)\exp(i\varphi_2)] \times (\alpha_1\beta_2 + \beta_1\alpha_2),$$

$$\psi_{0} = \frac{1}{\sqrt{2}}[Q(2)P(1)\exp(-i\varphi_1) - Q(1)P(2)\exp(-i\varphi_2)] \times \alpha_1\alpha_2,$$

$$\psi_{-1} = \frac{1}{2}[Q(2)P(1)\exp(-i\varphi_1) - Q(1)P(2)\exp(-i\varphi_2)] \times (\alpha_1\beta_2 + \beta_1\alpha_2),$$

$$\psi_{-2} = \frac{1}{\sqrt{2}}[Q(2)P(1)\exp(-i\varphi_1) - Q(1)P(2)\exp(-i\varphi_2)] \times \beta_1\beta_2,$$

where $P(k) = P(r_k, z_k)$ and $Q(k) = Q(r_k, z_k), k=1,2$. The two-electron basis functions are eigenfunctions of $J_z$,

$$J_z|\psi_{l}^j\rangle = J_z|\psi_{l}^j\rangle.$$  

(16)

The time-reversal operator $\hat{T}$ has the following effect on the diabatic electronic basis functions:

$$\hat{T} \left( \begin{array}{c} \psi_{+2}^j \\ \psi_{+1}^j \\ \psi_{0}^j \\ \psi_{-1}^j \\ \psi_{-2}^j \end{array} \right) = \left( \begin{array}{ccccc} -1 & 0 & 0 & 0 & 0 \\ 0 & -1 & +1 & 0 & 0 \\ 0 & 0 & -1 & +1 & 0 \\ 0 & 0 & 0 & -1 & +1 \\ 0 & 0 & 0 & 0 & -1 \end{array} \right) \cdot \psi_{l}^j.$$  

(17)

Using the six diabatic spin-electronic basis functions [Eq. (16)], the electronic Hamiltonian can be written as a 6 \times 6 vibronic matrix. The derivation of the 6 \times 6 spin-vibronic Hamiltonian is similar to the procedure outlined in Refs. 33–35. The determination of the matrix elements of $H_{el}$ can be simplified by using relations (17) and (18), and the Hermitian property of $H_{el}$. A Taylor series expansion of the matrix elements of the electronic Hamiltonian in powers of the bending distortion is performed, retaining the lowest-order nonvanishing term for each of the matrix elements. Further simplification of the vibronic Hamiltonian is achieved by the direct calculation of the individual coefficients, performing the integration over the angular variables $\varphi_1$ and $\varphi_2$ as well as over the discrete spin variables. The derivation of the 6 \times 6 spin-vibronic Hamiltonian is given in Appendix A. The result is

$$H = T_{N} + \begin{pmatrix} E_{II,1} & c_{\varphi}e^{2ix} & d_{\varphi}e^{ix} & 0 & 0 & 0 \\ c_{\varphi}e^{2ix} & E_{II,0} & 0 & -d_{\varphi}e^{ix} & 0 & 0 \\ d_{\varphi}e^{ix} & 0 & E_{II,1} & c_{\varphi}e^{2ix} & d_{\varphi}e^{ix} & 0 \\ 0 & -d_{\varphi}e^{-ix} & c_{\varphi}e^{2ix} & E_{II,1} & 0 & -d_{\varphi}e^{ix} \\ 0 & 0 & d_{\varphi}e^{-ix} & 0 & E_{II,0} & +c_{\varphi}e^{2ix} \\ 0 & 0 & 0 & -d_{\varphi}e^{-ix} & c_{\varphi}e^{2ix} & E_{II,2} \end{pmatrix}.$$  

(19)

$1$ is the 6 \times 6 unit matrix. $E_{II,0}$, $E_{II,1}$, and $E_{II,2}$ represent the energies of the three SO components ($^3\Pi_0$, $^3\Pi_1$, $^3\Pi_2$) of the $^3\Pi$ state at the linear geometry. From the time-reversal symmetry, it is obvious that $E_{II,2} = -E_{II,0}$ and $E_{II,1} = (E_{II,0} + E_{II,2})/2$. In terms of the SO splitting $\Delta$ of the $^3\Pi$ state, we can write $E_{II,2} = \Delta$, $E_{II,1} = 0$, and $E_{II,0} = -\Delta$. The relative ordering of the states depends on the sign of the SO splitting. The coupling term $c_\varphi$ is the well-known quadratic RT parameter of nonrelativistic (purely electrostatic) origin. All other coupling terms in Eq. (19) are of SO origin. While the nonrelativistic RT effect results in $^3\Pi_2 - ^3\Pi_0$ and $^3\Pi_1 - ^3\Pi_0$ coupling, the linear SO coupling term $d_{\varphi}e^{ix}$ is responsible for the coupling between $^3\Pi_2 - ^3\Pi_1$ and $^3\Pi_1 - ^3\Pi_0$. The linear SO coupling term is absent when the simplified phenomenological SO operator is employed.

The vibronic Hamiltonian (19) cannot be transformed to block-diagonal form by a constant unitary transformation. When $d=0$, then Hamiltonian (19) decouples into three 2
× 2 blocks which represent the pure orbital RT effect. In this case, the $^3\Pi$ RT-SO coupling problem (with SO splitting $\Delta$) decomposes into a $^3\Pi$ RT-SO coupling problem (with SO splitting $2\Delta$) and a $^1\Pi$ RT-SO coupling problem (with vanishing SO splitting).

### III. Vibronic Hamiltonian in the Adiabatic Representation

For fixed nuclei (i.e., $T_N=0$), the vibronic Hamiltonian (19) can be diagonalized analytically, yielding the following expressions for the eigenvalues:

$$U_{1,2}(\rho) = \frac{\omega}{2} \rho^2 \pm c \rho^2,$$

$$U_{3,4}(\rho) = \frac{\omega}{2} \rho^2 - W = \frac{\omega}{2} \rho^2 - \sqrt{\Delta^2 + c^2 \rho^4 + 2d^2 \rho^2},$$

$$U_{5,6}(\rho) = \frac{\omega}{2} \rho^2 + W = \frac{\omega}{2} \rho^2 + \sqrt{\Delta^2 + c^2 \rho^4 + 2d^2 \rho^2}. \quad (20)$$

In the nonrelativistic limit (i.e., $\Delta=0$ and $d=0$), two distinct adiabatic potential-energy terms are obtained which are degenerate at the linear geometry, i.e., $\rho=0$. This degeneracy is lifted in second order by the nonrelativistic RT coupling. Both potential-energy terms are threefold degenerate, representing the spin degeneracy. In the limit of vanishing RT coupling and nonzero SO coupling, the adiabatic terms are represented by three parabolas corresponding to the three SO components of the $^3\Pi$ state, see Fig. 1(a). Upon introduction of RT coupling ($c/\omega \neq 0$), the degenerate $^3\Pi_1$ state splits into two components (similar to the RT effect in a $^3\Pi$ state without SO splitting), whereas the $^3\Pi_2$ and $^3\Pi_0$ states exhibit a change of their curvatures (similar to the RT effect in a $^3\Pi$ state with SO splitting), see Fig. 1(b). At strongly bent geometries, the split potential-energy curves of the $^3\Pi_1$ state come close to the $^3\Pi_2$ and $^3\Pi_0$ potential-energy curves, see Fig. 1(b). This reflects the fact that the RT splitting of the degenerate $^3\Pi_1$ state is stronger than that of the SO-splitted $^3\Pi_2$ and $^3\Pi_0$ states. The near degeneracy of the $^3\Pi_1$-$^3\Pi_2$ and the $^3\Pi_1$-$^3\Pi_0$ potential-energy curves for large bending angles is lifted by the linear coupling term of SO origin, see Fig. 1(c).

The orthonormal eigenvectors $V_1, \ldots, 6$ of the fixed-nuclei Hamiltonian are given in Appendix B. The $V_i$, $i=1, \ldots, 6$, form the $6 \times 6$ eigenvector matrix $\mathcal{W}$ which is unitary. It transforms the potential matrix of Hamiltonian (19) to diagonal form. The same unitary matrix transforms the time-reversal operator $\hat{T}$ to block-diagonal form, i.e.,

$$\hat{T}_{ad} = \mathcal{W}^* \hat{T} \mathcal{W} = \begin{pmatrix} -1 & 0 \\ 0 & +1 \end{pmatrix} \begin{pmatrix} -\cos \theta_\perp & \sin \theta_\perp e^{2iX} & \sin \theta_\perp e^{2iX} & \cos \theta_\perp e^{2iX} \\ \sin \theta_\perp e^{2iX} & \cos \theta_\perp e^{2iX} & -\cos \theta_\perp & \sin \theta_\perp e^{2iX} \end{pmatrix} c.c. \quad (21)$$

The two $\rho$-dependent angles $\theta_\perp$ are defined by

$$\cos \theta_\perp = \frac{cd^2 \rho^4}{\Delta (\Delta^2 + 2d^2 \rho^2)} \div W(\Delta^2 + d^2 \rho^2) \quad (22)$$

and

$$-1 < \cos \theta_\perp \leq 0 \leq \cos \theta_\perp < 1 \quad (23)$$

The $2 \times 2$ matrices in the adiabatic representation of the time-reversal operator, given by Eq. (21), are unitary, whereas $\hat{T}_{ad}$ itself is antiunitary, and $\hat{T}_{ad}^2 = +1$. The operators $H_{cl}$ and $\hat{T}$ cannot be simultaneously diagonalized because of the presence of the $c.c.$ in Eq. (21).

The vibronic Hamiltonian (19) is characterized by an
additional symmetry, which is connected to the existence of two pairs of doubly degenerate eigenvalues. This symmetry property is restricted to the six-dimensional subspace of the eigenvectors.

The existence of additional symmetry operators giving rise to doubly degenerate eigenvalues can be seen as follows. It is evident that the $6 \times 6$ block-diagonal matrix

$$S_{6d} = \begin{pmatrix} 1 & 1 & & & & \\ 1 & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ \hat{C}_+ & \hat{C}_- \\ \hat{C}_+ & \hat{C}_- \\ \hat{C}_+ & \hat{C}_- \\ \hat{C}_+ & \hat{C}_- \\ \hat{C}_+ & \hat{C}_- \\ \hat{C}_+ & \hat{C}_- \end{pmatrix}$$

(24)

with

$$\hat{C}_+ = C_+^1 \hat{C}_x + C_+^2 \hat{C}_y + C_+^3 \hat{C}_z,$$

(25)

commutes with the (diagonal) Hamiltonian $\mathcal{H}/\hbar \omega \mathcal{V}$ and contains six real parameters $C_+^j, j=1, 2, 3$, which can be arbitrarily chosen. This proves that the vibronic Hamiltonian (19) possesses six matrix symmetry operators (in addition to the time-reversal symmetry operator $\hat{T}$). Each of these operators can be obtained from the general form of the matrix symmetry operator

$$S = \mathcal{W} S_{6d} \mathcal{V}',$$

(26)

if one of the constants $C_+^j$ is chosen to be 1 and the others are zero.

**IV. TOPOLOGICAL PHASES OF THE ADIABATIC ELECTRONIC STATES**

The adiabatic electronic states are obtained as

$$\psi^\alpha_{el} = \mathcal{V}_{\alpha}^T \psi_j(\rho, \chi), \quad j = 1, \ldots, 6,$$

(27)

where

$$\mathcal{V}_{\alpha}^T = (\psi_{\alpha 2}, \psi_{\alpha 1}, \psi_{\alpha 0}, \psi_{\alpha -1}, \psi_{\alpha -2}).$$

The well-known expression for the Berry phase$^{37-39}$ of the adiabatic electronic wave functions in $(\rho, \chi)$ space can be written in the simplified form

$$\gamma_j = i \oint_C \mathcal{V}_{\alpha}^T \psi_j(\rho, \chi) [\mathbf{V}_\rho \cdot \mathbf{V}_\chi \psi_j(\rho, \chi)] d^2 \mathbf{\rho},$$

(28)

where

$$d^2 \mathbf{\rho} = (d\rho, d\rho d\chi),$$

(29)

$$\mathbf{V}_\rho = \left( \frac{\partial}{\partial \rho}, -\frac{1}{\rho} \frac{\partial}{\partial \chi} \right).$$

Since the result of the integration does not depend on the form of the integration contour $C$, we can perform the integration along a circle with radius $R$ around the origin. Thus Eq. (28) reduces to

$$\gamma_j = i \int_0^{2\pi} \left[ \mathcal{V}_{\alpha}^T \psi_j(\rho, \chi) \frac{\partial}{\partial \chi} \psi_j(\rho, \chi) \right] d\chi.$$

(30)

For the eigenvectors $\psi_j(\rho, \chi) (j=1, \ldots, 6)$, Eq. (30) gives the following results:

$$\gamma_1 = \gamma_2 = 0,$$

(31)

$$\gamma_{3,5} = -2\pi \frac{2c^2 \Delta^2 R^6 + c^2 d^2 R^6 - d^2 R^6 (W \pm \Delta)^2}{2W (W \Delta^2 + d^2 R^2) \pm \Delta (\Delta^2 + 2 d^2 R^2)}$$

(32)

$$\gamma_{4,6} = \frac{4\pi}{N(R)^2} \left[ \left( \frac{c \Delta}{d^2} \mp c R^2 S(R) \frac{d}{dR} \right)^2 \right. \left. + \frac{1}{2} \left( \frac{\Delta + W}{d} \pm c R^2 \right)^2 \right. \left. + \frac{3c^2 R^2}{2d^2} (1 - WS(R)) \mp \Delta S(R) \right]$$

(33)

The functions $D(R)\psi, S(R)\mp N(R)\psi$ are defined in Appendix B. The phases $\gamma_1, \gamma_4, \gamma_5$, and $\gamma_6$ exhibit a complicated dependence on the integration radius $R$. It can be seen from Eqs. (32) and (33) that the geometric phases $\gamma_1 \cdots \gamma_6$ vanish both in the limit $R \to 0$ as well as in the limit $R \to \infty$. Such $R$-dependent geometric phases have previously been found for the $E \times E$ Jahn-Teller problem with SO coupling.$^{40-42}$ The result of integration does not depend on the form of the closed contour for a given area.$^{37}$ This implies that the whole area covered by the integration contour contributes to the geometric phase.

**V. CALCULATION OF VIBRATIONAL SPECTRA**

We consider a linear triatomic molecule which is initially in the vibrationless nondegenerate ground state $|\Psi_0\rangle$ and is excited by some operator $\mathcal{T}$ to an isolated $^3\Sigma$ electronic state. According to Fermi’s golden rule, the excitation spectrum is given by

$$P(E) = 2\pi \sum_n \left| \langle \Psi_0 | \mathcal{T} | \Psi_n \rangle \right|^2 \delta(E - E_0 - E_n),$$

(34)

where $E_0$ denotes the energy of the reference state $|\Psi_0\rangle$ and $E_n$ is the energy of the final vibronic state $|\Psi_n\rangle$. The final vibronic states $|\Psi_n\rangle$ are determined by

$$H|\Psi_n\rangle = E_n|\Psi_n\rangle,$$

(35)

with the Hamiltonian $H$ of Eq. (2). We solve Eq. (35) by the expansion of $\Psi_n$ in a complete basis which is constructed as the product of electronic $|\psi_{A,S}\rangle$ and vibrational $|n,l\rangle$ basis functions. The $|\psi_{A,S}\rangle, A = \pm 1, S = 0, \pm 1$, are the six diabatic electronic basis states which correspond to representation (19) of $H_{el}$. The $|n,l\rangle, n=0,1,2, \ldots, l=-n, -n+2, \ldots, n-2, n$, are the eigenfunctions of the two-dimensional isotropic harmonic oscillator.$^{43}$

Owing to the existence of the total angular momentum operator $\hat{J}_z$, which commutes with the Hamiltonian $H$, the Hamiltonian matrix decouples into submatrices corresponding to different eigenvalues (μ) of $\hat{J}_z$. The real symmetric Hamiltonian matrix is constructed and diagonalized by standard routines for a given value of μ. The vibrational basis is increased until convergence of the eigenvalues of interest has been achieved. These eigenvalues represent the vibronic en-
energy levels $E_\mu$ with vibronic angular momentum quantum number $\mu$. The square of the first component of the eigenvector represents the spectral intensity within the Condon approximation, assuming that the optical excitation takes place from the vibrational ground state $|0\rangle$.

VI. GENERIC ASPECTS OF LINEAR SO VIBRONIC COUPLING IN A $^3\Sigma$ STATE

In this section, we analyze the influence of the linear coupling term $d\rho e^{\pm i\chi}$ on the vibronic spectrum of a $^3\Pi$ electronic state. The effect of this coupling term is expected to become significant when the potentially interacting unperturbed levels are nearly degenerate. Since $d\rho e^{\pm i\chi}$ couples, in first order, levels with different spin quantum numbers which differ by one quantum of the bending mode, we expect pronounced effects when $\omega = \Delta$. We shall refer to the case $\omega = \Delta$ as the "resonant case" in the following.

For small values of the SO splitting and the RT coupling, the perturbative treatment of vibronic energy levels by Hougton provides excellent insight to the splitting pattern of the vibronic levels of the $^3\Pi$ state. This analysis fails, however, when the SO coupling is either comparable to or larger than the bending frequency $\omega$ and/or the RT coupling $c$. We shall consider here, as an example, the case $\Delta = \omega$ and $c < \omega$.

The vibronic energy levels of such a system are shown in Fig. 2 for the parameter values $d=0$, $\Delta/\omega = 0.8$, and $c/\omega = 0.2$. Upon introduction of the SO splitting $\Delta$, each of the unperturbed bending levels (shown in the left column) splits into three SO components, see the middle column of Fig. 2. The relative ordering of the spin multiplets depends on the sign of the SO splitting. Here we assume $\Delta$ to be positive. The energy levels obtained with the inclusion of RT coupling are shown in the last column of Fig. 2. The vibronic energy levels are assigned by the conventional spectroscopic terms.

The vibrational level $(v_1, n_2, v_3)$, where $v_1, n_2$, and $v_3$ are quantum numbers of the stretching modes and $n_2$ is the occupation number of the degenerate bending mode of the linear triatomic molecule, is denoted as $(n_2)$, since the stretching modes are absent in the present work. The degeneracy of the vibronic levels of $(0)^1\Pi_{0\alpha}$ has been discussed in Refs. 19 and 44. It should be mentioned that the assignment of individual vibronic levels becomes ambiguous for higher energies, especially in the case when several vibronic energy levels of the same $\mu$ value are close-by.

The example of Fig. 2 shows that the energy levels $(0)^3\Pi_1$ and $(1)^3\Delta_1$ are close in energy, as a consequence of $\Delta = \omega$. The same is true for the $(0)^3\Pi_2$ and $(1)^3\Delta_2$ levels. These quasidegenerate energy levels interact with each other when the linear vibronic-coupling term is taken into account.

Figure 3 displays the energy levels of this system as a function of the dimensionless parameter $d/\omega$. The energy levels with different values of $\mu$ are shown by different line types, see caption of Fig. 3. The figure reveals several significant level repulsions with increasing $d/\omega$. For example, the pair $(0)^3\Pi_1$ and $(1)^3\Delta_1$. On the other hand, the level $(1)^3\Sigma_1$ remains nearly unperturbed. The levels $(0)^3\Pi_2$, $(1)^3\Delta_2$, $(2)^3\Phi_2$, and $(2)^3\Pi_2$ exhibit a complicated interaction pattern. An avoided crossing between $(2)^3\Phi_2$ and $(2)^3\Pi_2$ can be seen at $d/\omega = 0.08$. An important observation is that the degenerate $(2)^3\Pi_{0\alpha}$ splits as a function of $d/\omega$. While one of the components remains nearly unaffected, the other appears to interact with the high-lying $(1)^3\Sigma_1^+$ state, resulting in a lowering of its energy with increasing $d/\omega$. Unlike the $(2)^3\Pi_{0\alpha}$ level, the $(0)^3\Pi_{0\alpha}$ level exhibits a minor splitting even for large values of $d/\omega$. Figure 3, in general, illustrates that even a small value of $d/\omega$ can lead to significant changes of the RT spectrum of a $^3\Pi$ state.

The mixing of the zero-order energy levels also has a significant effect on the intensity of the spectral lines. We
shall consider here the case of electronic excitation from the vibronic Hamiltonian significantly. The time-reversal symmetry reduces the number of independent matrix elements of the vibronic Hamiltonian significantly.

The vibronic Hamiltonian has been transformed to the adiabatic electronic representation. The adiabatic potential-energy functions and the transformation matrix \( V \) have been obtained in analytic form. The effect of the SO splitting \( \Delta \), the RT coupling parameter \( c \), and the linear SO coupling parameter \( d \) on the adiabatic potential-energy functions has been discussed. The topological phases of the six adiabatic electronic wave functions have been analyzed. While two of them exhibit no geometric phase, the other four exhibit complicated geometric phases which depend on the radius of integration in a nonmonotonic fashion.

The spectroscopic effects of the linear SO coupling term have been analyzed by variational calculations of the vibronic energy levels. It has been shown that the linear SO vibronic-coupling mechanism can lead to significant perturbations of the vibronic spectra when the SO splitting and the bending frequency are of similar magnitude.

It is well known that the lowest order (in the bending amplitude) for nonrelativistic RT coupling in a degenerate electronic state of electronic angular momentum \( \Lambda \) is \( 2 \Delta \). The existence of the linear SO vibronic-coupling term \( d \pi \) on the other hand, is independent of the angular momentum of the degenerate electronic state, since it couples the diabatic electronic states with the same orbital angular momentum quantum number and spin angular momentum number differing by one unit (see Appendix A). This implies that for \( \Delta \) or \( \Phi \) electronic states, where the nonrelativistic RT coupling term is of fourth or sixth order in the bending amplitude, respectively, the vibronic-coupling term of SO origin will be comparatively more important. In such cases, the SO vibronic coupling may dominate over the nonrelativistic RT coupling even in molecules with light atoms.

VII. CONCLUSIONS

The effect of SO coupling on the RT effect in a \( ^3 \Pi \) electronic state of a linear molecule has been analyzed by employing the microscopic expression for the two-electron Breit-Pauli SO operator. The microscopic RT-SO vibronic-coupling problem involves six coupled electronic states with electronic angular momentum projections \( \pm 2, \pm 1, \) and \( 0_a \). The \( 6 \times 6 \) vibronic Hamiltonian has been derived in the diabatic representation, employing a Taylor expansion up to second order in the bending displacement. It has been found that in addition to the well-known nonrelativistic quadratic

\[
(0)^3 \Pi_{0e} \quad (0)^3 \Pi_1 \quad (0)^3 \Pi_2 \quad (2)^3 \Pi_2 \quad (2)^3 \Pi_1 \quad (2)^3 \Pi_3
\]

\[
\text{Energy (units of } \omega \text{)}
\]

FIG. 4. Redistribution of the spectral intensity by the linear SO vibronic-coupling parameter \( d \) for \( \Delta/\omega=0.8 \) and (a) \( c=0, \ d=0 \), (b) \( c/\omega=0.2, \ d=0 \), and (c) \( c/\omega=0.2, \ d/\omega=0.15 \). Solid, dashed, and dotted lines represent energy levels with \( \mu=0, \ 1, \) and \( 2 \), respectively.

\[
(0)^3 \Pi_{0e} \quad (0)^3 \Pi_1 \quad (0)^3 \Pi_2 \quad (2)^3 \Pi_2 \quad (2)^3 \Pi_1 \quad (2)^3 \Pi_3
\]

\[
\text{Energy (units of } \omega \text{)}
\]

APPENDIX A: DERIVATION OF THE \( ^3 \Pi \) VIBRONIC HAMILTONIAN

The electronic Hamiltonian in the diabatic electronic basis [Eq. (16)] can be written as follows:

\[
H = \sum_i \epsilon_i | \Psi_i \rangle \langle \Psi_i | + \sum_{i<j} V_{ij} | \Psi_i \rangle \langle \Psi_j | + \sum_i \sum_{\alpha} \sum_{\beta} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \sum_{\tau} C_{\alpha \beta \mu \nu \sigma \tau} \langle \Psi_i | \alpha \beta \mu \nu \sigma \tau | \Psi_j \rangle | \Psi_i \rangle \langle \Psi_j |
\]

\[
H = \sum_i \epsilon_i | \Psi_i \rangle \langle \Psi_i | + \sum_{i<j} V_{ij} | \Psi_i \rangle \langle \Psi_j | + \sum_i \sum_{\alpha} \sum_{\beta} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \sum_{\tau} C_{\alpha \beta \mu \nu \sigma \tau} \langle \Psi_i | \alpha \beta \mu \nu \sigma \tau | \Psi_j \rangle | \Psi_i \rangle \langle \Psi_j |
\]

\[
H = \sum_i \epsilon_i | \Psi_i \rangle \langle \Psi_i | + \sum_{i<j} V_{ij} | \Psi_i \rangle \langle \Psi_j | + \sum_i \sum_{\alpha} \sum_{\beta} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \sum_{\tau} C_{\alpha \beta \mu \nu \sigma \tau} \langle \Psi_i | \alpha \beta \mu \nu \sigma \tau | \Psi_j \rangle | \Psi_i \rangle \langle \Psi_j |
\]
Hermitian conjugate of the upper triangular block. The lower triangular block of the vibronic Hamiltonian is the order in the degenerate bending coordinate Taylor series around the reference geometry up to second order, neglecting the quadratic SO coupling term, we have well as a spin-orbit part. By using the following definitions:

\[
\begin{align*}
\psi'_{\pm} & = \psi'_{\pm1} \quad \psi'_{0} \quad \psi'_{-1} \quad \psi'_{-2} \\

H'_{\pm12} & = \psi'_{\pm12} (0) + \frac{\partial H'_{\pm12}}{\partial Q_{\pm}} Q_{\pm} + \frac{1}{2} \frac{\partial^2 H'_{\pm12}}{\partial Q_{\pm}^2} Q_{\pm}^2 \\
& + \left( \frac{\partial^2 H'_{\pm12}}{\partial Q_{\pm} \partial Q_{-}} \right)_0 Q_{-} Q_{+} + \cdots .
\end{align*}
\]

(A1)

The lower triangular block of the vibronic Hamiltonian is the Hermitian conjugate of the upper triangular block.

1. Diagonal elements

Let us expand the diagonal matrix element \( H'_{\pm12} \) in a Taylor series around the reference geometry up to second order in the degenerate bending coordinate \( Q_{\pm} \),

\[
H'_{\pm12} = \psi'_{\pm12} (0) + \frac{\partial H'_{\pm12}}{\partial Q_{\pm}} Q_{\pm} + \frac{1}{2} \frac{\partial^2 H'_{\pm12}}{\partial Q_{\pm}^2} Q_{\pm}^2 \\
+ \left( \frac{\partial^2 H'_{\pm12}}{\partial Q_{\pm} \partial Q_{-}} \right)_0 Q_{-} Q_{+} + \cdots .
\]

(A2)

Using Eq. (17) it can be shown that only the totally symmetric terms in the above expansion can contribute to the matrix element \( H'_{\pm12} \). Thus, only the first and last terms survive. Furthermore, each of these two terms has an electrostatic as well as a spin-orbit part. By using the following definitions:

\[
\begin{align*}
H'_{\pm12} (\text{es}) (0) & = 0, \\
H'_{\pm12} (\text{SO}) (0) & = \Delta, \\
\left( \frac{\partial^2 H'_{\pm12} (\text{es})}{\partial Q_{\pm} \partial Q_{-}} \right)_0 & = \frac{\omega}{2},
\end{align*}
\]

and neglecting the quadratic SO coupling term, we have

\[
H'_{\pm12} = \Delta + \frac{1}{2} \omega \rho^2 = E_{1,2}.
\]

(A3)

Similarly,

\[
H'_{\pm11} = 0 + \frac{1}{2} \omega \rho^2 = E_{1,1},
\]

(A4)

\[
H'_{00} = - \Delta + \frac{1}{2} \omega \rho^2 = E_{1,0}.
\]

(A5)

Using time-reversal symmetry relation (18), we have

\[
H'_{\pm12} = H'_{-2-2}, \quad H'_{\pm11} = H'_{-1-1}, \quad H'_{00} = H'_{00}.
\]

(A6)

2. Off-diagonal elements

Using time-reversal symmetry (18) and employing the following definitions:

\[
\begin{align*}
H'_{\pm2-2} & = A, \\
H'_{-2-1} & = - H'_{+1-2} = B, \\
H'_{0-2} & = B'_{+1-1} = C.
\end{align*}
\]

(A7)

(A8)

(A9)

we obtain the 6 × 6 vibronic Hamiltonian

\[
H'_{\pm12} = \Delta + \frac{1}{2} \omega \rho^2 = E_{1,2},
\]

(A10)

\[
H'_{\pm10} = - H'_{0-1} = D_2,
\]

(A11)

\[
H'_{0-10} = - H'_{0} = D_3,
\]

(A12)

\[
H'_{00} = G,
\]

(A13)

\[
H'_{\pm12} = H'_{-2-2} = \mathcal{H},
\]

(A14)

Eq. (A1) can be written as

\[
\begin{array}{cccccccc}
\psi'_{\pm2} & \psi'_{\pm1} & \psi'_{-1} & \psi'_{-2} & \psi'_{0} & \psi'_{-3} & \psi'_{-2} \\
\psi'_{\pm2} & E_{1,2} & D_1 & \mathcal{H} & C & B & A \\
\psi'_{\pm1} & E_{1,1} & D_2 & D_3 & C & -B & \mathcal{H}
\end{array}
\]

(A15)

The matrix elements of the electronic Hamiltonian are expanded in a Taylor series in powers of the degenerate bending coordinate \( Q_{\pm} \). The terms with appropriate symmetry with respect to the symmetry operation \( \hat{J} \) on the corresponding electronic matrix elements survive. Using Eq. (17), it is found that the matrix element \( G \) is of zeroth order in the expansion: \( D_{1,2,3} \) are of first order, \( C \) and \( \mathcal{H} \) are of second order, \( B \) is of third order, while \( A \) is of fourth order.

Introducing the following abbreviations:

\[
G^{(0)} = g, \quad \left( \frac{\partial D_{1,2,3}}{\partial Q_{\pm}} \right)_0 = d_{1,2,3},
\]

\[
\left( \frac{\partial C}{\partial Q_{\pm}} \right)_0 = c, \quad \left( \frac{\partial H}{\partial Q_{\pm}} \right)_0 = h,
\]

(A16)

\[
\left( \frac{\partial A}{\partial Q_{\pm}} \right)_0 = a,
\]

\[
\left( \frac{\partial B}{\partial Q_{\pm}} \right)_0 = b
\]
The electrostatic part of the electronic Hamiltonian $H_{es}$ contributes to matrix elements with basis functions involving identical spin eigenstates. Hence only the matrix element $C$ will have contributions from the electrostatic Hamiltonian. Since the matrix elements $G$, $H$, and $A$ couple two orthogonal spin eigenstates $\alpha_1\alpha_2$ and $\beta_1\beta_2$, the relativistic contribution to these elements vanishes. Therefore,

$$a = h = g = 0.$$  \hspace{1cm} (A18)

On the other hand, the matrix elements $D_{1,2,3}$ and $B$ have a nonzero contribution from the SO operator.

Let us consider the matrix element $H_{+10}^+$. Using Eqs. (A1) and (16), we have

$$d_3pe^{i\chi} = \int d\tau_1d\tau_2(p_0^+)H_{+10}^+(p_0^-).$$

$$= \frac{1}{2\sqrt{2}} \int d^3r_1d^3r_2 \left[ Q(2)P(1)\exp(-i\varphi_1) - Q(1)P(2)\exp(-i\varphi_2) \right] \times \left[ Q(2)P(1)\exp(-i\varphi_1) - Q(1)P(2)\exp(-i\varphi_2) \right].$$

(A19)

where

$$d\tau_k = ds_z^{(k)} d^3r_k = ds_z^{(k)}r_1dr_2dz_1dz_2,$$

$$k = 1, 2$$

and

$$H_{+10}^{(1)} = \left( \frac{\partial H_{+10}}{\partial Q_{+1}} \right)_0.$$  \hspace{1cm} (A20)

Performing the integration over the spin variable $ds_z^{(k)}$ and the angular variable $d\varphi_k$, we obtain

$$d_3pe^{i\chi} = \frac{3^2\pi^2}{2\sqrt{2}} \frac{2.023}{4e^2} \int r_1r_2dr_1dr_2dz_1dz_2$$

$$\times \left[ \sum_{n=1}^3 \frac{r_1Q_n}{r_1^n} \left( \frac{r_2}{2\partial z_1} - \frac{z_2n}{2\partial r_1} \right) P^2(1)Q^2(2) \right] + \left[ \sum_{n=1}^3 \frac{r_2Q_n}{r_2^n} \left( \frac{r_1}{2\partial z_2} - \frac{z_1n}{2\partial r_2} \right) P^2(1)Q^2(2) \right].$$

(A21)

Similarly, the matrix element $H_{0+1}^+$ can be calculated as

$$\int d\tau_1d\tau_2(p_0^+)H_{0+1}^{(1)}(p_0^-) = -d_3e^{-i\chi}. \hspace{1cm} (A22)$$

The Hermiticity requirement gives

$$(H_{+10}^+)^* = H_{0+1}^+.$$  \hspace{1cm} (A23)

For the real parameter $d_3$, from Eqs. (A19), (A21), and (A22) it is obvious that

$$d_3 = 0.$$ \hspace{1cm} (A24)

In a similar way it can be shown that

$$d_1 = d_2.$$  \hspace{1cm} (A25)

Using relations (A18), (A23), and (A24) in Eq. (A17) and ignoring the third-order (relativistic) vibronic-coupling term $b$, we obtain final form (19) of the $6 \times 6$ vibronic Hamiltonian.

**APPENDIX B: ORTHONORMAL EIGENVECTORS**

Let $\mathbf{V}_{1,2}$ be the normalized factors.

$$\mathbf{V}_{1,2} = \frac{1}{N_{1,2}} \begin{pmatrix} \pm \exp(2i\chi) & -1 & \mp \exp(i\chi)(\Delta/d\rho) \\ -1 & \mp \exp(-i\chi)(\Delta/d\rho) & 0 \\ \exp(-2i\chi) & 0 & 
\end{pmatrix},$$

(B1)

where

$$N_1 = N_2 = 2\sqrt{1 + \Delta^2/(2d^2\rho^2)}.$$  \hspace{1cm} (B2)

are the normalization factors.

$$\mathbf{V}_{3,5} = \frac{1}{N_{3,5}} \begin{pmatrix} -\exp(2i\chi)(e\Delta/d^2) & D_3 & -\exp(i\chi)(\Delta + W/d\rho) \\ D_3 & \exp(-2i\chi)(e\Delta/d^2) & 0 \\ -\exp(i\chi)(\Delta + W/d\rho) & 0 & 
\end{pmatrix},$$

(B3)
\[
V_{4,6} = \frac{1}{N_{4,6}} \left( D_\pm + c^2 \rho^2 \Delta S_d / d^2 \right.
\exp\left(-2i\chi(c\Delta d^2 + c^2 \rho^2 S_d d)\right)
\exp(-i\chi)[(\Delta \mp Wd\rho) \pm c^2 \rho^2 S_d / d]
\exp(-3i\chi)(c\rho d)(1 - WS_d \mp \Delta S_d)
\exp(-2i\chi)
\mp c^2 \rho^2 S_d \exp(-4i\chi)\right)
\]

where
\[
D_\pm = 1 + \frac{\Delta(\Delta \pm W)}{d^2 \rho^2},
\]
\[
S_d = \frac{1}{W \pm \Delta \pm \Delta^2 \rho^2 / (\Delta^2 + d^2 \rho^2)},
\]
\[
N_{4,5} = \frac{1}{d^2 \rho^2} \left(2W[\Delta^2 + d^2 \rho^2] \pm \Delta(\Delta^2 + 2d^2 \rho^2)\right),
\]
\[
N_{4,6} = \frac{1}{d^2 \rho^2} \left(2W(\Delta^2 + d^2 \rho^2)(1 + c^2 \rho^4 S_d^2)
\mp 2W(\Delta^2 + 2d^2 \rho^2)(1 - c^2 \rho^4 S_d^2)
- 4c^2 \rho^2 WS_d(\Delta^2 + d^2 \rho^2)\right)^{1/2}.
\]