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THEORY OF A RESONANCE RAMAN SCATTERING FROM A NON-TOTALLY SYMMETRIC MODE THAT WEAKLY COUPLES THREE ELECTRONIC STATES. NAPHTHALENE*

By M. Z. Zgierski

Department of Theoretical Chemistry, Jagellonian University, Cracow**

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The excitation profiles (EP) and depolarization dispersion (DD) of a fundamental line of a non-totally symmetric, non-degenerate mode, that weakly couples three electronic states, two of them being of the same symmetry, are investigated. Such a situation exists, according to recent measurements by Ohta and Ito of a preresonance Raman scattering, in a naphthalene molecule. It is shown that the inclusion of the third electronic state, which is not in resonance with the laser beam, can lead to an extra maximum in DD, owing to interference between scattering from different pairs of electronic states. If this appears in the region of resonance with one of the electronic states, it can profoundly modify EP in this region. EP and DD curves for naphthalene's 511 cm^{-1}, 940 cm^{-1}, and 1163 cm^{-1} b_{1g} modes are calculated using the vibronic coupling parameters obtained by Ito and Ohta.

1. Introduction

The theory of resonance Raman scattering (RRS) has recently been developing very quickly, and it has been pointed out that it is a very powerful tool for investigating the dynamics of nuclei in molecules and couplings between electronic and nuclear motions in molecules (vibronic coupling). An excelent review of RRS in molecules is given in a very recent paper by Jacon, Mortensen and Siebrand [1]. The RRS by a non-totally symmetric mode was investigated in [2, 3]. The fundamental line cross-section can be greatly enhanced in the region of a resonance, only if a resonating electronic state interacts vibronically with some other electronic state via this very mode. This has been predicted a long time ago by Albrecht [4] and has found several experimental confirmations. The main feature of the excitation profile (EP) of such a fundamental line is an asymmetric doublet [3]; the cross-section peaks at $0-0$ and $0-1$ transitions, being larger at the $0-1$ one, because of non-adiabatic interactions. The depolarization dispersion (DD) curve peaks near the halfway point between $0-0$ and $0-1$ transitions, and its maximal value depends critically on the halfwidth, Γ, of intermediate states. Also the inhomogeneous broadening of inter-

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** Address: Instytut Chemii, Uniwersytet Jagielloński, Krupnicza 41, 30-060 Kraków, Poland.

mediate states can change the depolarization ratio [5]. When vibronic coupling starts to increase, but adiabatic potentials of interacting electronic states remain harmonic (harmonic coupling) EP becomes distorted keeping, however, its doublet structure, but DD diminishes and vanishes completely for zero energy gap between interacting electronic states [6]. For increasing anharmonic coupling, when an adiabatic potential of the lower electronic state forms a double minimum (pseudo Jahn-Teller effect) EP looses its doublet character, as Franck-Condon features start to appear [7]. In such a case EP resembles an EP of a totally-symmetric vibration, but the depolarization ratio is 0.75, that is typical for non-degenerate, non-totally symmetric vibrations, and exhibits some dispersion.

In some molecules there exist more than two, low energy, excited electronic states that are coupled by the same vibration. The very well known example forms the naphthalene molecule. The three lowest excited singlet electronic states in naphthalene are: $S_1({}^1B_{3u})$, $S_2({}^1B_{2u})$, and $S_3({}^1B_{3u})$ with electronic energies $E_1 = 32000\ \mathrm{cm}^{-1}$, $E_2 = 35900\ \mathrm{cm}^{-1}$, and $E_3 = 47500\ \mathrm{cm}^{-1}$ [8]. The pairs S_1, S_2 and S_2, S_3 are coupled by b_{1g} type vibrations. In the absorption and single vibronic level (SVL) fluorescence spectra of the first singlet modes $\bar{7}$ and $\bar{8}$ are active, their frequencies being 940 cm^{-1} [9] (938 cm^{-1} [8]), 511 cm^{-1} [9] (506 cm^{-1} [8]), respectively. The numbering of b_{1g} modes in naphthalene is given in [8a]. Ohta and Ito [9] found recently, that the preresonance Raman scattering indicates that other modes, not seen in absorption and SVL fluorescence spectra, are involved in vibronic coupling of the second and third excited singlets of a naphthalene molecule. These are $\bar{3}$, $\bar{4}$, $\bar{5}$, and $\bar{6}$ modes with frequencies equal to 1629 cm^{-1}, 1440 cm^{-1}, 1244 cm^{-1}, and 1164 cm^{-1}, respectively. In deuterated naphthalene also the $\bar{6}$ mode is present in SVL fluorescence spectra, because of the Fermi resonance with the $\bar{7}$ mode [8, 10].

In this paper we will investigate EP and DD curves of b_{1g} modes in a naphthalene molecule, using the vibronic coupling parameters calculated by Ohta and Ito [9]. We will show that the interference between RRS from S_1, S_2 and S_2, S_3 pairs leads to interesting modifications of EP and DD curves of the non-totally symmetric modes involved in vibronic coupling of three electronic states.

2. *General formulation*

Let us consider a molecule with three electronic excited states with the crude-adiabatic electronic wavefunctions ϕ_n^0, ϕ_m^0, and ϕ_k^0. The states ϕ_n^0 and ϕ_k^0 are of the same symmetry, and the state ϕ_m^0 can be vibronically coupled with two others via non-totally symmetric modes of proper symmetry with frequencies ω_{ai} and mass-weighted coordinates Q_{ai}. Next, we assume the coupling to be weak enough, so the adiabatic electronic wavefunctions have the form

$$\phi_n = \phi_n^0 + \sum_i \lambda_i^{nm}(2\omega_{ai})^{1/2} Q_{ai}\phi_m^0, \tag{1a}$$

$$\phi_m = \phi_m^0 - \sum_i \lambda_i^{nm}(2\omega_{ai})^{1/2} Q_{ai}\phi_n^0 + \sum_i \lambda_i^{km}(2\omega_{ai})^{1/2} Q_{ai}\phi_k^0, \tag{1b}$$

$$\phi_k = \phi_k^0 - \sum_i \lambda_i^{km}(2\omega_{ai})^{1/2} Q_{ai}\phi_m^0 \tag{1c}$$

where λ_i^{nm}, λ_i^{km} are the vibronic coupling constants for the i-th mode, and n, m, and k, m pairs of electronic states, respectively. They are given by

$$\lambda_i^{nm} = (2\omega_{ai})^{-1/2} \frac{\langle \phi_n^0 | \frac{\partial h}{\partial Q_{ai}} | \phi_m^0 \rangle}{E_n - E_m} \equiv \frac{h_i^{nm}}{E_n - E_m} \tag{2}$$

h being the electronic hamiltonian of a molecule, and $E_n(E_m)$ are electronic excitation energies of the n-th (m-th) electronic states. A similar relation holds for λ_i^{km}.

We are assuming that frequencies ω_{ai} are the same in all electronic states, including the ground state ϕ_g^0. We also neglect the rotation of vibrational coordinates upon electronic excitation (Dushinsky effect). Apart of these non-totally symmetric vibrations, there will also be active totally symmetric vibrations in absorption spectra. The necessary condition is the appearance of nuclear displacements upon electronic excitation. In order to keep our formulas transparent, we will assume that there exists only one such totally symmetric vibration with frequency ω_s. This has to be taken into account as it will modify EP and DD curves, as excited states with excited totally-symmetric vibrations will also serve as intermediate states in RRS. Let us now denote by $\vec{M}_{g\beta}^{w_i 0_s, w_i' v_s}$ ($w_i = 0, 1$; $w_i' = 0, 1$; $w_i' = w_i + 1$; $\beta = n, m, k$) the vibronic dipole moment for the transition $\phi_g^0 \Lambda_{w_i}(Q_{ai}) \Lambda_0(Q_{aj\neq i}) \Lambda_0^g(Q_s) \rightarrow \phi_\beta^0 \Lambda_{w_i'}(Q_{ai}) \Lambda_0(Q_{aj\neq i}) \Lambda_{v_s}^\beta(Q_s)$ where $\Lambda_{w_i}(Q_{ai})$ are harmonic oscillator wavefunctions for the i-th non-totally symmetric mode, and $\Lambda_{v_s}^\beta(Q_s)$ are such functions for a totally symmetric mode. These last ones depend on the electronic state as the equilibrium configuration for this mode will depend on electronic excitation. Neglecting the modification of vibronic coupling by Franck-Condon factors [11], that can be done for not too large displacements between pairs of interacting states, and not too small energy gaps $E_{mn} = E_m - E_n$, $E_{km} = E_k - E_m$, we will get, proceeding along the lines presented in [12], the following expressions for the vibronic transition moments (up to the first order in $\lambda_i^{\alpha\beta}$):

$$\vec{M}_{gn}^{0_i 0_s, 1_i v_s} = \lambda_i^{nm} \frac{E_{mn} S_{0v}^{gn}}{E_{mn} - \omega_{ai}} \vec{M}_{gm}, \tag{3a}$$

$$\vec{M}_{gn}^{1_i 0_s, 0_i v_s} = \lambda_i^{nm} \frac{E_{mn} S_{0v}^{gn}}{E_{mn} + \omega_{ai}} \vec{M}_{gm}, \tag{3b}$$

$$\vec{M}_{gm}^{0_i 0_s, 1_i v_s} = -\lambda_i^{nm} \frac{E_{mn} S_{0v}^{gm}}{E_{mn} + \omega_{ai}} \vec{M}_{gn} + \lambda_i^{km} \frac{E_{km} S_{0v}^{gm}}{E_{km} - \omega_{ai}} \vec{M}_{gk}, \tag{3c}$$

$$\vec{M}_{gm}^{1_i 0_s, 0_i v_s} = -\lambda_i^{nm} \frac{E_{mn} S_{0v}^{gm}}{E_{mn} - \omega_{ai}} \vec{M}_{gn} + \lambda_i^{km} \frac{E_{km} S_{0v}^{gm}}{E_{km} + \omega_{ai}} \vec{M}_{gk}, \tag{3d}$$

$$\vec{M}_{gk}^{1_i 0_s, 0_i v_s} = -\lambda_i^{km} \frac{E_{km} S_{0v}^{gk}}{E_{km} - \omega_{ai}} \vec{M}_{gm}, \tag{3e}$$

$$\vec{M}_{gk}^{0_i 0_s, 1_i v_s} = -\lambda_i^{km} \frac{E_{km} S_{0v}^{gk}}{E_{km} + \omega_{ai}} \vec{M}_{gm}, \tag{3f}$$

where

$$\vec{M}_{g\beta} = \langle \phi^0_{g} | \hat{\vec{M}} | \phi^0_\beta \rangle, \text{ and } S^{g\beta}_{0v} = B^v_\beta (2^v v!)^{-1/2} \exp(-B^2_\beta/4), \ (\beta = n, m, k) \tag{3g}$$

are the Franck-Condon overlap integrals, and B_β is the displacement parameter for the β-th state.

Now, the scattering tensor describing a fundamental line of a non-totally symmetric mode Q_{ai} can be written as (only three excited electronic states are assumed to contribute significantly to RRS in the region of the first and second excited states)

$$(\alpha^{0_i \to 1_i})_{\varrho,\sigma} = \sum_{\beta = m,n,k} \sum_{v_s} \frac{(\vec{M}^{0_i 0_s, 0_i v_s}_{g\beta})_\varrho (\vec{M}^{0_i v_s, 1_i 0_s}_{\beta g})_\sigma}{E_\beta + v_s \omega_s - \Omega - i\Gamma}$$

$$+ \sum_{\beta = m,n,k} \sum_{v_s} \frac{(\vec{M}^{0_i 0_s, 1_i v_s}_{g\beta})_\varrho (\vec{M}^{1_i v_s, 1_i 0_s}_{\beta g})_\sigma}{E_\beta + \omega_{ai} + v_s \omega_s - \Omega - i\Gamma} + \text{antiresonance term}, \qquad \varrho, \sigma = x, y, z. \tag{4}$$

Here Ω is the frequency of the laser beam, and Γ is the bandwidth of intermediate states (for simplicity assumed to be the same for all of them). We will neglect all inhomogeneous broadening effects [5, 13]. We do not write the explicit form of the antiresonance term as it is much smaller than the resonance terms and does not play any important role. Let us now assume that $\vec{M}_{gn}$ and $\vec{M}_{gk}$ are parallel to the z axis, whereas $\vec{M}_{gm}$ is parallel to the x axis, then, taking into account that $\vec{M}^{w_i 0_s, w_i v_s}_{g\beta} = \vec{M}_{g\beta} S^{g\beta}_{0v}$, we get for resonance terms

$$\tilde{\alpha}^{0_i \to 1_i}_{xz} = -(E_{mn} + \omega_{ai})^{-1} \sum_v \left\{ \frac{(S^{gm}_{0v})^2}{E_m + \omega_{ai} + v\omega_s - \Omega - i\Gamma} - \frac{(S^{gn}_{0v})^2}{E_n + v\omega_s - \Omega - i\Gamma} \right\}$$

$$+ A_i (E_{km} - \omega_{ai})^{-1} \sum_v \left\{ \frac{(S^{gm}_{0v})^2}{E_m + \omega_{ai} - v\omega_s - \Omega - i\Gamma} - \frac{(S^{gk}_{0v})^2}{E_k + v\omega_s - \Omega - i\Gamma} \right\}, \tag{5a}$$

$$\tilde{\alpha}^{0_i \to 1_i}_{zx} = -(E_{mn} - \omega_{ai})^{-1} \sum_v \left\{ \frac{(S^{gm}_{0v})^2}{E_m + v\omega_s - \Omega - i\Gamma} - \frac{(S^{gn}_{0v})^2}{E_n + \omega_{ai} + v\omega_s - \Omega - i\Gamma} \right\}$$

$$+ A_i (E_{km} + \omega_{ai})^{-1} \sum_v \left\{ \frac{(S^{gm}_{0v})^2}{E_m + v\omega_s - \Omega - i\Gamma} - \frac{(S^{gn}_{0v})^2}{E_n + \omega_{ai} + v\omega_s - \Omega - i\Gamma} \right\} \tag{5b}$$

all other terms of the scattering tensor being equal to zero. In Eqs (5a), (5b) we have put

$$\tilde{\alpha}^{0_i \to 1_i}_{\varrho\sigma} = \alpha^{0_i \to 1_i}_{\varrho\sigma} / h^{nm}_i |\vec{M}_{gn}| \, |\vec{M}_{gm}| \tag{5c}$$

and

$$A_i = h^{km}_i |\vec{M}_{gk}| / h^{nm}_i |\vec{M}_{gn}|. \tag{5d}$$

If the displacement parameters (and therefore Franck-Condon integrals) are the same for all excited electronic states Eqs. (5a), (5b) can be simplified and written in the form

$$\tilde{\alpha}_{xz}^{0_i\to 1_i} = \sum_{\beta=n,k}\sum_{v} \frac{S_{0v}^2(\delta_{\beta n}+A_i\delta_{\beta k})}{(E_m+\omega_{ai}+v\omega_s-\Omega-i\Gamma)\,(E_\beta+v\omega_s-\Omega-i\Gamma)}, \tag{6a}$$

$$\tilde{\alpha}_{zx}^{0_i\to 1_i} = \sum_{\beta=n,k}\sum_{v} \frac{S_{0v}^2(\delta_{\beta n}+A_i\delta_{\beta k})}{(E_m+v\omega_s-\Omega-i\Gamma)\,(E_\beta+\omega_{ai}+v\omega_s-\Omega-i\Gamma)}. \tag{6b}$$

From Eqs. (6a), (6b) one can easily see, that for $S_{0v} = \delta_{0v}$ (no displacements in a totally symmetric mode) the components of the scattering tensor will go to zero for energies $\Omega_1 = (E_k+A_iE_n)\,(1+A_i)^{-1}$ for α_{xz}, and $\Omega_2 = \Omega_1+\omega_{ai}$, for α_{zx}.

At these energies α_{xz} and α_{zx} change their signs, so for $\Omega_1 < \Omega < \Omega_2$ they will have opposite signs and the antisymmetric scattering will be greater than in neighbouring regions. This will lead to an increase of the depolarization ratio of the linearly polarized incident light, and thus the depolarization ratio, ϱ_l, will peak at the energy close to

$$\Omega_\varrho^{(i)} = \frac{E_k+A_iE_n}{1+A_i} + \tfrac{1}{2}\,\omega_{ai}. \tag{7}$$

This effect is the result of the interference between scattering coming from two different pairs of coupled electronic states, and will appear for such A_i that $\Omega_\varrho^{(i)} > 0$.

If $S_{0v} \neq \delta_{0v}$ then different terms with the same v will go to zero for energies differing by ω_s. However, this will almost never lead to separate maxima in DD, as only the leading term will give such maximum, its magnitude being smaller, as other terms will not scatter antisymmetrically. In this situation instead of E_k, and E_n values that correspond to 0–0 transition energies, one should use rather $E_\beta+0.5B_\beta^2\,\omega_s$ in Eq. (7). These values corrected by Stockes' shifts, correspond to vertical transition energies.

If $A_i < 0$, $\Omega_\varrho^{(i)} < E_n$ and we will get an extra maximum in DD and the corresponding extra minimum in EP in the preresonance region. This will form a 'ghost' resonance-antiresonance coincidence in EP-DD curves. If $A_i > 0$ then $\Omega_\varrho^{(i)} > E_n$, and these extra features can appear between two resonances or in the region of a resonance with the m-th electronic state. For $|A_i| \gg 1$ (stronger coupling within the m-k pair, and/or $|\vec{M}_{gk}| \gg |\vec{M}_{gn}|$), $\Omega_\varrho^{(i)}$ is close to E_n. This will lead to a prominent distortion of the EP and DD curves of a non-totally symmetric fundamental line in comparison to those predicted by the two-electronic model [3]. If A_i is close to unity, $\Omega_\varrho^{(i)}$ can easily enter the region of a resonance with the m-th state distorting its EP and DD curves strongly ($A_i > 0$), or can lie far in the preresonance region ($A_i < 0$). In this latter case, however, the approximation (4) for the scattering tensor may be invalid (very small cross-section for the scattering) and one must include contributions from all higher electronic states (ordinary Raman scattering). This contribution is independent of Ω and can be incorporated into our treatment just by adding constant terms to α_{xz}, α_{zx}, so we put $\alpha_{\varrho\sigma} \to \alpha_{\varrho x}+\gamma, \varrho, \sigma = x, z$). We will discuss this in the next section.

3. *Calculations for the naphthalene molecule*

There are six b_{1g} modes in a naphthalene molecule that are active in the vibronic coupling of S_1, S_2, and S_3 electronic states. According to the SVL fluorescence spectra published by Stockburger et al. [8], the totally symmetric mode which forms the most prominent progressions in these spectra is the C–C stretching mode with the frequency $\omega_s = 1147\ \mathrm{cm}^{-1}$. One can estimate the displacement parameter B_n for this mode from the vibronic intensity distribution in the Franck-Condon progression of this mode. This estimation gives the value $B = 1.0$.

Ohta and Ito [9] have calculated the vibronic coupling parameters, which are just equal to those denoted in this paper by $h_i^{\alpha\beta}(2\omega_{ai})^{1/2}$, with the help of a semiempirical method developed by Murrell and Pople [14]. We will use these values to calculate A_i parameters for all b_{1g} modes. To do this we take the following experimental values of electronic transition dipole moments [9]: $|M_{gn}|^2 = 0.002$, $|M_{gm}|^2 = 0.18$, $|M_{gk}|^2 = 1.7$. The so-obtained values of A_i are listed in Table I.

$\omega_{ai}[\mathrm{cm}^{-1}]$	$\|A_i\|$
511	37.24
940	3.88
1164	104.86
1237	1070.77
1440	174.93
1629	258.71

We present the $511\ \mathrm{cm}^{-1}$, $940\ \mathrm{cm}^{-1}$, and $1164\ \mathrm{cm}^{-1}$ modes EP and DD curves in figures 1, 2, 3, respectively, for the value of $\Gamma = 200\ \mathrm{cm}^{-1}$ and $E_n = 32000\ \mathrm{cm}^{-1}$, $E_m = 35900\ \mathrm{cm}^{-1}$, and $E_k = 47500\ \mathrm{cm}^{-1}$ [8], for both signs of A_i. EP and DD curves are given with and without inclusion of participation of the totally symmetric $1147\ \mathrm{cm}^{-1}$ mode, with $B_n = B_m = B_k = 1.0$ and $B_n = B_m = B_k = 0.0$, respectively. We see that for this value of displacement parameters, typical for a naphthalene molecule, there are only minor differences in EP and DD with respect to the situation where no totally symmetrical mode participates in RRS.

For $511\ \mathrm{cm}^{-1}$ mode $\Omega_Q^{(i)}$ lies near the resonance with the first excited electronic singlet state, forming an extra maximum in DD on the low energy ($A_i < 0$) and high energy ($A_i > 0$) side of the 0–0 transition of the S_1 state. The EP in this region is therefore strongly perturbed with respect to that in the two-level model. For $A_i > 0$ the asymmetry of the doublet, resulting from non-adiabatic interactions, is no longer seen, and for $A_i < 0$ the asymmetry is observed only because the doublet lies on the steeply increasing cross-section resulting from the scattering from the S_2–S_3 pair. The EP and DD curves in the region of a resonance with the second excited singlet state look much the same as in the two-level model.

The opposite situation arises for $940\ \mathrm{cm}^{-1}$ mode and $A_i > 0$. Here $\Omega_Q^{(i)}$ lies near $36000\ \mathrm{cm}^{-1}$ perturbing very strongly EP and DD curves near the resonance with the second singlet. A huge maximum in DD curve is produced by an accidental coincidence of two interferences: one occurring between scatterings from different electronic pairs, and the second from 0–0 and 0–1 transition in the second singlet. The maximal value of $\varrho_{l,\max}^{(i)}$ depends very critically on the accurate displacement parameters, and on the participation of an ordinary Raman scattering in this region of energies. So for $B_n = B_m = B_k = 1.0$ we get $\varrho_{l,\max}^{(i)} \approx 500.0$, whereas for $B_n = B_m = B_k = 0.0$, $\varrho_{l,\max}^{(i)} \approx 20.0$. Similarly, the ordinary Raman scattering cross-section equal to 0.003 of the value of that for RRS near 32000 cm^{-1}, lowers $\varrho_{l,\max}^{(i)}$ to 225 or 60 depending whether they interfere constructively or destructively in the preresonance region. For $A_i < 0$ EP and DD curves look very much the same as in the two level model, but an extra maximum $\varrho_{l,\max}^{(i)} = 7.0$ is produced near $\Omega_\varrho^{(i)} = 27450$ cm^{-1}, the cross section being very small at this point (6×10^{-6} of that at 32000 cm^{-1}).

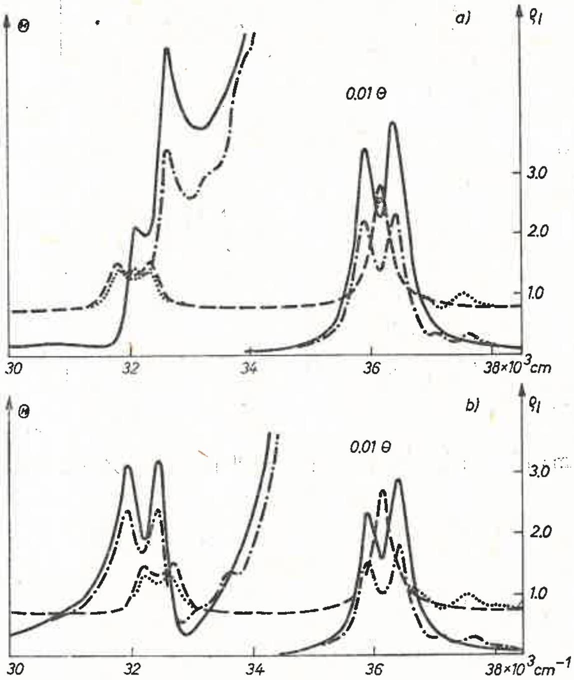

Fig. 1. Excitation profiles (———, –·–·–) and depolarization dispersion (– – – –, ·····) for 511 cm^{-1} mode of naphthalene. The displacement parameters for 1147 cm^{-1} totally symmetrical mode are assumed to be the same for all three states and equal to 0.0 (———, – – – –), and 1.0 (–·–·–, ·····). a) $A = 37.24$, b) $A = -37.24$

Changes of displacement parameters have minor influence on ϱ_l in this region, however, constructively interfering ordinary Raman scattering of large enough amplitude (say 0.0001 of RRS cross section at 32000 cm^{-1}) damps entirely this ‘ghost’ resonance-antiresonance DD–EP coincidence. If the ordinary Raman scattering interferes destructively with RRS in this region then it only diminishes $\varrho_{l,\max}^{(i)}$ and shifts $\Omega_\varrho^{(i)}$ towards slightly higher energies.

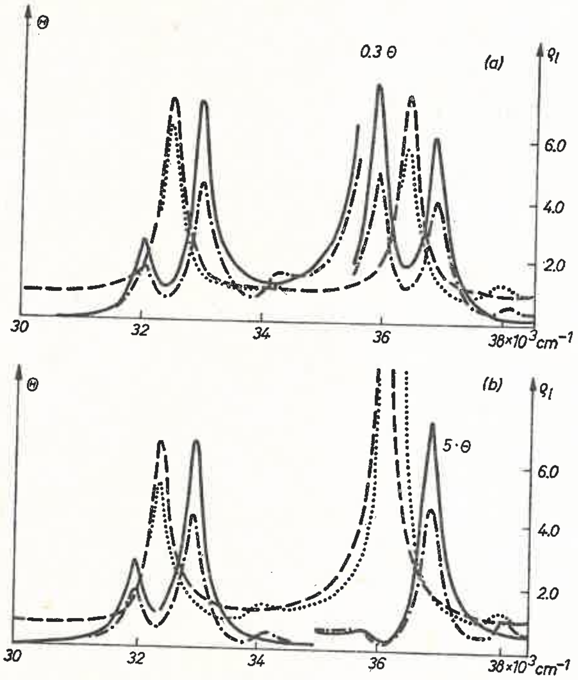

Fig. 2. The same plot as in Fig. 1 for 940 cm^{-1} mode. a) $A = 3.88$, b) $A = -3.88$

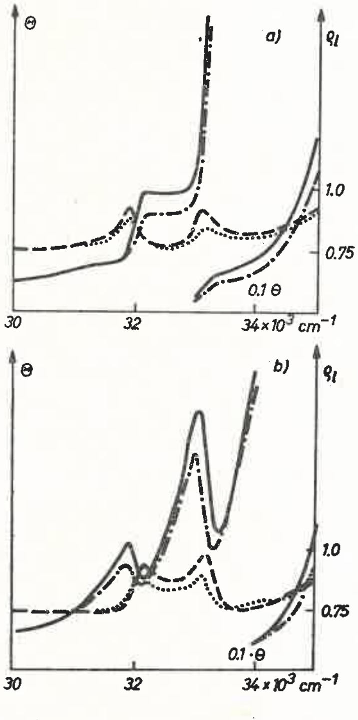

Fig. 3. The same plot as in Fig. 1 for 1164 cm^{-1} mode. a) $A = 104.86$, b) $A = -104.86$

The 1164 cm^{-1} mode EP and DD curves look very much the same as those for the other three b_{1g} modes with higher frequencies, where the bulk of the contribution to RRS comes from the S_2-S_3 pair of electronic states. The S_1-S_2 pair scattering forms only tiny structures in the region of the first singlet state on the steeply rising RRS cross section. For the 1237 cm^{-1} mode even these tiny structures disappear almost completely. Here, an extra, small maximum in ϱ_l is formed in the region of the first singlet state, and for $A_i < 0$ one can observe three plateaus in EP. The EP and DD curves near the second singlet look just the same as those in the two-level model, and therefore are not depicted in Figs 3a, 3b.

The above presented calculations do not need to give exactly EP and DD curves to be experimentally observed in naphthalene in the future, as the vibronic coupling parameters calculated by Ohta and Ito do not need to be the exact ones. However, we believe that the general structure of EP and DD curves will be much the same as that depicted in Figs. 1, 2, 3. We see that a lot of information on vibronic couplings can be extracted from RRS measurements for fundamental lines of b_{1g} modes in naphthalene. Such measurements can also give interesting information on the amplitude of the ordinary Raman scattering in the region of the first two singlets. We hope, such measurements will be done in the near future with the use of a tunable laser with frequency doubling.

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