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Vibronic spectra of a molecule in a laser field

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Abstract. The problem of optical spectra of a molecule in a strong monochromatic field is considered within the framework of a simple numerically solvable quantum mechanical model. In this model two nondegenerate electronic states and one vibrational mode with different equilibrium positions in different electronic states are taken into account. The calculated spectra show a new vibrational structure, with the quantum exceeding that of a free molecule, and also weak satellites of strong lines. Considerable changes of spectra with a small variation of laser frequency in the region of resonances with vibronic transitions and some other effects are also found and discussed. It is shown that orientational averaging does not lead to the disappearance of peculiarities in the spectrum.

1. Introduction

The interaction of atoms with a strong resonant laser field is an actual topic of nonlinear optics, which is investigated intensively both theoretically and experimentally. Such phenomena as the dynamic Stark effect, nutational oscillations of emitted intensity, antibunching of photons etc, have been thoroughly studied. The relevant references can be found in the review of Knight and Milonni (1980).

A laser field can also affect molecule systems, rearranging their configuration and dynamics and, as a result, changing their optical spectra. Essential alterations of that kind are naturally to be expected only in a sufficiently strong field, greater than or approximately equal to $10^8\ \mathrm{V\,m^{-1}}$, but in some special cases (molecules absorbed on a rough metal surface, large-size localised Frenkel excitons in molecular crystals) it may be one to three orders weaker (Loorits *et al* 1983).

Although the intensities mentioned are achievable nowadays, systematical studies of molecules and their optical spectra in a strong laser field are still in a very early stage. Trifonov and Troshin (1970) have considered the case when the Rabi frequency is small in comparison with the vibration frequencies of a molecule and only one pair of vibronic levels falls into resonance. They took both energetic and phase relaxation into account. Derbov *et al* (1979) have used the quasi-energy method (see Zel'dovich 1973) and discussed the problem of identifying different types of secondary radiation of molecules. Kiselev and coworkers have studied the problem of the configurational stability of a molecule in a strong monochromatic field (see references in Kiselev and Bordo (1981)). Federov *et al* (1975) have found the conditions for use of the adiabatic approximation in the case of a strong field and indicated the possibility of a considerable change of molecular adiabatic surfaces. Kovarskii *et al* (1979) have calculated emission (scattering) spectra beyond the frames of the adiabatic approximation; however, the WKB method used allows only some parts of the spectrum to be described correctly.

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In the present work we study the gradual changes occurring in the optical spectra of a molecule with the increase of light intensity. Under consideration it is an exactly solvable quantum mechanical model with two (ground and excited) electronic states and one vibrational mode. The latter one is supposed to have different equilibrium positions in different electronic states. We use the method of dressed vibronic states analogous to that of dressed atomic states (Cohen-Tannoudji and Reinaud 1977). To find the dressed states of a molecule in a laser field an algebraic eigenvalue problem for a semi-infinite five-diagonal matrix must be solved. The solution is obtained numerically. Using calculated dressed states the optical spectra of a molecule in a strong laser field are found.

Let us remark that an analogous approach can also be used in studying the optical spectra of a molecule with degenerated electronic states in a strong laser field (Loorits *et al* 1983).

2. The Hamiltonian

Let us regard the energy spectrum and stationary states of a molecule in a monochromatic laser field. It is known that in the rotating-wave approximation the dipole matrix element describing the interaction of the electronic system with the electromagnetic mode is of the form

$$\langle N'|\langle e|\boldsymbol{d}\boldsymbol{\mathscr{E}}|g|N\rangle = \Gamma_N \delta_{N',N-1}. \tag{1}$$

Here $|g\rangle$ and $|e\rangle$ are the ground and excited electronic states of an atom or a molecule, $|N\rangle$ is the N-photon state of the mode, $\boldsymbol{d}$ is the dipole transition momentum, $\boldsymbol{\mathscr{E}}$ is the electric field strength. Such structure of the interaction operator makes the following choice of the basis of electron–photon states purposeful: $\ldots|g\rangle|N\rangle$, $|e\rangle|N\rangle$, $|g\rangle|N+1\rangle$, $|e\rangle|N+1\rangle\ldots$. In this basis the Hamiltonian of the molecule + laser mode acquires the form of the matrix

$$H = \begin{pmatrix} \vdots & \cdots & \cdots & \vdots \\ H_{N-1} & 0 & 0 & \\ 0 & H_N & 0 & \\ 0 & 0 & H_{N+1} & \\ \vdots & \cdots & \cdots & \vdots \end{pmatrix} \tag{2}$$

with the blocks

$$H_N = \begin{array}{c} \\ \\ \end{array}\begin{array}{cc} |e\rangle|N-1\rangle & |g\rangle|N\rangle \\ \multicolumn{2}{c}{\begin{pmatrix} H_e + (N-1)\omega_{\rm L} & \Gamma_N \\ \Gamma_N & H_g + N\omega_{\rm L} \end{pmatrix}} \end{array} \tag{3}$$

on the main diagonal. Here $\hbar = 1$, $\omega_{\rm L}$ is the frequency of the laser mode, H_g and H_e are the vibrational Hamiltonians of the ground and excited electronic states. In the harmonic approximation

$$H_g = E_g + \frac{1}{2}\left(-\frac{\partial^2}{\partial q^2} + q^2\right) = E_g + a^+ a + \tfrac{1}{2} \tag{4a}$$

$$H_e = E_e + \frac{1}{2}\left(-\frac{\partial^2}{\partial q^2} + (q - \bar{q})^2\right) = E_e + (a^+ + D^{1/2})(a + D^{1/2}) + \tfrac{1}{2} \tag{4b}$$

where q is the dimensionless vibrational coordinate, $\bar{q}$ is the shift of the equilibrium position of the coordinate in the electronic transition, $D = \bar{q}^2/2$, a^+ and a are the operators of phonon creation and annihilation; the vibrational quantum is taken per energy unit. Then

$$H_N = E_e + (N-1)\omega_{\mathrm{L}} + \tfrac{1}{2} + \tilde{H}_N \tag{5}$$

where

$$\tilde{H}_N = \begin{pmatrix} (a^+ + D^{1/2})(a + D^{1/2}) & \Gamma_N \\ \Gamma_N & a^+a + \Delta \end{pmatrix} \tag{6}$$

and

$$\Delta = \omega_{\mathrm{L}} + E_g - E_e \tag{7}$$

is the difference between the laser and pure electronic transition frequencies.

The eigenstates (dressed states) of the Hamiltonian $\tilde{H}_N$ may be written in the form

$$|\nu, N\rangle = \sum_n \left(c_{en}^{\nu,N}|n\rangle|e\rangle|N-1\rangle + c_{gn}^{\nu,N}|n\rangle|g\rangle|N\rangle\right) \tag{8}$$

where $|n\rangle$ are the n-phonon eigenstates of the Hamiltonian H_g. The stationary Schrödinger equation

$$\tilde{H}_N|\nu, N\rangle = E_\nu^N|\nu, N\rangle \tag{9}$$

reduces to the following five-diagonal matrix equation

$$\begin{pmatrix} D-E_\nu & \Gamma & D^{1/2} & 0 & 0 & 0 & \vdots \\ \Gamma & \Delta-E_\nu & 0 & 0 & 0 & 0 & \vdots \\ D^{1/2} & 0 & D+1-E_\nu & \Gamma & (2D)^{1/2} & 0 & \vdots \\ 0 & 0 & \Gamma & \Delta+1-E_\nu & 0 & 0 & \vdots \\ 0 & 0 & (2D)^{1/2} & 0 & D+2-E_\nu & \Gamma & \vdots \\ 0 & 0 & 0 & 0 & \Gamma & \Delta+2-E_\nu & \vdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} c_{e0}^\nu \\ c_{g0}^\nu \\ c_{e1}^\nu \\ c_{g1}^\nu \\ c_{e2}^\nu \\ c_{g2}^\nu \\ \vdots \end{pmatrix} = 0. \tag{10}$$

Here ν enumerates the eigenstates of $\tilde{H}_N$ (for simplicity the indices N are omitted).

3. Optical spectra

Let us now consider the absorption and spontaneous emission of photons of nonlaser modes. The dipole matrix elements of one-photon transitions have the form

$$\begin{aligned} M_{\mathrm{e}}^{\mu,\nu} &= \langle\nu, N+1|d|\mu, N\rangle \propto \sum_n c_{en}^{\mu,N} c_{gn}^{\nu,N+1} \\ M_{\mathrm{a}}^{\mu,\nu} &= \langle\nu, N-1|d|\mu, N\rangle \propto \sum_n c_{gn}^{\mu,N} c_{en}^{\nu,N-1} \end{aligned} \tag{11}$$

for emission and absorption respectively. Here $|\mu, N\rangle$ is the initial state, d is the projection of the operator $\boldsymbol{d}$ on to the polarisation vector of the emitted (absorbed) photon. Note that the factors under the sums in (11) are the eigenvector components of the adjacent blocks of the total block diagonal Hamiltonian (2). These blocks differ from each other due to the dependence of Γ_N on N (Γ_N is proportional to $N^{1/2}$).

In the case of a strongly excited laser mode the essential values of N are very large and differ little from the mean value: $\langle (N-\bar{N})^2\rangle^{1/2} \ll \bar{N} \propto \langle |\mathscr{E}|^2\rangle$. Therefore we must solve the eigenvalue problem only for $\Gamma = \Gamma_N$, and there is no need for further use of subscripts and superscripts N. For the same reason, no question about averaging the considered quantities over N arises any longer.

In the present work we neglect the radiative width of the dressed levels. In this approximation the optical spectra consist of zero-width lines. By applying the Fermi golden rule to the transitions considered the intensities of the lines are proportional to $|M^{\mu,\nu}_{\mathrm{e(a)}}|^2$. Then the normalised one-photon emission and absorption spectra are

$$I_{\mathrm{e}}(E) = \sum_{\nu} \delta(E_\mu + E - E_\nu) \left(\sum_n c^{\mu}_{en} c^{\nu}_{gn}\right)^2$$
$$I_{\mathrm{a}}(E) = \sum_{\nu} \delta(E_\mu + E - E_\nu) \left(\sum_n c^{\mu}_{gn} c^{\nu}_{en}\right)^2 \tag{12}$$

where the frequency of emission $\omega_{\mathrm{e}} = \omega_{\mathrm{L}} - E$ and that of absorption $\omega_{\mathrm{a}} = \omega_{\mathrm{L}} + E$. Actually the absorption of a weak probe field consists of two parts—the real absorption and the stimulated emission leading to the beam amplification. In accordance with the Einstein relation between the probabilities of spontaneous and stimulated emission the spectrum of the latter is equal to $-I_{\mathrm{e}}(\omega_{\mathrm{L}} - \omega_{\mathrm{a}})$. Therefore, the total absorption spectrum

$$\kappa(\omega_{\mathrm{a}}) = I_{\mathrm{a}}(\omega_{\mathrm{a}} - \omega_{\mathrm{L}}) - I_{\mathrm{e}}(\omega_{\mathrm{L}} - \omega_{\mathrm{a}}). \tag{13}$$

A special point should also be made about the interpretation of the emission described by equation (11). Within the framework of a weak light field the emission classification is based on the role of relaxation processes (Rebane *et al* 1976). We hold that this classification is also applicable in the case of a strong field. In our model the relaxation processes are supposed to be slow and not taken into account. Therefore the emission considered should be classified as Raman scattering. Correspondingly, the intensities of the lines in spectrum (11) determine the cross sections δ of Raman scattering:

$$\delta_{\nu-\mu} \propto \left(\sum_n c^{\mu}_{en} c^{\nu}_{gn}\right)^2 / \Gamma^2. \tag{14}$$

Here $\nu - \mu$ is the order of Raman scattering.

Let us determine now the initial state $|\mu, N\rangle$. Suppose that before the switch on of the interaction between the molecule and the mode the former was in the lowest stationary state $|0\rangle|g\rangle$. The duration of the laser pulse is considered to be large in comparison with the vibration frequency but short compared with the characteristic radiation decay time. In this case the regime of adiabatic switch on of the interaction is realised, and only one level $|\mu, N\rangle$, arising from the zero vibrational level of the ground electronic state $|0\rangle|g\rangle$, will be populated. The number of this level is determined as follows: if $\Delta < 0$, then $\mu = 0$ but if $\Delta > 0$, then μ is the entire part of Δ (see figure 1, the eigenstate of $\tilde{H}_N$ with the lowest energy is supposed to have the zero number).

4. Results of numerical calculations

The eigenvalues E_ν and eigenvectors $c^{\nu}_{g(e)}$ of the Hamiltonian $\tilde{H}_N$ and the optical spectra (11) and (12) were calculated on a computer taking into account 100–150

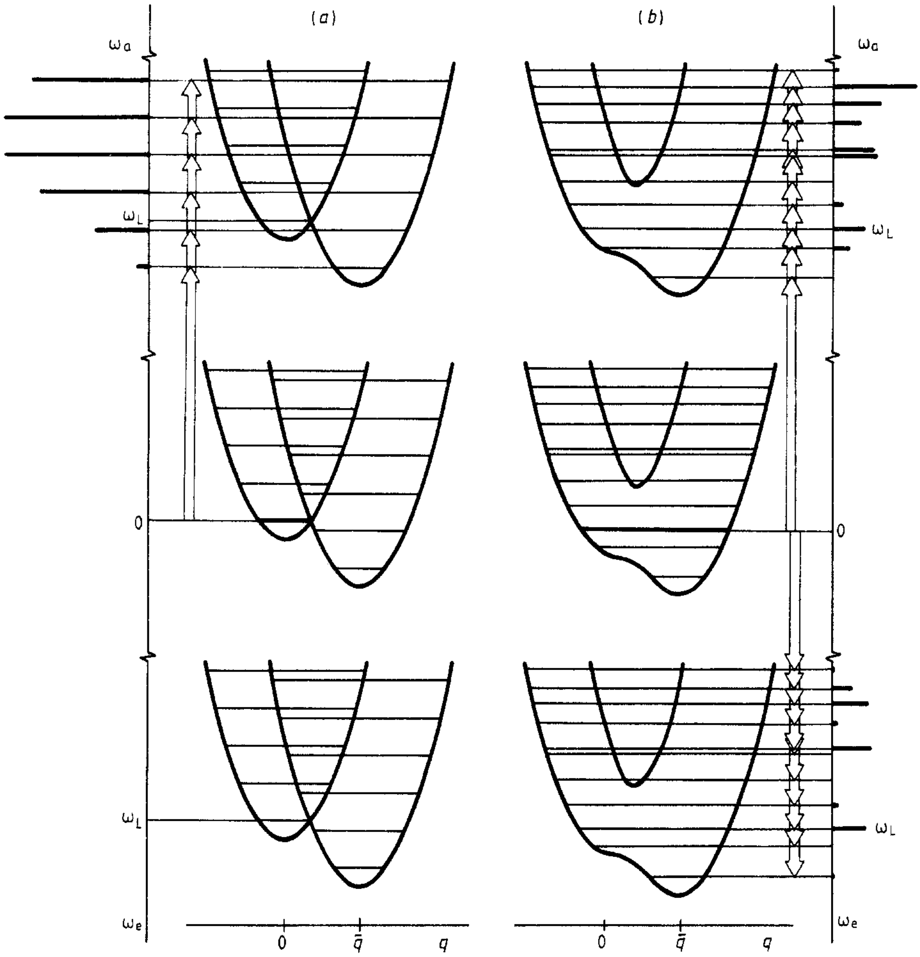

Figure 1. The adiabatic surfaces and dressed energy levels of a molecule in a resonance laser field for $\Delta = 1.25$, $D = 4$: (a) $\Gamma = 0$ (no interaction between the field and the molecule); (b) $\Gamma = 1$. The arrows show the one-photon (optical) transitions from the initially populated level (thick curve); fragments of the corresponding spectra are presented on the left and right sides of the figure.

vibrational levels in equation (9). For all used Γ, D and Δ it turned out to be sufficient; this was checked by comparing the results of computation for various numbers of included vibrational levels. The results of the calculations are presented in figures 1–4.

In figure 1 one can see the positions of dressed levels for $\Gamma = 0$ and $\Gamma = 1$ and in figure 2, their dependence on Γ, which is proportional to the absolute value of electric field strength. For most of the levels this dependence is essentially nonmonotonous. Such behaviour of the dressed levels is caused by their anticrossing, which may be easily understood, based on the adiabatic description of the dressed states. This description uses the eigenstates of the adiabatic Hamiltonians

$$H_{u,l} = -\frac{1}{2}\frac{\partial^2}{\partial q^2} + W_{u,l}(q) \tag{15}$$

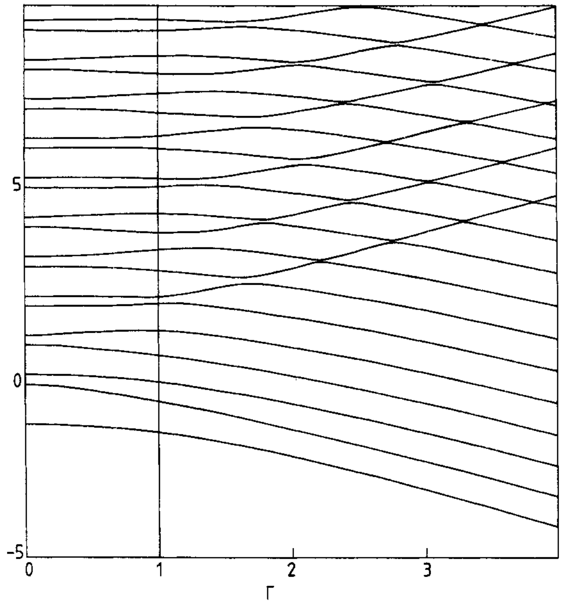

Figure 2. The positions of the lowest ($\nu = 0, 1, \ldots, 20$) dressed energy levels of a molecule as a function of the resonant laser field strength parameter Γ. The values $\Delta = 1.25$ and $D = 4$ are the same as in figure 1. Anticrossings of the levels are caused by the nonadiabatic mixing of the corresponding adiabatic dressed states of the molecule. The case $\Gamma = 1$ corresponds to the dressed level positions in figure 1.

for the basis states. Here

$$W_{u,l}(q) = \tfrac{1}{2}\{q^2 - \bar{q}q + \tfrac{1}{2}\bar{q}^2 + \Delta \pm [(\bar{q}q - \tfrac{1}{2}\bar{q}^2 - \Delta)^2 + 4\Gamma^2]^{1/2}\} \tag{16}$$

are the upper and lower branches of the adiabatic potential (see figure 1). The potentials $W_u(q)$ and $W_l(q)$ depend differently on Γ. Therefore the levels of the adiabatic Hamiltonian H_u cross with the upper levels of the adiabatic Hamiltonian H_l. The anticrossing effect is then caused by nonadiabaticity, which is most important near the crossing points†.

Let us now consider the calculated optical spectra (see figures 3 and 4). The first noteworthy feature of these spectra is the structure with a quantum exceeding that of a free molecule (see spectra for $\Gamma > 1$). This structure reflects the configurational and dynamical rearrangement of the molecule in a strong light field and can be interpreted as transitions to the levels of the upper branch W_u of the adiabatic potential (see figure 1). The satellites near some of these strong lines in the spectra reflect an anticrossing effect—they are caused by a nonadiabatic mixing of the levels with the nearest levels of the lower branch W_l of the adiabatic potential. The effect of the mixing is the higher the less is the energetic distance between the levels, which is typical of Fermi resonance for the states of various branches of the adiabatic potential (see Loorits 1980).

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† If Δ is integer or $\Delta \geqslant D$, then the initially populated level μ gets to the crossing area. Then the adiabatic switch on regime may be unrealisable because of small splittings of the levels in anticrossing points. In this work we considered the cases when the adiabatic switch on regime is realisable.

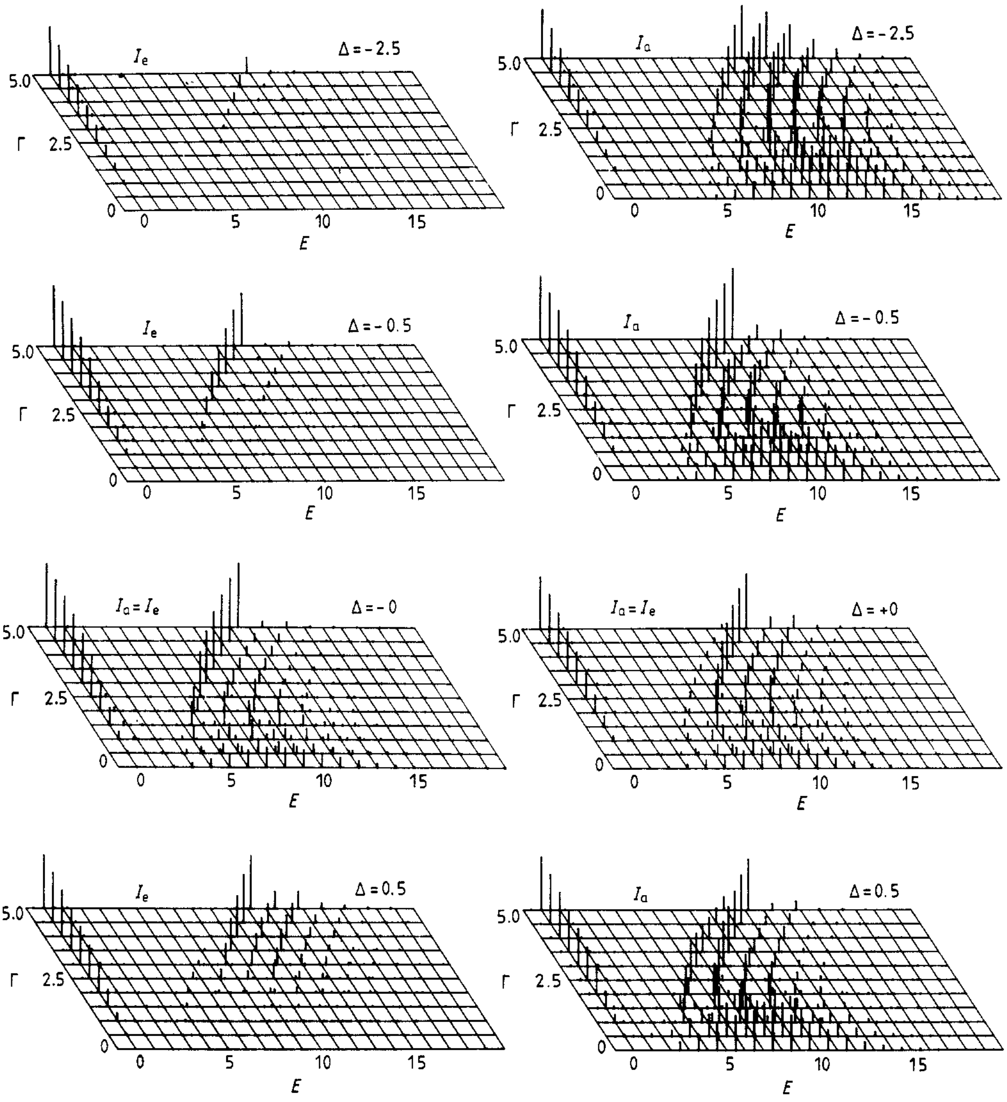

Figure 3. The dependence of optical spectra $I_e(E)$ and $I_a(E)$ of a molecule on the resonant laser field strength parameter Γ.

The presence of lines in the anti-Stokes region for $\Delta > 0$ is remarkable (in figure 5 these lines have negative numbers). At $T = 0$ the corresponding transitions appear as a result of the dressing (see figure 1). In the weak-field limit their intensity tends to zero as Γ^2. Note that in the Stokes region lines also exist, whose intensity tends to zero as Γ^2 (see e.g. curve in figure 5 for $\Delta = -2.5$).

The next conclusion following from our calculations is a considerable change of the spectra at small variation of laser frequency in the region of resonance with vibronic transitions (see for example spectra at $\Delta = +0$ and $\Delta = -0$). This change includes a jump-like part and a continuous one. The former is related to the jump-like change of the number of the initially populated level. The latter with the remarkable alteration of the wavefunction of the initial level in the region of tunnel transition frequencies.

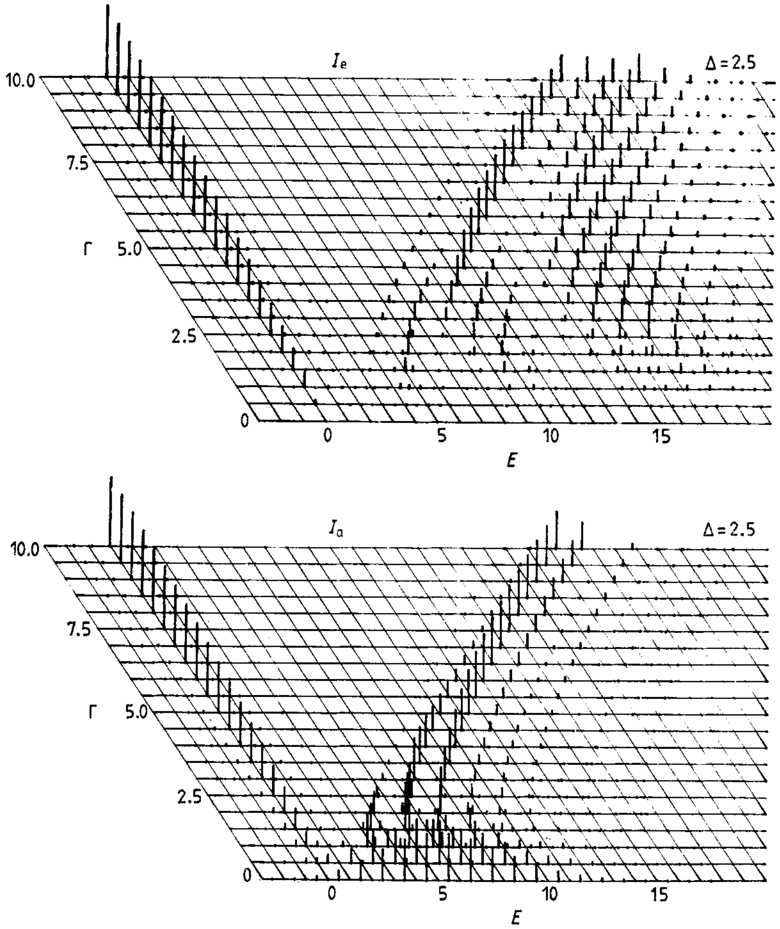

Figure 4. The dependence of optical spectra $I_e(E)$ and $I_a(E)$ of a molecule on the resonance laser field strength parameter.

One more effect deserves attention: the disappearance of lines for some parameter values (see, e.g. the I_e spectrum in figure 3 for $\Gamma = 5$, $E \simeq 15$ but also sharp minima in figure 4). This disappearance is caused by the change of the $M^{\mu,\nu}_{e(g)}$ sign (see equation (10)) with variation of Γ. Let us mention that such effect is absent in the case of a two-level system in a strong monochromatic field.

In connection with interpreting emission (11) as a Raman scattering it is essential to underline that in a strong-field case ($\Gamma \geqslant 1$) the cross sections and the frequencies of scattering depend remarkably on the light intensity parameter Γ^2 (see figure 4). Strong dependence of the scattering spectrum on the frequency of the exciting light is also noteworthy (see I_e spectra in figures 3 and 4).

5. Orientational averaging

The possible systems for application of the above-presented theory are molecules in viscous solutions or in solid (amorphous or polycrystal) matrices. In these cases one

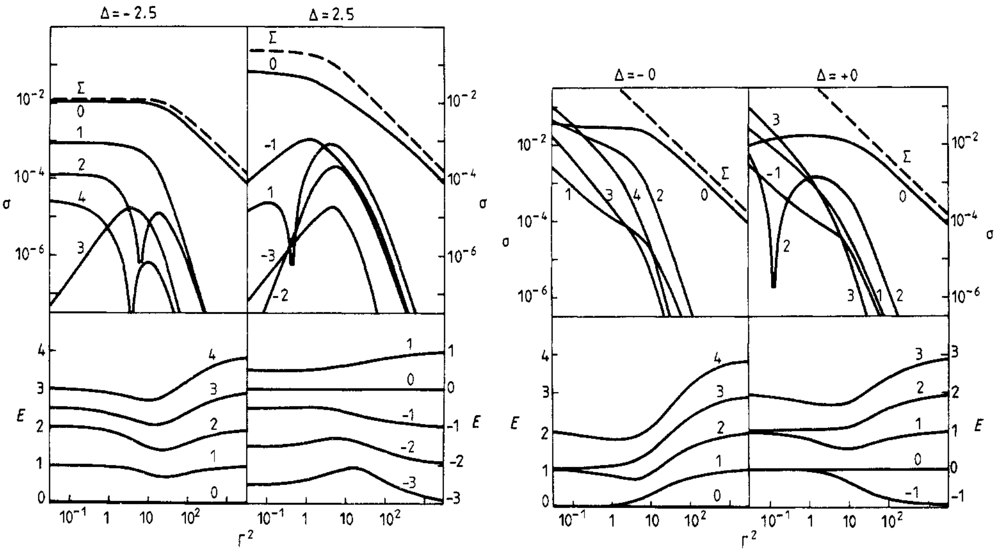

Figure 5. The cross sections (at the top) and the frequencies (at the bottom) of different order Raman scatterings (full curve) and total cross section Σ (broken curve). Numbers above the lines indicate the scattering orders.

should consider additionally the arbitrary orientation of molecules with respect to the field strength vector. Therefore the interaction constant varies for different molecules and the spectrum becomes smoothed. To find the lineshape one should evidently average the line positions over Γ with the distribution function $\rho(\Gamma)$. It is essential, however, that this averaging does not necessarily lead to the disappearance of peculiarities in the spectrum.

To illustrate what was said above, regard $\rho(\Gamma)$ for the allowed electronic transitions of a linear molecule in a polarisation perpendicular to its axis. For such a transition

$$\rho(\Gamma)=\tfrac{1}{2}\int_0^{\pi}\delta(\Gamma_{\max}\sin\Theta-\Gamma)\sin\Theta\,d\Theta=\frac{\Gamma}{\Gamma_{\max}(\Gamma_{\max}^2-\Gamma^2)^{1/2}} \tag{17}$$

($\Gamma_{\max}$ is the value of Γ for an orientation of the dipole transition moment along the electric field of the laser, Θ is the angle between the axis of the molecule and the field strength). We can see that here the function $\rho(\Gamma)$ and also the lineshape have a square-root-type peculiarity. In the case of optical transitions resolved in a polarisation parallel to the axis of the molecule, no such feature in $\rho(\Gamma)$ appears. Indeed, for such a transition

$$\rho(\Gamma)=\tfrac{1}{2}\int_0^{\pi}\delta(\Gamma_{\max}\cos\Theta-\Gamma)\sin\Theta\,d\Theta=1/2\Gamma_{\max}. \tag{18}$$

And even here part of the lines in the spectrum can be observed in the form of peculiarities. These are the lines with a nonmonotonic dependence of their frequencies on Γ. Near the extremal (turning) points this dependence has the form $\omega=\omega_{\text{turn}}+\frac{1}{2}\alpha(\Gamma_{\text{turn}}-\Gamma)^2$. The shape of such lines near ω_{turn} is the following:

$$I(\omega)\propto|d\omega/d\Gamma|^{-1}_{\omega\simeq\omega_{\text{turn}}}=[\alpha(\omega-\omega_{\text{turn}})]^{-1/2}. \tag{19}$$

It should be emphasised that peculiarities of such a type should always appear if $\Gamma_{\max} \geqslant \Gamma_{\text{turn}}$. This applies also to laser pulses of non-square form, for which it is essential to consider the change of Γ within the pulse action.

Let us mention that the orientational averaging procedure presented here is not applicable for free molecules, because the orientational motion is essentially affected by a strong laser field.

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