POTENTIAL CURVES FOR BENDING VIBRATIONS IN THE RENNER EFFECT

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The decoupling conditions for the vibronic equation of the Renner effect are analysed. For the higher vibronic states the proposed decoupling procedure is shown to be sufficiently accurate and leads to separate effective potentials for nuclear movements.

In electronically degenerate states of linear polyatomic molecules strong coupling of the electronic motions with the degenerate bending vibrations occurs [1, 2]. The Born-Oppenheimer approximation is valid no more for such a case, and vibronic coupling which results lead to significant changes in the optical properties of molecules. The degeneracy of vibronic states is removed and the optical selection rules are changed. The sum of the electronic and vibrational angular momenta is now a good quantum number although neither electronic nor vibrational angular momentum is separately. In such a case a two--dimensional matrix Hamiltonian describes the nuclear motions and no separate (single valued) potentials for the nuclear motions are determined at all.

In this note we shall study the conditions under which the vibrations strongly coupled with the electronic motions can be connected with a given potential curve. We consider a three atomic linear molecule in an electronic state of type Π and suppose all other electronic states to be well separated. In this case the stretching vibration does not couple with electronic motions, and the vibronic wavefunction has the form [2]:

$$\Psi(q, Q_0, Q_x, Q_y) = \alpha(Q_0) \left[\Psi_+(q)\, \eta_+(Q_x, Q_y) + \Psi_-(q)\, \eta_-(\hat{Q}_x, Q_y) \right] \qquad (1)$$

where Q_0 denotes the normal coordinate for the stretching vibration, and Q_x, Q_y denote the bending ones. $\Psi_+(q)$ and $\Psi_-(q)$ are the degenerate electronic functions which depend parametrically on the nuclear normal coordinates, and η_+, η_- are vibronic functions which are to be determined.

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Insertion of (1) into the Schrödinger equation of a molecule, integration over electronic coordinates, and separation of the stretching mode leads to the following equation determining η_+ and η_- [2]:

$$
\begin{pmatrix}
\dfrac{1}{2}\lambda\varrho^2 + \dfrac{1}{2M\varrho^2}[(\varrho P_\varrho)^2 + P_\Phi^2] & \dfrac{1}{2}\varepsilon\lambda\varrho^2 \overline{e}^{2i\Phi} \\[2mm]
\dfrac{1}{2}\varepsilon\lambda\varrho^2 e^{2i\Phi} & \dfrac{1}{2}\lambda\varrho^2 + \dfrac{1}{2M\varrho^2}[(\varrho P_\varrho)^2 + P_\Phi^2]
\end{pmatrix}
\begin{pmatrix}
\eta_+(\varrho,\Phi) \\
\eta_-(\varrho,\Phi)
\end{pmatrix}
= E\begin{pmatrix}\eta_+ \\ \eta_-\end{pmatrix},
\tag{2}
$$

where

$$
\varrho = (Q_x^2 + Q_y^2)^{1/2}, \quad \Phi = \operatorname{arctg}\frac{Q_x}{Q_y}, \tag{3a}
$$

$$
W(Q_0) + \frac{1}{2}\lambda\varrho^2 = \int \psi_+^* H(Q)\psi_+ dq = \int \psi_-^* H(Q)\psi_- dq, \tag{3b}
$$

$$
\frac{1}{2}\varepsilon\lambda\varrho^2 e^{-2i\Phi} = \int \psi_+^* H(Q)\psi_- dq = \left(\int \psi_-^* H(Q)\psi_+ dq\right)^*, \tag{3c}
$$

and higher than quadratic terms in normal coordinates in development of electronic matrix elements were neglected. $W(Q_0)$ is the function of the stretching mode and is not intersesting for us, ε is the coupling constant in the Renner effect, λ is the force constant for an unperturbed problem, P_ϱ and P_Φ are the momenta canonically conjugated with coordinates ϱ, Φ, and $H(Q)$ is the Hamiltonian of electrons with fixed position of nuclei.

Putting

$$
\begin{pmatrix}\eta_+ \\ \eta_-\end{pmatrix} = \begin{pmatrix} R_+^K(\varrho)\, e^{i(K-1)\Phi} \\ R_-^K(\varrho)\, e^{i(K+1)\Phi}\end{pmatrix}, \quad \begin{pmatrix} R_+^K \\ R_-^K \end{pmatrix} = \chi^K \tag{4}
$$

we obtain

$$
H^K\chi^K = E^K\chi^K
$$

and

$$
H^K = \left[\frac{1}{2}\lambda\varrho^2 + \frac{(\varrho P_\varrho)^2}{2M\varrho^2} + \frac{\hbar^2(K^2+1)}{2M\varrho^2}\right]\mathbf{1} - \frac{K\hbar^2}{M\varrho^2}\sigma_3 + \frac{1}{2}\varepsilon\lambda\varrho^2\sigma_1 \tag{5}
$$

where K is the quantum number of the total angular momentum (sum of electronic and vibrational ones in an electronic π state), and σ_i are the Pauli matrices.

Introduce

$$
\chi^K = \frac{1}{\sqrt{2}}\begin{pmatrix} R_+^K + R_-^K \\ R_+^K - R_-^K \end{pmatrix} \equiv \begin{pmatrix} R_1^K \\ R_2^K \end{pmatrix}
$$

then

$$
\tilde{H}^K = \left[\frac{1}{2}\lambda\varrho^2 + \frac{P_\varrho^2}{2M} - \frac{i\hbar}{2M\varrho}P_\varrho + \frac{\hbar^2(K^2+1)}{2M\varrho^2}\right]\mathbf{1} + \frac{1}{2}\varepsilon\lambda\varrho^2\sigma_3 - \frac{K\hbar^2}{M\varrho^2}\sigma_1 \tag{6}
$$

and the term proportional to $\boldsymbol{\sigma}_1$ couples electronic and nuclear motions. We introduce now the dimensionless quantities, as follows

$$q = \varrho \left(\frac{M\omega}{\hbar}\right)^{1/2}, \, p = \boldsymbol{P}_\varrho(\hbar M\omega)^{-1/2}, \, \omega^2 = \frac{\lambda}{M} \tag{7}$$

then

$$\frac{\tilde{\boldsymbol{H}}^K}{\hbar\omega} = \left[\frac{1}{2} (p^2 + q^2) - \frac{i}{2q} p + \frac{K^2 + 1}{2q^2}\right] \mathbf{1} + \frac{1}{2} \varepsilon q^2 \boldsymbol{\sigma}_3 - \frac{K}{q^2} \boldsymbol{\sigma}_1 \tag{8}$$

We put $K \neq 0$ and transform the Hamiltonian (8) by the unitary transformation

$$\boldsymbol{H}'^K = \boldsymbol{U}\tilde{\boldsymbol{H}}^K\boldsymbol{U}^{-1} \tag{9a}$$

where

$$\boldsymbol{U} = \cos\alpha \cdot \boldsymbol{\sigma}_3 + \sin\alpha \cdot \boldsymbol{\sigma}_1 \tag{9b}$$

$$\operatorname{ctg} 2\alpha = -\frac{\varepsilon}{2K} q^4 \tag{9c}$$

then

$$\frac{\boldsymbol{H}'^K}{\hbar\omega} = \left[\frac{1}{2} (p^2 + q^2) + \frac{K^2 + 1}{2q^2} - \frac{i}{2q} p + \frac{1}{2} \left(\frac{d\alpha}{dq}\right)^2\right] \mathbf{1} +$$

$$+ \frac{1}{2q^2} \sqrt{\varepsilon^2 q^8 + 4K^2} \, \boldsymbol{\sigma}_3 + \frac{d\alpha}{dq} \boldsymbol{\sigma}_2 \cdot p - \frac{i}{2} \frac{d^2\alpha}{dq^2} \boldsymbol{\sigma}_2 - \frac{i}{2q} \frac{d\alpha}{dq} \boldsymbol{\sigma}_2 \tag{10}$$

We note that all terms proportional to $\boldsymbol{\sigma}_2$ have upper limits, namely

$$\left|\frac{d\alpha}{dq}\right| \leqslant \left(\frac{\varepsilon}{K}\right)^{1/4}, \quad \left|\frac{d^2\alpha}{dq^2}\right| \leqslant 2 \left(\frac{\varepsilon}{K}\right)^{1/2}; \quad \left|\frac{1}{q} \frac{d\alpha}{dq}\right| \leqslant \left(\frac{\varepsilon}{K}\right)^{1/2} \tag{11}$$

Assuming that derivatives of R_1 and R_2 are not excessively high we may neglect the coupling terms in (10) if only the term proportional to $\boldsymbol{\sigma}_3$ is larger than the largest term with $\boldsymbol{\sigma}_2$ in the whole region of the q-space. It is easy to see that we have always

$$\frac{1}{2q^2} (\varepsilon^2 q^8 + 4K^2)^{1/2} \gg K \left(\frac{\varepsilon}{K}\right)^{1/2} \tag{12}$$

Also the condition for neglecting the nondiagonal terms in (10) reads

$$\text{for} \quad \varepsilon \leqslant K, \quad K^3 \varepsilon \gg 1$$

$$\text{for} \quad \varepsilon > K, \quad K \gg 1 \tag{13}$$

and practically for all vibronic states for which the quantum number K satisfies $K^3 \gg \varepsilon^{-1}$ we can obtain two uncoupled equations which determine the functions R_1 and R_2. The condition (13) can be hardly satisfied for vibronic Π-states. The solutions of the so-obtained

uncoupled equations give better approximation for vibronic states with larger quantum number K. Substitute

$$\tilde{\chi}^K = \Phi^K q^{-\frac{1}{2}}; \quad \Phi^K = \begin{pmatrix} \varphi_+^K(q) \\ \varphi_-^K(q) \end{pmatrix} \tag{14}$$

then we obtain

$$\left[\frac{1}{2} p^2 + V_{\pm,K}^{\text{eff}}(q) \right] \varphi_\pm^K(q) = E_\pm^K \varphi_\pm^K(q) \tag{15}$$

where

$$V_{\pm,K}^{\text{eff}}(q) = \frac{1}{2} q^2 + \frac{4K^2+3}{8q^3} \pm \frac{(\varepsilon^2 q^8 + 4K^2)^{\frac{1}{2}}}{2q^2}, \tag{16}$$

and

$$\begin{pmatrix} R_+^K(q) \\ R_-^K(q) \end{pmatrix} = \frac{q^{-\frac{1}{2}}}{\sqrt{2}} \left[(\cos\alpha + \sin\alpha)\, \mathbf{1} - i(\cos\alpha - \sin\alpha)\boldsymbol{\sigma_2} \right] \begin{pmatrix} \varphi_+^K(q) \\ \varphi_-^K(q) \end{pmatrix} \tag{17}$$

Therefore for $K = 2, 3, 4\ldots$ and not too small ε the functions R_+^K, R_-^K can be obtained from the solution of the Schrödinger equation with an effective potential (16) which includes the effect of the electronic-vibrational coupling. We now see that for $K = 0$, equation (6) is uncoupled and gives (15) with $V_{\pm,0}^{\text{eff}}(q)$, therefore also the vibronic states with $K = 0$ can be obtained from (15).

We see that we can speak about the potential energy of vibrations only for vibronic states with a sufficiently large projection of the total angular momentum on the long axis of the molecule, i. e., for Δ, Φ, Γ, ... states including also Σ states, providing that the coupling parameter ε is not too small. Vibronic Π-states are practically never connected with any potential curve in a simple sense, and a one-dimensional effective Hamiltonian for such states cannot be obtained.

We see, further, that in this sense large angular momentum number and a not too small coupling parameter ε in the Renner effect is an analogue of the strong coupling in vibronic effects in dimers [3].

The difference in potentials in the "plus" and "minus" modes leads to the splitting of all previously degenerate vibronic levels. Equation (15) should be solved numerically as analytical solutions are not available.

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