Study of strong $\Sigma$–$\Pi$ and spin–orbit vibronic coupling effects in linear triatomic molecules

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Abstract

The vibronic coupling between $^2P$ and $^2R$ electronic states of a linear molecule is considered with the inclusion of the spin–orbit coupling of the $^2P$ electronic state, employing the microscopic (Breit–Pauli) spin–orbit coupling operator in the single-electron approximation. The $6 \times 6$ Hamiltonian matrix in a diabatic spin-electronic basis is derived by an expansion of the molecular Hamiltonian in powers of the bending amplitude up to second-order. The symmetry properties of the Hamiltonian are analyzed. It is pointed out that there exist zeroth-, first-, and second-order $\Sigma$–$\Pi$ vibronic-coupling terms of spin–orbit origin, which are absent when the usual phenomenological form of the spin–orbit coupling operator is used instead of its microscopic form. The influence of the $\Sigma$–$\Pi$ and spin–orbit vibronic-coupling terms on the adiabatic potential energy curves as well as on the vibronic spectra is analyzed for selected models. It is demonstrated that the interplay of strong $\Sigma$–$\Pi$ vibronic-coupling and strong spin–orbit splitting of the $\Pi$ state can result in unexpectedly complex vibronic spectra.

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1. Introduction

The original paper of Renner [1], describing the vibronic interactions in degenerate $\Pi$ electronic states of linear molecules, has been fundamental for molecular spectroscopy. Experimental observations of Renner’s predictions in the spectrum of the NH$_2$ radical [2,3] stimulated early methodological developments for the treatment of the Renner–Teller (RT) effect [4–6]. These early theoretical descriptions, which were based on perturbation theory, were later supplemented by variational methods for the calculation of RT spectra [7–9]. For a detailed survey of the RT effect, we refer to the review by Rosmus and Chambaud [10].

The spectra of isolated $^2\Pi$ electronic states in many triatomic and tetra-atomic molecules have been quantitatively analyzed by these methods. Quite often, however, the interaction of a degenerate $^2\Pi$ state with other closely lying electronic states is also important. Examples are the absorption spectra of NCO [11] and NCS [12] and the photoelectron spectra of HCN [13,14], N$_2$O [15], and C$_2$N$_2$ [16]. In radicals like C$_3$H [17–20], C$_3$F [21], and C$_2$Cl [22,23], the vibronic interaction of closely spaced $^2\Pi$ and $^2\Sigma$ states leads to very complex vibronic energy-level spectra. Some selected effects of $\Sigma$–$\Pi$ vibronic coupling (VC) have been calculated by perturbation theory, e.g. corrections to rotational energy levels [11,24], modifications of Zeeman orbital g-factors [24,25], and intensity borrowing effects [24]. A comprehensive discussion of the effects associated with the weak perturbation of a $\Pi$ electronic state by a $\Sigma$ electronic state has been given by Aarts [26]. A detailed analysis of strong VC of closely spaced $^2\Sigma$ and $^2\Pi$ states of
a linear molecule has been given by Köppel et al. [27], using variational methods.

The inclusion of the spin of the unpaired electron in the analysis of vibronic spectra of linear molecules was first considered by Pople [28]. He treated the spin–orbit (SO) coupling as a perturbation of the RT Hamiltonian of a $^2\Pi$ state and obtained the spin-vibronic energy corrections up to second-order. Since then, numerous studies on the situation where a degenerate $^2\Pi$ electronic state and a nondegenerate $^2\Sigma$ state of a linear triatomic molecule are closely spaced and coupled by the degenerate bending mode. The vibronic Hamiltonian of this system is written as ($\hbar = 1$),

$$H = T_N + H_{el} = T_N + H_{\text{el}} + H_{\text{SO}}, \quad (2)$$

$$T_N = \left[ -\frac{\omega^2}{2} \left( \frac{1}{\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right) + \frac{\omega}{2} \sigma_z^2 \right], \quad (3)$$

$$H_{\text{el}} = -\frac{1}{2} \nabla^2 - \sum_{n=1}^{3} \frac{e Q_n}{r_n}, \quad (4)$$

$$H_{\text{SO}} = A_x \cdot \sigma_x + A_y \cdot \sigma_y + A_z \cdot \sigma_z. \quad (5)$$

Here, $H_{\text{el}}$ is the electrostatic part of the electronic Hamiltonian that includes the kinetic energy of the unpaired electron and the electronic–nuclear interaction term. The $Q_n$ are effective nuclear charges. The coupling of the spin and orbital motion of the electron in the field of three nuclei is given by the Breit–Pauli SO operator, $H_{\text{SO}}$, $A_x$, $A_y$, and $A_z$ being differential operators in electronic coordinate space, the explicit form of which is given in Appendix A. The $\sigma_x$, $\sigma_y$, and $\sigma_z$ are the Pauli spin matrices. $\omega$ is the harmonic bending frequency. $T_N$ is the nuclear kinetic energy operator, described in polar coordinates ($\rho, \phi$), where $\rho$ and $\phi$ are the radial and angular part of the degenerate bending vibrational mode, respectively. In terms of the Cartesian bending normal coordinates $Q_x$ and $Q_y$, they are defined as

$$\rho e^{\pm i \phi} = Q_x = Q_x \pm i Q_y. \quad (6)$$

It should be noted that we have suppressed the totally symmetric stretching modes in the Hamiltonian (2). The stretching modes generally “tune” the energy gap of the vibronically coupled $^2\Sigma$ and $^2\Pi$ states and are, therefore, not separable from the bending motion in the $\Sigma-\Pi$ VC problem [37]. Since the aim of this work is to understand the generic effects of $\Sigma-\Pi$ VC as well as SO coupling rather than to calculate spectra of specific molecular systems, the omission of the stretching modes is appropriate for simplicity and clarity. The extension of the present formalism to include the stretching modes is straightforward.

The electronic Hamiltonian $H_{\text{el}}$ can be shown to commute with the $z$-component of the electronic angular momentum operator

$$j_z = -i \frac{\partial}{\partial \theta} + \sigma_z, \quad (7)$$

where $\theta$ is the angular coordinate and $\sigma_z$ is the spin angular momentum. $j_z$ describes a continuous symme-
try, generating an one-parametrical group of unitary transformations

\[ J_z(\epsilon) = e^{i\epsilon J_z} . \]  

(8)

Here, \( \epsilon \) is the angular group parameter. It is evident that

\[ [H_{el}, J_z(\epsilon)] = 0. \]  

(9)

The electronic Hamiltonian \( H_{el} \) also possesses time-reversal (TR) symmetry. For odd-electronic systems, the TR operator \( \hat{T} \) is an antiunitary operator that satisfies [38,39]

\[ \langle \hat{T} \psi_1 \rangle \hat{T} \psi_2 \rangle = \langle \psi_1 | \psi_2 \rangle^*. \]  

(10)

The full Hamiltonian \( H \) of Eq. (2), satisfies, in addition to the TR property,

\[ [H, J_z] = 0 \]  

(11)

with

\[ J_z = j_z - i \frac{\partial}{\partial \phi}. \]  

(12)

Here, \( j_z \) is the \( z \)-component of the total angular momentum operator (including the nuclear angular momentum). The eigenvalues (\( \mu \)) of \( J_z \) are half-integer (\( \mu = \pm 1/2, \pm 3/2, \ldots \)). The eigenvalues of \( H \) are doubly degenerate (Kramer’s degeneracy [40]), which is a consequence of the TR symmetry.

Let’s define \( |\psi_{\pm}\rangle \) and \( |\psi_0\rangle \) as diabatic [41–43] electronic basis set associated with the two components of the degenerate \( 2\Sigma \) electronic state (with electronic orbital angular momentum quantum numbers \( \Lambda = \pm 1 \)) and the nondegenerate \( 2\Sigma \) state (\( \Lambda = 0 \), respectively. The coupling of the spin motion with the orbital motion of the electron gives rise to six SO-coupled states. Hence, a complete diabatic electronic basis set is given by \( |\psi_{\pm}\rangle \), \( |\psi_{\pm}\rangle \), \( |\psi_0\rangle \), and \( |\psi_{0\delta}\rangle \), where the notation \( |\psi_{\pm}\rangle \) stands for \( |\psi_{\pm}\rangle |x\rangle \). Here, \( x \) and \( \beta \) represent the two spin eigenstates of the single unpaired electron.

For linear molecules with cylindrical symmetry, the following relationship is fulfilled by the diabatic electronic basis,

\[ J_z(\epsilon) |\psi_{A,\alpha}\rangle = e^{i(\Delta \alpha \phi)} |\psi_{A,\alpha}\rangle. \]  

(13)

The TR operator \( \hat{T} \) has the following effect on the diabatic electronic basis functions:

\[ \hat{T} |\psi_{\pm\alpha\delta}\rangle = |\psi_{\pm\alpha\delta}\rangle, \quad \hat{T} |\psi_{0\alpha\delta}\rangle = |\psi_{0\alpha\delta}\rangle; \]  

\[ \hat{T} |\psi^{-\pm\alpha\delta}\rangle = -|\psi^{-\pm\alpha\delta}\rangle, \quad \hat{T} |\psi^-_{0\alpha\delta}\rangle = -|\psi^-_{0\alpha\delta}\rangle. \]  

(14)

Using the above defined six diabatic spin-electronic basis functions, the electronic Hamiltonian can be written as a \( 6 \times 6 \) vibronic matrix. The determination of the vibronic matrix elements can be simplified by using the TR symmetry, Eqs. (10) and (14), 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 up to second-order in the bending coordinate. The derivation of the \( 6 \times 6 \) spin-vibronic Hamiltonian is given in Appendix B. The result is

\[ H = T_{N1} \]

\[ + \begin{pmatrix}
E_{1\Sigma}/2 & \lambda |e^2| & \lambda |e^{2\delta}| & g & h |e^{2\delta}| & h |e^{2\delta}| & 0 \\
\lambda |e^{2\delta}| & E_{1\Sigma}/2 & \lambda |e^{2\delta}| & g & -h |e^{2\delta}| & -d |e^{2\delta}| & 0 \\
\lambda |e^{2\delta}| & \lambda |e^{2\delta}| & E_{1\Sigma}/2 & 0 & -g & -d |e^{2\delta}| & 0 \\
g & g & 0 & E_{1\Sigma}/2 & \lambda |e^{2\delta}| & \lambda |e^{2\delta}| & 0 \\
-h |e^{2\delta}| & -h |e^{2\delta}| & -d |e^{2\delta}| & -d |e^{2\delta}| & \lambda |e^{2\delta}| & \lambda |e^{2\delta}| & \lambda |e^{2\delta}| \\
0 & -h |e^{2\delta}| & -d |e^{2\delta}| & -d |e^{2\delta}| & -d |e^{2\delta}| & \lambda |e^{2\delta}| & \lambda |e^{2\delta}| \\
0 & 0 & 0 & 0 & 0 & 0 & E_{1\Sigma}/2 \\
\end{pmatrix}. \]  

(15)

Here, \( I \) is the six-dimensional unit matrix and \( E_{1\Sigma}/2, E_{1\Sigma}/2, \) and \( E_{1\Sigma}/2 \) are the electronic energies at the reference geometry (\( \rho = 0 \)). To simplify the notation, we introduce the \( \Sigma - \Pi \) energy gap \( \Delta \) and the SO splitting \( \zeta \) as follows

\[ \Delta = E_{1\Sigma} - E_{1\Sigma}, \]  

(16)

\[ \zeta = E_{1\Sigma}/2 - E_{1\Sigma}/2. \]  

(17)

Here, \( E_{1\Sigma} \) and \( E_{1\Sigma} \) are the electrostatic energies at the reference geometry, while \( E_{1\Sigma}/2 \) and \( E_{1\Sigma}/2 \) are the reference energies with inclusion of SO coupling. \( c \) is the well-known nonrelativistic quadratic RT coupling constant [1–4], \( \lambda \) is the linear \( \Sigma - \Pi \) coupling constant [27], while \( g \) and \( h \) are purely relativistic \( \Sigma - \Pi \) coupling constants of zeroth- and second-order in the bending coordinate, respectively. The parameter \( d \) is the relativistic linear RT coupling constant introduced in Ref. [34]. The zeros appearing along the cross diagonal are a consequence of the TR symmetry. The two \( 3 \times 3 \) diagonal blocks of the vibronic Hamiltonian (15) have the same form as the nonrelativistic \( \Sigma - \Pi \) Hamiltonian (\( \zeta = 0 \)) [27]. The off-diagonal \( 3 \times 3 \) blocks of the vibronic Hamiltonian (15) are, necessarily, of purely relativistic origin.

For linear geometry (\( \rho = 0 \)), all off-diagonal elements of the Hamiltonian matrix (15) vanish, with the exception of the zeroth-order off-diagonal coupling SO matrix element \( g \). This special case of the \( \Sigma - \Pi \) SO Hamiltonian has been considered in Ref. [44]. It has been shown that the \( 6 \times 6 \) matrix can be block-diagonalized in this case to two \( 3 \times 3 \) matrices by a constant (\( \rho \) independent) unitary transformation. It should be realized, however, that this transformation mixes the \( 2\Sigma \) and \( 2\Pi \) diabatic states. The transformed basis states thus are no longer diabatic electronic states, if, for example, a \( \Sigma - \Pi \) crossing occurs as a function of the stretching coordinates. In the general case (\( \rho \neq 0 \)) the Hamiltonian matrix (15) cannot be decoupled into smaller submatrices.

Although the adiabatic approximation fails to describe the vibronic energy levels of nearly degenerate electronic states, the adiabatic potential energy (PE) surfaces are nevertheless very helpful for the qualitative interpretation of the vibronic spectra. The adiabatic PE surfaces are obtained by diagonalizing \( H - T_N \) at a fixed nuclear geometry. The derivation of analytic expressions for the eigenvalues of the \( 6 \times 6 \) matrix is unfeasible even with the help
of symbolic-mathematical tools. The adiabatic PE surfaces therefore have been obtained by numerical diagonalization of the $6 \times 6$ matrix.

3. Calculation of spectra

For a given value of the good quantum number $\mu$, we expand $|\Psi^{(\mu)}_k\rangle$ in a complete basis, which is constructed as the product of electronic $|\psi^{(\mu)}_{\sigma}\rangle$ and vibrational $|n\ell\rangle$ basis functions, where $\Lambda = \pm 1.0$ (for the $2\Pi$ and the $2\Sigma$ state, respectively) and $\sigma = \pm 1/2$. The $|n\ell\rangle$, $n = 0, 1, 2\ldots$ and $\ell = -n, -n+2, \ldots n-2, n$, are the eigenfunctions of the two-dimensional isotropic harmonic oscillator [45]. Within the Condon approximation, only the vibronic levels with $\mu = \pm 1/2$ and $\pm 3/2$ can carry intensity, assuming optical excitation from a closed-shell and vibrationless ground state.

The real symmetric Hamiltonian matrix is constructed and diagonalized for a given value of $\mu$. The vibrational basis is increased until convergence of the eigenvalues of interest has been achieved. A standard diagonalization method for real symmetric matrices has been used. The eigenvalues represent the vibronic energy levels for the given vibronic angular momentum quantum number $\mu$. While $\mu = 3/2$ levels gain intensity only from the $2\Pi_{3/2}$ state, $\mu = 1/2$ levels gain intensity from both the $2\Sigma_{1/2}$ and $2\Pi_{1/2}$ states (we assume equal oscillator strengths of all three states). For $\mu = 3/2$, the square of the eigenvector corresponding to the $|2\Pi_{3/2}\rangle\langle 00|$ basis state gives the intensity. For $\mu = 1/2$, on the other hand, two eigenvector components, corresponding to the $|2\Pi_{1/2}\rangle\langle 00|$ and $|2\Sigma_{1/2}\rangle\langle 00|$ basis states, may give intensity. In the case of strong $\Sigma$–$\Pi$ mixing, both components of the eigenvectors become comparable. In this case, we assume, for clarity, that either the $2\Sigma_{1/2}$ or the $2\Pi_{1/2}$ oscillator strength is zero.

4. Results and discussion

In this section, we analyze the influence of the $\Sigma$–$\Pi$ VC and SO coupling on the energy levels and the spectral intensity distribution for the photoinduced transition from an unperturbed initial state into the vibronically coupled $2\Sigma$ and $2\Pi$ final states. For brevity, we consider only the case where the $2\Sigma$ state is higher in energy than the $2\Pi$ state. Since the $6 \times 6$ $\Sigma$–$\Pi$ vibronic Hamiltonian contains many coupling parameters, a systematic study of the effects of all parameters is beyond the scope of this article. We will limit ourselves to the investigation of a few selected and particularly interesting cases.

The effect of nonrelativistic RT coupling (parameter $c$) and linear relativistic VC (parameter $d$) within a $2\Pi$ state is well understood. Therefore, we do not consider these coupling mechanisms in the present study. The coupling term $h$ is purely relativistic and quadratic in the bending distortion and hence will be ignored in the following. It should be kept in mind that all coupling parameters, in particular $\Delta$ and $\zeta$, may be functions of the stretching modes, which is not taken into account here.

4.1. Variation of the $\Sigma$–$\Pi$ coupling strength

The nonrelativistic $\Sigma$–$\Pi$ VC mechanism has been analyzed in detail in Ref. [27]. For weak SO coupling, it is straightforward to include the SO effects by perturbation theory. Hence we shall focus here on the cases where the SO splitting ($\zeta$) of the $2\Pi$ state is relatively large, being comparable to the $\Sigma$–$\Pi$ energy gap ($\Delta$).

4.1.1. Case I

Here, we discuss a system with $\Delta/\omega = 5.0$ and $\zeta/\omega = -2.0$. This represents a typical case of a relatively large $\Sigma$–$\Pi$ gap and moderate SO splitting of a $2\Pi$ state, which can be found in many linear molecules with moderately heavy atoms. Fig. 1a–c shows the adiabatic PE curves of this system for $\lambda/\omega = 0$, 2.0, and 4.0, respectively. All other coupling parameters in Eq. (15) are set to zero. The solid, dashed, and dotted lines correspond to the $2\Pi_{3/2}$, $2\Pi_{1/2}$, and $2\Sigma_{1/2}$ states, respectively. For $\lambda = 0$, the adiabatic PE curves are parabolas which are separated by the zero-order splittings ($\Delta$ and $\zeta$). With increasing $\lambda/\omega$, the $2\Pi_{3/2}$ PE functions develop a double-minimum shape, while the PE function of the $2\Pi_{1/2}$ state becomes very flat in the vicinity of $\rho = 0$.

The corresponding vibronic spectra are shown in Fig. 2a–c. For $\lambda/\omega = 0$, the result is trivial, showing three purely electronic transitions of equal intensity, see Fig. 2a. The intensities of these lines get distributed over vibronic levels when $\lambda/\omega$ becomes nonzero. The increase in the curvature of the uppermost adiabatic PE curve (the $2\Sigma_{1/2}$ state), leads to a substantial increase of the zero-point energy, thus shifting the corresponding lines to higher energy. The VC effects are most pronounced in the $2\Pi$ state, where the adiabatic PE function develops a bent geometry. Strong $\Sigma$–$\Pi$ coupling ($\lambda/\omega = 4.0$) leads to very complicated vibronic structures of the $2\Pi_{3/2}$ and $2\Pi_{1/2}$ states, see Fig. 2c. It is noteworthy that the vibronic spectra of the two components of the $2\Pi$ state are very different from each other in this case. This possibility of very different vibronic structures of the two SO components of a $2\Pi$ state apparently has never been considered so far in the assignment of observed spectra.

4.1.2. Case II

Here, we investigate the case of very large SO splitting ($\zeta/\omega = -20.0$) and moderate $\Sigma$–$\Pi$ gap ($\Delta/\omega = 5.0$). This combination of parameters leads to the interesting situation where the nondegenerate $2\Sigma$ state lies between the two SO components of the $2\Pi$ state. This situation may arise for excited states of molecules containing relatively heavy atoms, as is well known for diatomic molecules [46].

Fig. 3a–c shows the adiabatic PE curves for $\lambda/\omega = 0$, 2.0, and 4.0. For $\lambda/\omega = 0$, the adiabatic PE curves are harmonic and the $2\Sigma_{1/2}$ state lies in between the two SO
Fig. 1. Adiabatic PE curves of the $^3\Pi_{3/2}$ (solid), $^3\Pi_{1/2}$ (dashed), and $^3\Sigma_{1/2}$ (dotted) states for $\Delta/\omega = 5.0$, $\zeta/\omega = -2.0$, and $\lambda/\omega = 0$ (a), 2.0 (b), and 4.0 (c).

Fig. 2. $\Sigma$–$\Pi$ vibronic spectra for $\Delta/\omega = 5.0$, $\zeta/\omega = -2.0$, and $\lambda/\omega = 0$ (a), 2.0 (b), and 4.0 (c). The solid, dashed, and dotted lines represent the vibronic levels which gain intensity from the $^3\Pi_{3/2}$, $^3\Pi_{1/2}$, and $^3\Sigma_{1/2}$ states, respectively.
Fig. 3. Adiabatic PE curves of the 3Π\( \frac{3}{2} \) (solid), 3Π\( \frac{1}{2} \) (dashed), and 3Σ\( \frac{1}{2} \) (dotted) states for \( D/\omega = 5.0, \kappa/\omega = 20.0, \) and \( \lambda/\omega = 0 \) (a), 2.0 (b), and 4.0 (c).

Fig. 4. Σ–Π vibronic spectra for \( D/\omega = 5.0, \kappa/\omega = -20.0, \) and \( \lambda/\omega = 0 \) (a), 2.0 (b), and 4.0 (c). The solid, dashed, and dotted lines represent the vibronic levels which gain intensity from the 3Π\( \frac{3}{2} \), 3Π\( \frac{1}{2} \), and 3Σ\( \frac{1}{2} \) states, respectively.
components of the $^2\Pi$ state, see Fig. 3a. For $\lambda/\omega = 2.0$, the PE function of the $^2\Pi_{3/2}$ state becomes very flat near $\rho = 0$, while the PE function of the $^2\Sigma_{1/2}$ state has developed a slight double minimum. With further increasing $\lambda/\omega$, both the $^2\Pi_{3/2}$ as well as the $^2\Sigma_{1/2}$ PE functions develop minima at bent geometries, see Fig. 3c. Fig. 4a–c shows the corresponding absorption spectra. For $\lambda/\omega = 2.0$, the close-lying $^2R_{1/2}$ and $^2P_{1/2}$ states show weak indications of vibronic interaction, while the far-lying $^2P_{3/2}$ state remains nearly unperturbed. Compared to Fig. 2b, the effect of $\Sigma$–$\Pi$ coupling is less pronounced here because of the larger SO splitting. For $\lambda/\omega = 4.0$, the spectrum of the $^2P_{3/2}$ state exhibits a pronounced progression in the bending mode, which reflects the nonlinear equilibrium geometry, see Fig. 3c. The $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$ states exhibit rather complex vibronic spectra which are dominated by quasi-degeneracy effects, see Fig. 4c. This again shows that the two SO components of the $^2\Pi$ state can exhibit completely different vibronic spectra.

4.2. The $^2P_{1/2}$–$^2R_{1/2}$ resonance case

Here, we consider the case of accidental degeneracy of the $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}$ states. The $\Sigma$–$\Pi$ gap ($A$) and the SO splitting ($\zeta$) are adjusted such that the $^2\Pi_{1/2}$ component of the $^2\Pi$ state and the $^2\Sigma_{1/2}$ state are degenerate at the reference geometry. For a sufficiently large value of $A$, the $^2\Pi_{3/2}$ can be considered to be decoupled from the $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}$ states. The $6 \times 6$ vibronic Hamiltonian can thus be truncated to $4 \times 4$ form

$$H = T_N 1 + \begin{pmatrix} E_{\Sigma_{1/2}} & \lambda \rho e^{i\phi} & g & 0 \\ \lambda \rho e^{-i\phi} & E_{\Pi_{1/2}} & 0 & -g \\ g & 0 & E_{\Pi_{1/2}} & \lambda \rho e^{i\phi} \\ 0 & -g & \lambda \rho e^{-i\phi} & E_{\Sigma_{1/2}} \end{pmatrix}, \quad (18)$$

where $1$ is the four-dimensional unit matrix. The above Hamiltonian is isomorphic to the Hamiltonian of the linear $E \times E$ Jahn–Teller (JT) effect with SO coupling in trigonal symmetry, see Ref. [47]. $\lambda$ is equivalent to the linear JT coupling parameter, while $g$ is equivalent to the matrix elements of the $A_1 \sigma_x + A_2 \sigma_y$ term of the SO coupling operator.

4.2.1. Case I

In this special case of accidental degeneracy of the $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$ states, we have investigated the effect of the zeroth-order coupling parameter $g$. Fig. 5a–c exhibits the adiabatic PE curves of a system with $A/\omega = 5.0$, $\zeta/\omega = -10.0$, $\lambda/\omega = 1.0$, while $g/\omega$ takes the value 0, 0.2, and 0.5. Fig. 5a shows that the $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}$ PE functions touch each other at the reference geometry ($\rho = 0$). With increasing

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Fig. 5. Adiabatic PE curves of the $^2\Pi_{1/2}$ (solid), $^2\Pi_{3/2}$ (dashed), and $^2\Sigma_{1/2}$ (dotted) states for $A/\omega = 5.0$, $\zeta/\omega = -12.0$, and $\lambda/\omega = 1.0$ with $g/\omega = 0$ (a), 0.2 (b), and 0.5 (c).
Fig. 6. Σ-Π vibronic spectra for $\Delta \hbar \omega = 5.0$, $\zeta / \omega = -12.0$, and $\lambda / \omega = 1.0$ with $g / \omega = 0$ (a), 0.2 (b), and 0.5 (c). The solid and dashed lines represent the vibronic levels gaining intensity from the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states, respectively.

Fig. 7. Adiabatic PE curves of the $^2\Pi_{3/2}$ (solid), $^2\Pi_{1/2}$ (dashed), and $^2\Sigma_{1/2}$ (dotted) states for $\Delta \hbar \omega = 5.0$, $\zeta / \omega = -12.0$, and $\lambda / \omega = 4.0$ with $g / \omega = 0$ (a), 0.5 (b), and 1.0 (c).
g, this degeneracy is removed, see Fig. 5b and c, while the adiabatic PE curve of the $^2\Sigma_{3/2}$ state remains essentially unchanged. Fig. 6a–c shows the corresponding vibronic spectra, assuming vanishing oscillator strength of the $^2\Pi_{1/2}$ state (the alternative case will lead to a spectrum with same line positions, but different intensities). In Fig. 6a, the $^2\Pi_{1/2}$ state exhibits a vibronic spectrum which corresponds to a moderately strong $E \times E$ JT effect, each vibronic line being doubly degenerate. With increasing $g/\omega$, these degenerate vibronic lines split proportional to $g/\omega$. The coupling parameter $g$ thus removes the accidental degeneracy of the vibronic levels (due to the $^2\Sigma_{1/2}$-$^2\Pi_{1/2}$ accidental degeneracy) in zeroth-order.

4.2.2. Case II

In this final example, we investigate the resonance case in the limit of very strong $\Sigma-\Pi$ nonrelativistic coupling ($\lambda/\omega = 4.0$). Fig. 7a–c shows the adiabatic PE functions for $\Delta/\omega = 5.0$, $\zeta/\omega = -10.0$, while $g/\omega$ takes the values 0, 0.5, and 1.0. The lowest adiabatic PE curve develops a minimum at a strongly bent geometry as a consequence of the strong $\Sigma-\Pi$ coupling, see Fig. 7a. The accidental degeneracy of the $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}$ states in Fig. 7a is lifted by finite values of $g/\omega$, see Fig. 7c. Fig. 8a–c shows the corresponding vibronic spectra. For $g/\omega = 0$, the $^2\Pi_{1/2}$ state shows vibronic structure which is typical for strong JT coupling. Note in particular, the double-hump shape of the spectral envelope. The well separated $^2\Pi_{3/2}$ state, on the other hand, exhibits the characteristic extended Franck–Condon progression of a linear-to-bent transition. With increasing $g/\omega$, each of the $^2\Pi_{1/2}$ lines splits into two, as described earlier. However, in addition to changes in the vibronic structure of the $^2\Pi_{1/2}$ state, the parameter $g$ also strongly affects the vibronic structure of the $^2\Pi_{3/2}$ state, see Fig. 8b. In this case of large $\lambda/\omega$, the $^2\Pi_{3/2}$ state cannot be decoupled from the $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$ states. For $g/\omega = 0.5$, the density of intensity carrying lines in the $^2\Pi_{3/2}$ state is doubled, see Fig. 8b. Interestingly, further increase of $g/\omega$ to 1.0 essentially restores the line density observed for $g/\omega = 0$, see Fig. 8c. In the latter case, the levels of the $^2\Pi_{3/2}$ state are again doubly degenerate.

5. Conclusions

The combined effects of strong SO coupling and the strong VC of closely spaced $^2\Pi$ and $^2\Sigma$ electronic states of a linear molecule has been investigated, employing the Breit–Pauli SO operator. The 6x6 vibronic Hamiltonian has been derived in the diabatic representation up to second-order in the bending displacement. It has been found that there exists, in addition to the well-known nonrelativistic (quadratic) RT coupling term and nonrelativistic (linear) $\Sigma-\Pi$ coupling term, three coupling terms of relativistic origin. While the two components of the $^2\Pi$ state are coupled by a relativistic linear term, the $^2\Sigma$ and $^2\Pi$ states are relativistically coupled in zeroth- and second-order of the bending displacement. The quadratic coupling term of SO origin has been ignored in the present study, while the effects of the zeroth-order term have been studied explicitly.
The combined effects of nonrelativistic Σ-Π coupling and strong SO splitting of the 2Π state have been investigated by variational calculations of the vibronic energy levels. It has been shown that this problem is very rich and that very complex vibronic spectra can arise. For example, the 2Π1/2 and 2Π3/2 states can exhibit completely different vibronic structures when both the SO splitting and the non-relativistic Σ-Π coupling are strong.

The effect of zeroth-order relativistic Σ-Π coupling has been shown to be important when 2Σ1/2–2Π1/2 near degeneracies occur. In this case, for a sufficiently large SO coupling, the 2Π1/2 state gets approximately decoupled, and the 2Π3/2 and 2Σ1/2 states exhibit a linear JT type interaction.

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Appendix A. The Breit–Pauli SO operator

The differential operators $A_x$, $A_y$, and $A_z$ of Eq. (5) in cylindrical coordinates are given by

$$A_x = -i g \beta \sum_{n=1}^{3} \frac{Q}{r^2} \left[ \sin \phi \frac{\partial}{\partial z} - z_n \left( \sin \phi \frac{\partial}{\partial r} + \cos \phi \frac{\partial}{\partial \phi} \right) \right]$$

$$A_y = -i g \beta \sum_{n=1}^{3} \frac{Q}{r^2} \left[ z_n \left( \cos \phi \frac{\partial}{\partial r} - \sin \phi \frac{\partial}{\partial \phi} \right) - r \cos \phi \frac{\partial}{\partial z} \right]$$

$$A_z = -i g \beta \sum_{n=1}^{3} \frac{Q}{r^2} \frac{\partial}{\partial \phi}$$

where $g \simeq 2.0023$ is the g-factor of the electron and $\beta = \frac{e}{2m_e}$ is the Bohr magneton.

Appendix B. Derivation of the Σ–Π spin-vibronic Hamiltonian

The electronic Hamiltonian in the diabatic electronic basis can be written as follows

$$H_{xx} = \psi_{+\alpha}^\dagger H^{0+0}_{\alpha \alpha} \psi_{+\alpha} + \psi_{-\alpha}^\dagger H^{0-0}_{\alpha \alpha} \psi_{-\alpha} + \psi_{+\beta}^\dagger H^{0+0}_{\beta \beta} \psi_{+\beta} + \psi_{-\beta}^\dagger H^{0-0}_{\beta \beta} \psi_{-\beta}$$

$$H_{\text{es}} = H^{+\alpha\beta}_{\alpha \beta} + H^{+\beta\alpha}_{\beta \alpha} + H^{-\alpha\beta}_{\alpha \beta} + H^{-\beta\alpha}_{\beta \alpha}$$

$$H^{+\alpha\beta}_{\alpha \beta} = \psi_{+\alpha}^\dagger H^{0+0}_{\alpha \alpha} \psi_{+\alpha} \psi_{+\beta}^\dagger H^{0+0}_{\beta \beta} \psi_{+\beta}$$

$$H^{+\beta\alpha}_{\beta \alpha} = \psi_{+\beta}^\dagger H^{0+0}_{\beta \beta} \psi_{+\beta} \psi_{+\alpha}^\dagger H^{0+0}_{\alpha \alpha} \psi_{+\alpha}$$

$$H^{-\alpha\beta}_{\alpha \beta} = \psi_{-\alpha}^\dagger H^{0-0}_{\alpha \alpha} \psi_{-\alpha} \psi_{+\beta}^\dagger H^{0-0}_{\beta \beta} \psi_{+\beta}$$

$$H^{-\beta\alpha}_{\beta \alpha} = \psi_{-\beta}^\dagger H^{0-0}_{\beta \beta} \psi_{-\beta} \psi_{+\alpha}^\dagger H^{0-0}_{\alpha \alpha} \psi_{+\alpha}$$

$$H^{+\alpha\beta}_{\alpha \beta} = \psi_{+\alpha}^\dagger H^{0+0}_{\alpha \alpha} \psi_{+\alpha} \psi_{+\beta}^\dagger H^{0+0}_{\beta \beta} \psi_{+\beta}$$

$B.1. Diagonal elements$

Let us expand the diagonal matrix element $H^{++}_{xx}$ in a Taylor series around the reference geometry up to second-order in the degenerate bending coordinate ($Q_{\pm}$).

$$H^{++}_{xx} = H^{++}_{xx}^{(0)} + \left( \frac{\partial H^{++}_{xx}}{\partial Q_{\pm}} \right)_0 Q_{\pm} + \frac{1}{2} \left( \frac{\partial^2 H^{++}_{xx}}{\partial Q_{\pm}^2} \right)_0 Q_{\pm}^2 + \cdots$$

Using Eq. (13) it can be shown that only the totally symmetric terms in the above expansion can contribute to the matrix element $H^{++}_{xx}$. Thus, only the first and last terms survive. Furthermore, each of these two terms has an electrostatic as well as spin–orbit part. By using the following definitions;

$$H^{++}_{xx}^{(es)} = -A \frac{C}{2},$$

$$H^{++}_{xx}^{(SO)} = \frac{\zeta}{2},$$

$$\frac{1}{2} \left( \frac{\partial^2 H^{++}_{xx}^{(es)}}{\partial Q_{\pm}^2} \right)_0 = \frac{\omega}{2},$$

and neglecting the quadratic SO coupling term, we have,

$$H^{++}_{xx} = -A + \frac{\zeta}{2} + \frac{1}{2} \frac{\omega r^2}{2} = E_{\Pi 3/2} + \frac{1}{2} \frac{\omega r^2}{2}.$$ (B.3)

Similarly,

$$H^{--}_{xx} = -A + \frac{\zeta}{2} + \frac{1}{2} \frac{\omega r^2}{2} = E_{\Sigma 1/2} + \frac{1}{2} \frac{\omega r^2}{2}.$$ (B.4)

$$H^{00}_{xx} = A + \frac{1}{2} \frac{\omega r^2}{2} = E_{\Sigma 1/2} + \frac{1}{2} \frac{\omega r^2}{2}.$$ (B.5)

Using the TR symmetry relations of Eqs. (10) and (14), we have

$$H^{++}_{xx} = H^{--}_{xx} + H^{00}_{xx} = H^{++}_{xx} + H^{00}_{xx}.$$ (B.6)

B.2. Off-diagonal elements

Using the TR symmetry, Eqs. (10) and (14), we have

$$H^{\alpha \beta} = H^{++}_{\alpha \beta} = H^{00}_{\alpha \beta} = 0.$$ (B.7)

We define

$$H^{0+0}_{xx} = (H^{0+0}_{\beta \beta})^* = H^{0-0}_{\beta \beta} = (H^{0-0}_{\alpha \alpha})^* = (H^{0+0}_{\alpha \alpha})^*.$$ (B.8)

$$H^{0-0}_{xx} = (H^{0-0}_{\beta \beta})^* = H^{0+0}_{\beta \beta} = (H^{0+0}_{\alpha \alpha})^* = (H^{0-0}_{\alpha \alpha})^*.$$ (B.9)

$$H^{+\alpha\beta}_{\alpha \beta} = (H^{+\alpha\beta}_{\beta \alpha})^* = H^{+\beta\alpha}_{\beta \alpha} = (H^{+\beta\alpha}_{\alpha \beta})^* = (H^{+\alpha\beta}_{\alpha \beta})^* = (H^{+\beta\alpha}_{\beta \alpha})^*.$$ (B.10)

$$H^{+\alpha\beta}_{\alpha \beta} = (H^{+\alpha\beta}_{\alpha \beta})^* = (H^{+\alpha\beta}_{\alpha \beta})^* = (H^{+\alpha\beta}_{\alpha \beta})^* = (H^{+\alpha\beta}_{\alpha \beta})^*.$$ (B.11)

$$H^{+\alpha\beta}_{\alpha \beta} = (H^{+\alpha\beta}_{\alpha \beta})^* = (H^{+\alpha\beta}_{\alpha \beta})^* = (H^{+\alpha\beta}_{\alpha \beta})^* = (H^{+\alpha\beta}_{\alpha \beta})^*.$$ (B.12)
Using the above definitions, Eq. (B.1) can be written as

<table>
<thead>
<tr>
<th>$\psi_{+\alpha}$</th>
<th>$\psi_{0\alpha}$</th>
<th>$\psi_{-\alpha}$</th>
<th>$\psi_{+\beta}$</th>
<th>$\psi_{0\beta}$</th>
<th>$\psi_{-\beta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{\alpha}$</td>
<td>$E_{\Sigma,1/2}$</td>
<td>$L$</td>
<td>$G$</td>
<td>$0$</td>
<td>$-H$</td>
</tr>
<tr>
<td>$H_{\beta}$</td>
<td>$E_{\Pi,1/2}$</td>
<td>$L$</td>
<td>$G$</td>
<td>$0$</td>
<td>$-H$</td>
</tr>
<tr>
<td>$H_{\gamma}$</td>
<td>$E_{\Pi,1/2}$</td>
<td>$L$</td>
<td>$G$</td>
<td>$0$</td>
<td>$-H$</td>
</tr>
</tbody>
</table>

(B.13)

The electrostatic part of the electronic Hamiltonian $H_{es}$ contributes to matrix elements with the basis functions involving identical spin eigenstates. Hence the matrix elements $\mathcal{L}$ and $\mathcal{G}$ will have contributions from the electrostatic Hamiltonian. The contribution of $H_{SO}$ to the matrix elements of the electronic Hamiltonian is determined in the following way,

$$\mathcal{L}_{SO} = \langle \psi_{+z} | H_{SO} | \psi_{0z} \rangle = \frac{1}{2} \langle \psi_{+z} | A_x | \psi_{0z} \rangle = 0,$$

(B.14)

$$\mathcal{G}_{SO} = \langle \psi_{+z} | H_{SO} | \psi_{-z} \rangle = \frac{1}{2} \langle \psi_{+z} | A_z | \psi_{-z} \rangle = 0,$$

(B.15)

$$\mathcal{D}_{SO} = \langle \psi_{+z} | H_{SO} | \psi_{+\beta} \rangle = \frac{1}{2} \langle \psi_{+z} | A_x - i A_y | \psi_{+\beta} \rangle \neq 0,$$

(B.16)

$$\mathcal{G}_{SO} = \langle \psi_{0z} | H_{SO} | \psi_{+\beta} \rangle = \frac{1}{2} \langle \psi_{0z} | A_x - i A_y | \psi_{+\beta} \rangle \neq 0,$$

(B.17)

$$\mathcal{H}_{SO} = \langle \psi_{0z} | H_{SO} | \psi_{-\beta} \rangle = \frac{1}{2} \langle \psi_{0z} | A_x - i A_y | \psi_{-\beta} \rangle \neq 0.$$

(B.18)

The matrix elements of the electronic Hamiltonian are expanded in a Taylor series up to second-order in the degenerate bending mode ($Q_{\pm}$). The terms with appropriate symmetry with respect to the symmetry operation $J_{\pm}(\epsilon)$ on the corresponding electronic matrix elements survive. Using Eq. (13), it is found that the matrix element $\mathcal{G}$ is of zeroth-order in the expansion; $\mathcal{L}$ and $\mathcal{D}$ are of first-order; while $\mathcal{G}$ and $\mathcal{H}$ are of second-order.

The following abbreviations are introduced to arrive at the final form of the $6 \times 6$ vibronic Hamiltonian (15):

$$\mathcal{G}^{0}(\epsilon) = g \left( \frac{\partial \mathcal{L}}{\partial Q_{+}} \right)_0 = \lambda \left( \frac{\partial \mathcal{G}}{\partial Q_{+}} \right)_0 = d,$$

(B.19)

$$\left( \frac{\partial \mathcal{G}}{\partial Q_{-}} \right)_0 = c \left( \frac{\partial \mathcal{H}}{\partial Q_{-}} \right)_0 = h.$$

**References**