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# PRE-RESONANCE RAMAN SCATTERING BY THE *t*-TYPE MODE NEAR THE $A \to T$ ELECTRONIC TRANSITION*

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The excitation profiles (EP) and dispersion of the depolarization ratios (DD) for the two first lines of the *t*-type vibration in preresonance Raman scattering are analysed. It is shown that small changes in the quadratic Jahn–Teller coupling within $T \times t$ vibronic states may change considerably the EP and DD of the first overtone in the near-resonance range.

## 1. *Introduction*

It is well known that in the non-degenerate excited electronic states a quadratic vibronic coupling leads to changes in frequency of the active mode. This coupling gives two important effects in the low-temperature absorption spectrum. Firstly, we get the blue or red shift for the vibronic progression of the absorption spectrum. The directions of these shifts depend on the sign of the difference between the vibration frequencies in the excited and ground electronic states. Secondly, we can observe the broadening of the absorption spectrum. In the degenerate excited electronic states in which the degenerate vibrations are Jahn–Teller active, the quadratic coupling can provide additional effects especially in Resonance Raman Scattering (RRS).

Recently, we analysed the RRS in molecules which possessed the doubly degenerate state coupled by the *e*-type mode [1]. It was shown that the quadratic coupling causes activation of new channels in RRS. Consequently, we observe the dispersion of depolarization ratios for overtones of the *e*-type vibration. It should be noted, however, that the weak quadratic coupling only very weakly modifies the absorption spectrum.

An analysis of RRS for molecules with triple degenerate excited states leads to a similar conclusion for the DD for overtones of the *e*-type vibration in the resonance region of scattering [2]. When the energy of laser light is smaller than the energy of $A \to T$ elec-

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tronic transition (pre-resonance Raman Scattering, PRRS) the dispersion or depolarization ratios can exhibit extremes due to the presence of quadratic coupling within the $T\times e$ vibronic states. In the absence of quadratic coupling, the depolarization ratios are equal to 3/14 and 9/22 for the first and second overton, respectively. On the other hand, for triply degenerate modes which are active in the $T\times t$ vibronic states, the DD for overtons also exists when the quadratic Jahn–Teller coupling vanishes. In the off-resonance region, however, for the weak and intermediate linear Jahn-Teller coupling, the depolarization ratios tend asymptotically to 1/4 and 1/2 for first and second overtones. Simultaneously, the intensities of these lines increase monotonously with the energy of laser light. These conclusions do not hold when we take into account a quadratic coupling within the $T\times t$ vibronic states.

In this paper, we investigate in detail the EP and DD curves for the fundamental line and the first overton of the $t$-type vibration in the pre-resonance region. We will show that the three types of quadratic interactions which are possible in $T\times t$ vibronic states lead to important changes in the distribution of intensity for the first overtone. As an example, for the EP of this line, instead of the monotonous decay of intensity we can obtain the minimum of intensity in the off-resonance region. In this region the DD curve may have two extremes with positions that are strongly altered by quadratic interactions.

## 2. *The model*

Let us consider the simple molecular model using the following assumptions:

(*i*) The triply degenerate singlet excited electronic state that contributes to scattering is coupled only by one triply degenerate harmonic oscillation. This oscillation has the normal co-ordinates, $Q_{xy}$, $Q_{xz}$, $Q_{yz}$, which transform as $xy$, $xz$, $yz$, respectively. For simplicity, we assume that the triply degenerate state under consideration is well separated in the Born–Oppenheimer sense from other electronic states.

(*ii*) The electronic ground state is totally symmetric and is decoupled from other electronic states. In this case, the vibronic wavefunctions are the simple products of crude adiabatic electronic function and the vibrational functions. The vibrational functions which are important in a discussion of the fundamental line and first overton have the form [2]:

$$\phi_1(T_{2xy}) = \phi_{100},$$

$$\phi_2(A_1) = \frac{1}{\sqrt{3}}(\phi_{200}+\phi_{020}+\phi_{002}), \qquad \phi_2(T_{2xy}) = \phi_{011},$$

$$\phi_2(E_\theta) = \frac{1}{\sqrt{6}}(\phi_{200}+\phi_{020}-2\phi_{002}). \tag{1.1}$$

(*iii*) Further we assume that the vibronic coupling in the $T$ electronic state is realized by a linear and quadratic interaction. It is well known that the quadratic interaction for the $t$-type vibration in the $T$ electronic state is composed of three types of elements [4]. Each of these elements belongs to a different representation of the octahedral or tetrahedral point groups. These elements are:

$$B_0^{(a)} = Q_{xy}^2+Q_{xz}^2+Q_{yz}^2, \tag{1.2a}$$

$$B_\theta^{(e)} = Q_{yz}^2+Q_{xz}^2-2Q_{xy}^2, \quad B_\varepsilon^{(e)} = -\sqrt{3}\,(Q_{xz}^2-Q_{yz}^2), \tag{1.2b}$$

$$B_{xy}^{(t)} = Q_{xz}Q_{yz}, \quad B_{xz}^{(t)} = Q_{xy}Q_{yz}, \quad B_{yz}^{(t)} = Q_{xy}Q_{xz}, \tag{1.2c}$$

where the superscripts refer to the symmetry of each components. The elements (1.2a), (1.2b) are connected with the diagonal parts of the matrix of coupling (vide infra) and this leads to changes of the frequency in the excited electronic state. The element (1.2c) mixes the electronic functions with different polarizations.

With these assumptions, the vibronic hamiltonian in the matrix form may be written as:

$$\boldsymbol{H} = 1(\hat{h}_0+E_0)+\frac{\alpha}{\sqrt{\omega}}\boldsymbol{A}+\left(\frac{\alpha}{\sqrt{\omega}}\right)^2\boldsymbol{B} \tag{1.3}$$

with

$$\hat{h}_0 = \frac{\omega}{2}\sum_{\mu=xy,xz,yz}(P_\mu^2+Q_\mu^2), \tag{1.4}$$

$$\boldsymbol{A} = Q_{xy}\boldsymbol{\sigma}_{xy}+Q_{xz}\boldsymbol{\sigma}_{xz}+Q_{yz}\boldsymbol{\sigma}_{yz}, \tag{1.4a}$$

$$\boldsymbol{B} = 2/3\eta_a\mathbf{1}B_0^{(a)}+1/3\eta_e(\boldsymbol{\sigma}_\theta B_\theta^{(e)}+\boldsymbol{\sigma}_\varepsilon B_\varepsilon^{(e)})+\eta_t(\boldsymbol{\sigma}_{xy}B_{xy}^{(t)}+\boldsymbol{\sigma}_{xz}B_{xz}^{(t)}+\boldsymbol{\sigma}_{yz}B_{yz}^{(t)}), \tag{1.4b}$$

where $\alpha$, $\omega$ are the linear Jahn–Teller parameters and the vibration frequency, respectively, $E_0$ is the vertical electronic excitation energy and $\eta_a$, $\eta_e$, $\eta_t$ are the quadratic Jahn–Teller parameters. The matrix $\boldsymbol{\sigma}_\mu$ for $\mu = \theta, \varepsilon, xy, xz, yz$ has the following form:

$$\mathbf{1} = \begin{Bmatrix}1, & 0, & 0\\ 0, & 1, & 0\\ 0, & 0, & 1\end{Bmatrix}, \quad \boldsymbol{\sigma}_\theta = 1/2\begin{Bmatrix}1, & 0, & 0\\ 0, & 1, & 0\\ 0, & 0, & -2\end{Bmatrix}, \quad \boldsymbol{\sigma}_\varepsilon = \sqrt{3}/2\begin{Bmatrix}1, & 0, & 0\\ 0, & -1, & 0\\ 0, & 0, & 0\end{Bmatrix},$$

$$\boldsymbol{\sigma}_{xy} = \begin{Bmatrix}0, & 1, & 0\\ 1, & 0, & 0\\ 0, & 0, & 0\end{Bmatrix}, \quad \boldsymbol{\sigma}_{xz} = \begin{Bmatrix}0, & 0, & 1\\ 0, & 0, & 0\\ 1, & 0, & 0\end{Bmatrix}, \quad \boldsymbol{\sigma}_{yz} = \begin{Bmatrix}0, & 0, & 0\\ 0, & 0, & 1\\ 0, & 1, & 0\end{Bmatrix}. \tag{1.5}$$

As mentioned above, both diagonal terms in Eq. (1.4b) lead to a change in the frequency of vibration in the excited state. However, the parameters $\eta_b$, $\eta_e$ modify the excitation profiles and DD curves for overtones in a different way. In particular, for the first overtone, the changes $\eta_a$, $\eta_e$ alter the distribution of intensity of the channels $A \to A$, $A \to E$. Similarly, the parameter $\eta_t$, alters the intensity of the channel $A \to T_2$. The consequences of these changes in PRRS for the first overtone are discussed in Section 4.

### 3. Pre-resonance Raman scattering

We will consider the Stokes Raman scattering when the energy of laser light is smaller by several vibration quanta than the energy of the $A \to T$ electronic excitation. If we additionally assume that only the $T$ electronic state contributes to scattering, we can apply the time-independent Green's function of the operator (1.3) to the description of PRRS. The tensor elements can be expressed as the trace of the products of the Green function and the matrices (1.5). For the channels: $A_1 \to A_1$, $A_1 \to E$, $A_1 \to T_2$, the tensor elements have the following form:

$$S_n = \frac{c}{3} \sum_{s=+,-} \langle \phi_n(A_1) | \operatorname{Tr} [\mathbf{1}\hat{G}_s] | \phi_0(A_1) \rangle,$$

$$q_n = \frac{2c}{3} \sum_{s=+,-} \langle \phi_n(E_\theta) | \operatorname{Tr} [\sigma_\theta \hat{G}_s] | \phi_0(A_1) \rangle,$$

$$r_n = \frac{c}{2} \sum_{s=+,-} \langle \phi_n(T_{2xy}) | \operatorname{Tr} [\sigma_{xy} \hat{G}_s] | \phi_0(A_1) \rangle, \tag{2.1}$$

where $\langle \ldots \rangle$ denotes the integration over the normal co-ordinates of the vibration, $c$ is the constant which is proportional to the square of the dipole transition moment and the index $n = 1, 2$ refers to the fundamental line and first overtone. As for RRS [2], [3], we have also $S_1 = q_1 = 0$, $r_1 \neq 0$ and $S_2 \neq 0$, $q_2 \neq 0$, $r_2 \neq 0$. The Green functions $\hat{G}_-$, $\hat{G}_+$ correspond to the resonance and antiresonance parts of the tensor. Both the functions satisfy Dyson's equation,

$$\hat{G}_\pm(\Omega_\pm) = \mathbf{1}\hat{g}_\pm(\Omega_\pm) - \hat{G}_\pm(\Omega_\pm) W \hat{g}_\pm(\Omega_\pm) \tag{2.2}$$

with

$$\hat{g}_\pm(\Omega_\pm) = (\hat{h}_0 + E_0 \pm \Omega_\pm - i\Gamma)^{-1}, \tag{2.2a}$$

where $\Omega_-$, $\Omega_+ (= \Omega_- - n\omega)$ are the energies for the incoming (laser) and outgoing (scattered) light. $\Gamma$ is a positive constant. The matrix, $W$, is the sum of the two last terms in the hamiltonian (1.3). It is easy to see from (2.2), (1.3) and (1.4a)–(1.4b) that $\hat{G}_\pm$ can be expanded in the power series into $\alpha/\sqrt{\omega}$. Assuming that the linear Jahn–Teller interaction is weak, i.e., $\alpha/\sqrt{\omega}$ is small, the power series can be cut off on the third term. We obtain

$$\hat{G}_\pm = \mathbf{1}\hat{g}_\pm - \alpha/\sqrt{\omega}\, \hat{g}_\pm A \hat{g}_\pm + (\alpha/\sqrt{\omega})^2 \hat{g}_\pm (A \hat{g}_\pm A - B) \hat{g}_\pm. \tag{2.3}$$

The first, second and third terms contribute to the Rayleigh line, fundamental line and first overtone. This follows from the parity of these terms and the parity of the function (1.1). Inserting (2.3) into (2.1) and taking into account (1.1) after algebraic calculations, we obtain for the fundamental line,

$$r_1 = \frac{\alpha/\sqrt{\omega}}{\sqrt{2}} \sum_{s=+,-} \langle \hat{g}_s \rangle_1 \langle \hat{g}_s \rangle_0 \tag{2.4}$$

and for the first overtone

$$S_2 = \frac{2(\alpha/\sqrt{\omega})^2}{\sqrt{6}} \sum_{s=+,-} \langle \hat{g}_s\rangle_2 \langle \hat{g}_s\rangle_1 \langle \hat{g}_s\rangle_0 \left(1 - \frac{\eta_a}{\langle \hat{g}_s^{-1}\rangle_1}\right),$$

$$q_2 = \frac{-(\alpha/\sqrt{\omega})^2}{\sqrt{3}} \sum_{s=+,-} \langle \hat{g}_s\rangle_2 \langle \hat{g}_s\rangle_1 \langle \hat{g}_s\rangle_0 \left(1 - \frac{\eta_e}{\langle g_s^{-1}\rangle_1}\right),$$

$$r_2 = \frac{(\alpha/\sqrt{\omega})^2}{2} \sum_{s=+,-} \langle \hat{g}_s\rangle_2 \langle \hat{g}_s\rangle_1 \langle \hat{g}_s\rangle_0 \left(1 - \frac{\eta_t}{\langle g_s^{-1}\rangle_1}\right), \tag{2.5}$$

where $\langle \hat{g}_\pm \rangle_k$ is defined as

$$\langle \hat{g}_\pm \rangle_k = (\omega k + E_0 \pm \Omega_\pm - i\Gamma)^{-1}. \tag{2.6}$$

In the next step we will use Eqs. (12), (13) from [2].

Assuming that the molecule is randomly oriented, the depolarization ratios and excitation profiles for the fundamental line and first overtone can be calculated from

$$\theta_n \sim 10|S_n|^2 + 7|q_n|^2 + 14|r_n|^2,$$

$$\varrho_n = \frac{6|r_n|^2 + 3|q_n|^2}{10|S_n|^2 + 7|q_n|^2 + 14|r_n|^2}. \tag{2.7}$$

The elements (2.4), (2.5) with (2.7) are the starting point for the considerations discussed in the next section.

## 4. *Results and discussion*

Firstly, it should be noted that in our approximation the excitation profile of the fundamental line does not show any unusual properties. We observe only that the intensity of this line increases directly with the energy of laser light. The depolarization ratio is equal to 3/4. This is far from the resonance where $|E_0 \pm \Omega_\pm| \gg \omega$. From Eqs. (2.4) and (2.7) we can obtain:

$$\theta_1 \sim \frac{4(E_0^2 + \Omega_-^2)^2}{(E_0^2 - \Omega_-^2)^4}. \tag{3.1}$$

Multiplying Eq. (3.1) by $\Omega_+^4$, we obtain the intensity of the fundamental line which is consistent with Albrecht's theory [6]. For the first overtone, however, the changes introduced by the quadratic Jahn–Teller interaction are quite remarkable. The representative samples of calculations for $\varrho_2$ and $\theta_2$ obtained from Eqs (2.5) and (2.7) are shown in Figs 1 and 2. We see that for the excitation profile the quadratic interactions can produce the minimum

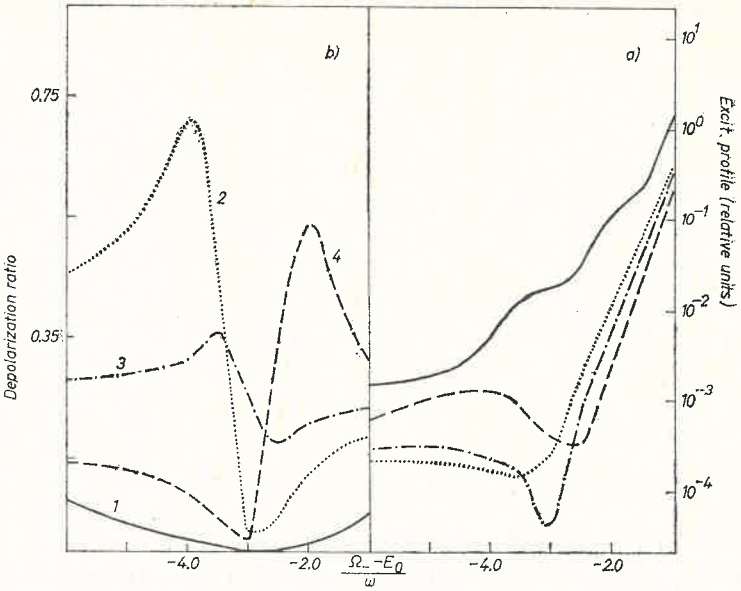

Fig. 1. Excitation profiles (a) and depolarization ratios (b) for the first overtone. The parameters are: $\eta_e = 0.25$, $\eta_t = 0\ 25$, $E_0 = 15$, $\Gamma = 0.2$ (in units $\omega$); *1* — $\eta_a = -0.10$, *2* — $\eta_a = 0.20$, *3* — $\eta_a = 0.24$, *4* — $\eta_a = 0.30$

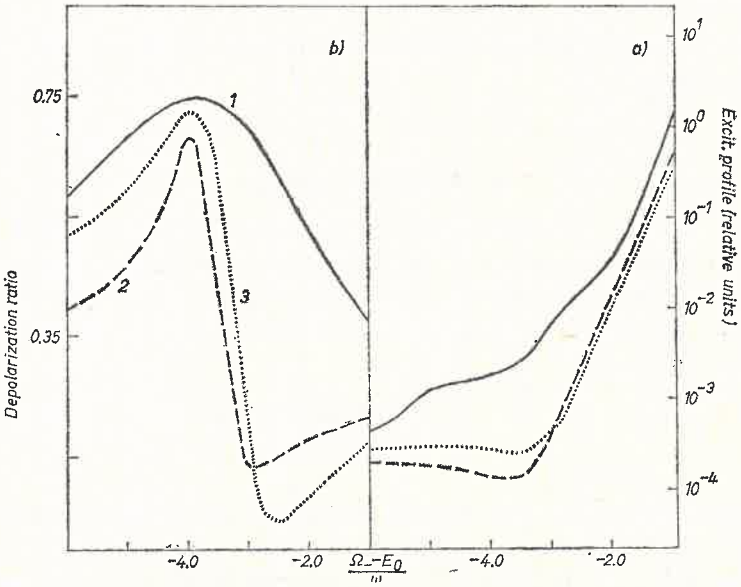

Fig. 2. Excitation profiles (a) and depolarization ratios (b) for the first overtone. The parameters are: $\eta_a = 0.20$, $\eta_t = 0.25$, $E_0 = 15$, $\Gamma = 0.2$ (in units $\omega$); *1* — $\eta_e = -0.10$, *2* — $\eta_e = 0.20$, *3* — $\eta_e = 0.30$

near the resonance. Indeed, neglecting for simplicity the antiresonance terms in Eq. (2.5), we can find the simple formula for $\theta_2$ which is

$$\theta_2 \sim Z(\tilde{\Omega})\,\{40[1+\eta_a(\tilde{\Omega}-\omega)]^2+21[1+\eta_t(\tilde{\Omega}-\omega)]^2 + 14[1+\eta_e(\tilde{\Omega}-\omega)]^2+(40\eta_a^2+21\eta_t^2+14\eta_e^2)\Gamma^2\} \tag{3.2}$$

with

$$Z(\tilde{\Omega}) = [\tilde{\Omega}^2+\Gamma^2]^{-1}[(\tilde{\Omega}-\omega)^2+\Gamma^2]^{-1}[(\tilde{\Omega}-2\omega)^2+\Gamma^2]^{-1}, \tag{3.2a}$$

where $\tilde{\Omega} = E_0-\Omega_-$ is the energy of laser light calculated from the "vertical" electronic calculation. From Eq. (3.2) we see that the minimum is strongly marked when $\eta_a = \eta_e = \eta_t > 0$. In other cases, the excitation profile changes in a different manner. Particularly, when all parameters of the quadratic coupling are negative the minimum does not lie in the pre-resonance region. Figs. 1b, 2b show several dispersion curves which correspond to the excitation profile in Figs 1a, 2a. Now we see that the quadratic coupling also significantly changes the dispersion of the depolarization ratio. In particular, we can observe the minimum and maximum near the resonance. Assuming for simplicity that the anti-resonance terms are neglected and additionally putting $\Gamma = 0$ into Eq. (2.5), the depolarization ratio can be approximated by

$$\varrho_2 = \frac{3}{4}\,\frac{2[1+\eta_e(\tilde{\Omega}-\omega)]^2+3[1+\eta_t(\tilde{\Omega}-\omega)]^2}{10[1+\eta_a(\tilde{\Omega}-\omega)]^2+2[1+\eta_e(\tilde{\Omega}-\omega)]^2+3[1+\eta_t(\tilde{\Omega}-\omega)]^2}. \tag{3.3}$$

Now, we see clearly that the depolarization ratio has extremes at

$$\tilde{\Omega}_{\max} = \omega-\eta_a^{-1}, \qquad \tilde{\Omega}_{\min} = \omega-\frac{3(\eta_t-\eta_a)+2(\eta_e-\eta_a)}{3(\eta_t-\eta_a)\eta_t+2(\eta_e-\eta_a)\eta_e}. \tag{3.4}$$

It is easy to see from Eq. (3.4) that small changes in the quadratic Jahn–Teller parameters can introduce large changes for $\tilde{\Omega}_{\min}$ and $\tilde{\Omega}_{\max}$. In consequence this can alter dramatically the depolarization dispersion. Of course, for $\eta_a = \eta_e = \eta_t$, the dispersion of the depolarization ratio does not appear because the ratios $|S_2/q_2|$ and $|S_2/r_2|$ from Eqs (2.5) are constant. In particular, the depolarization ratio, $\varrho_2$, is equal to 1/4 when we only take into account the linear Jahn–Teller effect. This is also true for the intermediate linear Jahn–Teller coupling [2]. Therefore, we conclude that in the range of weak and intermediate linear coupling, the DD and EP of the first overtone depend mainly on quadratic coupling. For strong linear coupling our results are not correct because the power series (2.3) is too short. In this case, the EP and DD curves depend strongly on the linear Jahn–Teller interaction and a numerical treatment is more appropriate.

Finally, it should be noted that the presence of other vibrations, i.e., totally symmetric and doubly degenerate ones, only quantitatively perturbes the results reported here. First of all, the presence of Franck–Condon factors of *a*-type and *e*-type modes in Eqs. (2.5) can cause the shifts in the EP and DD curves. Simultaneously, the shapes of the EP and DD curves are only insignificantly modified. In this context, we believe that our results can be used to estimate the quadratic Jahn–Teller interactions within triply degenerate electronic states.

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