Nonresonant scattering of intense light by a molecule

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Scattering of intense radiation by a molecule is considered in the case when such radiation alters the rotational spectrum of the molecule. If the energy of interaction with radiation is comparable with the rotational constant, the selection rules governing the rotational quantum number are modified and the scattering spectrum acquires new branches which are equidistant in an asymptotically strong field. If the radiation power is low and the polarization is linear or circular, the Stark splitting of magnetic sublevels results in a linear dependence of the line width on the intensity of the exciting light. However, if the radiation is strong and eliptically polarized, the magnetic quantum numbers are not conserved and the dependence of the scattering line width on the intensity of the incident light may be more complex. An analytic solution is obtained of the nonstationary Schrödinger equation for a three-dimensional rotator which has an induced dipole and is subjected to an alternating field whose frequency is considerably higher than the rotational frequency. The solution is expressed in terms of spheroidal functions.

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1. INTRODUCTION

Scattering of light by molecules is governed largely by the rotational structure of the molecular wave function. Changes in the rotational quantum numbers caused by scattering govern the Rayleigh and Raman scattering line profiles and widths. If the scattered radiation is sufficiently intense, the dynamic Stark effect modifies the rotational spectrum of the molecule and this should be manifested as a dependence of the profile and width of the scattering line on the radiation intensity. The present paper is concerned with the influence of this modification in the rotational spectrum on the scattering.

The Stark effect of the rotational levels of a molecule in a static electric field is treated in many papers. In weak fields the rotational levels are shifted and split in respect of the projection of the momentum, and this shift and splitting depend linearly or quadratically on the field intensity for dipole and nonpolar molecules, respectively.[1] In a sufficiently strong field the problem has only axial symmetry and, therefore, the total momentum is not conserved. This occurs if the interaction of a molecule with such a field becomes comparable with the distance (energy separation) between the rotational levels. The states of a molecule with different momenta become mixed and the spectrum can no longer be found in the lowest order of the perturbation theory. An analysis of the spectrum of a three-dimensional rotator with a permanent dipole moment [2,3] shows that, in a very strong field, the spectrum becomes equidistant and corresponds to small harmonic oscillations of the dipole moment relative to the field direction.

The perturbation of the rotational spectrum of a molecule in a weak alternating field of nonresonant frequency is a quadratic function of the field intensity irrespective of whether or not the molecule has a dipole moment. The formulas for the polar molecules are given by Townes and Schawlow.[1] The same case is discussed by Yakovlev et al.[4] on the basis of the well-known Kapitza method. However, the virtual states in these investigations of the quadratic Stark effect of the rotational levels are effectively only the states belonging to the same vibronic term as the initial state differing from the latter solely by the rotational quantum number. These states make a contribution B/ω times smaller than the other vibronic states (B is the rotational constant and ω is the frequency of the external field). Clearly, in contrast to the radiofrequency range, this parameter is very small at optical and infrared frequencies.

We shall consider the modification of the rotational spectrum of a molecule by a method developed by us earlier in the theory of the dynamic Stark effect.[5] This method allows us to extend the theory to a very interesting range of strong fields. In the case of weak fields the results obtained for $B \ll \omega$ give a different dependence of the shift and splitting of the levels on the total momentum and its projection on an axis fixed in space than the dependence obtained in [1,4].

In the second section we shall consider the field-induced modification of the rotational spectrum of a symmetric top molecule whose rotational degrees of freedom are described in the rigid rotator approximation. In the next section we shall show that in some special cases the spectrum of such a molecule in an alternating field is identical with the spectrum of a rotator in a static field, and the interaction between the field and the rotator is governed by the latter's polarizability and not by its dipole moment. The solution of the appropriate Schrödinger equation is then expressed in terms of spheroidal functions. In the fourth section we shall obtain general formulas for the change in the rotational spectrum of a diatomic molecule in the Hund coupling cases a and b and for an arbitrary elliptic polarization of the field. In the last section we shall discuss the Raman scattering of intense radiation, corresponding to a transition of a molecule between quasistationary states formed as a result of its interaction with the field. In the weak-field case these formulas reduce to the well-known results of the theory of scattering in a line wing.

We shall confine ourselves to the case of a nonresonant external field frequency. Makarov and Fedorov[6] considered the change in the rotational spectrum of a molecule in a field which is in resonance with a vibrational transition frequency. In that case the adiabatic potential energy of rotating molecule can be obtained in the high-field limit.

2. SYMMETRIC TOP MOLECULE IN A NONRESONANT FIELD

The wave functions of a symmetric top molecule are of the form

$$|nJKM\rangle=\left(\frac{2J+1}{8\pi^2}\right)^{1/2}D^J_{KM}(\theta_i)\,|n\rangle. \tag{1}$$

Here, J is the total momentum of the molecule; K is the projection of the momentum on the axis 3 of a coordinate system linked to the molecule; M is the projection of the momentum on the z axis in a fixed system of coordinates; n are the quantum numbers representing vibronic states; $|n\rangle$ is the wave number of internal motion; θ_i are the Euler angles. The energy of a molecule in the state (1) is

$$E_{nJK}=E_n+BJ(J+1)+(C-B)K^2,$$

where E_n is the energy of a vibronic state; B and C are the rotational constants.[1] We shall ignore the centrifugal perturbation of the rotational constants and the vibrational-rotational interaction; we shall also assume that $\hbar = 1$.

We shall seek the wave function of a molecule in a field $\mathscr{E}_z(t) = F\cos\omega t$ in the form

$$\psi_{nM}(t)=\sum_{JK}a_{JK}(t)\,e^{-iE_nt}|nJKM\rangle, \tag{2}$$

where, because of the linear polarization of the field, M remains an integral of motion.

We shall assume that the field frequency ω and the detuning of this frequency from the frequencies of the vibronic transitions between the term n under consideration and all the other dipole-coupled terms is considerably greater than the separation between the rotational energy levels. In this case the equations for the coefficients α_{JK} become:[5]

$$i\dot a_{JK}=[BJ(J+1)+(C-B)K^2]a_{JK}-F\cos\omega t\sum_{J'K'}\langle nJKM|d_z|nJ'K'M\rangle a_{J'K'}$$
$$-\frac{F^2}{4}\sum_{J'}(c_{zz})_{JKM,\,J'K'M}\,a_{J'K'}, \tag{3}$$

$$(c_{ij})_{JKM,\,J'K'M'}=\sum_{n_1J_1K_1M_1}\frac{2\omega_{n_1n}}{\omega^2_{n_1n}-\omega^2}\langle nJKM|d_i|n_1J_1K_1M_1\rangle$$
$$\times\langle n_1J_1K_1M_1|d_j|nJ'K'M'\rangle, \tag{4}$$

where c_{ij} is the tensor representing the scattering of light by a molecule;[7] $\omega_{nn'} = E_n - E_{n'}$; **d** is the dipole moment operator.

The second term on the right-hand side of Eq. (3) governs the change in the wave function due to the dipole moment of the molecule and the third term describes the change due to its dynamic polarizability. It is important to note that the influence of a permanent dipole moment is negligible in the optical frequency range. This is physically self-evident because at high frequencies of an external field a dipole moment does not have sufficient time to become oriented along the field and, therefore, the terms linear in the field do not alter the energy. The presence of these terms simply gives rise to quasi-energy harmonics in the wave function[8] but the weight of these harmonics is given by the factor d_0F/ω (d_0 is the dipole moment), which is always very small at field intensities such that we can still speak of quasistationary molecular state. However, the order of smallness of the terms quadratic in the field and originating from the dipole moment (compared with the polarization terms) is given by the ratio B/ω. This is demonstrated most easily by a simple iteration analysis of the equations in the system (3).

Following this discussion, we drop the second term from the system (3) and obtain a system of differential equations with constant coefficients. Allowance for just the terms diagonal in JK and J′K′ in the polarization sum of the system (3) gives the shift of the energy levels in a weak field when the mixing can be ignored. The corresponding matrix element of the scattering tensor gives the amplitude of the elastic scattering of a photon of frequency ω by a level JK. The nondiagonal elements govern both the mixing of the levels by the field and the inelastic scattering JK → J′K′ in the wing of a Rayleigh line. Therefore, we can say that the system (3) allows not only for the elastic channel but also for the contribution of the low-lying inelastic channels to the quasistationary states of a molecule in a field.

Integrating the system (4) with respect to the Euler angles, we obtained the following differential equations in the matrix form for the column of coefficients α_{JK}:

$$i\dot{\mathbf{a}}=\mathbf{Q}\mathbf{a},$$
$$Q_{JK,\,J'K'}=[BJ(J+1)+(C-B)K^2]\delta_{JJ'}\delta_{KK'}-\frac{F^2}{4}\left(\frac{2J'+1}{2J+1}\right)^{1/2}$$
$$\times\sum_{J_1K_1m}(-1)^{2J_1+K+K_1}C^{JK}_{J_1K_11m}C^{JM}_{J_1M10}C^{J_1K_1}_{J'K'10}C^{J_1M}_{J'M10}\alpha_m, \tag{5}$$
$$\alpha_m=\sum_{n_1}\frac{2\omega_{n_1n}}{\omega^2_{n_1n}-\omega^2}\langle n|\bar d_m|n_1\rangle\langle n_1|\bar d_{-m}|n\rangle,$$

where $\bar{\mathbf{d}}$ is the dipole moment operator in a system of coordinates linked rigidly to a molecule.[7]

A general solution of the system (5) can be expressed in terms of the eigenvectors of the matrix **Q**:

$$\mathbf{a}=\sum_r C_re^{-iq_rt}\mathbf{f}_r,\quad \mathbf{Q}\mathbf{f}_r=q_r\mathbf{f}_r, \tag{6}$$

where C_r are arbitrary constants governed by the initial conditions. Substituting Eq. (6) into Eq. (2), we can see that the spectrum of a molecule in a field is governed by the eigennumbers q_r.

The matrix **Q** is generally of infinite rank, but beginning from certain values of J and K, the nondiagonal elements in this matrix can be ignored compared with the diagonal elements which increase proportionally to J^2 and K^2. Numerical results can be obtained if we know the values of the longitudinal α_0 and transverse $\alpha_{\pm1}$ polarizabilities of a molecule. We shall consider the simplest case of $\alpha_{\pm1} = 0$. This is satisfied well for diatomic molecules in the infrared range because the main contribution to the polarizability is then made by the virtual states which belong to the same electron term as the initial state and which differ from the latter only by the vibrational quantum number ("vibrational" polarizability). In this case the matrix **Q** is diagonal in respect of the index K and it is of the form

$$Q^{(K)}_{JJ}=BJ(J+1)+(C-B)K^2-\frac{\alpha_0F^2}{4}\left\{\frac{(J^2-K^2)(J^2-M^2)}{J^2(2J+1)(2J-1)}\right.$$
$$\left.+\frac{K^2M^2}{J^2(J+1)^2}+\frac{[(J+1)^2-K^2][(J+1)^2-M^2]}{(J+1)^2(2J+1)(2J+3)}\right\}, \tag{7}$$
$$Q^{(K)}_{J,J+1}=Q^{(K)}_{J+1,J}=-\frac{\alpha_0F^2KM}{2J(J+1)(J+2)}\left\{\frac{[(J+1)^2-K^2][(J+1)^2-M^2]}{(2J+1)(2J+3)}\right\}^{1/2},$$
$$Q^{(K)}_{J,J+2}=Q^{(K)}_{J+2,J}=-\frac{\alpha_0F^2}{4(J+1)(J+2)(2J+3)}\cdot$$
$$\left\{\frac{[(J+1)^2-K^2][(J+2)^2-K^2][(J+1)^2-M^2][(J+2)^2-M^2]}{(2J+1)(2J+5)}\right\}^{1/2}.$$

The quantities $Q^{(K)}_{JJ}$ give the energy shift in a weak field. In the special case of K = 0, we have

$$q_J(K=0)\approx Q_{JJ}^{(0)}=BJ(J+1)-\frac{\alpha_0F^2}{4}\frac{2J^2+2J-1-2M^2}{(2J-1)(2J+3)}. \tag{8}$$

Comparing this expression with the results of other investigations[4] we see that allowance for the polarization terms (instead of the terms associated with the permanent dipole moment) gives rise to different functional dependences of the shift and splitting of the levels on J and M.

We can analyze qualitatively the behavior of the energy levels in the limit of a strong field by considering a truncated matrix **Q** of order n. If n is sufficiently high and M and K are fixed, the main matrix elements satisfy $J^2 \gg M^2$ and $J^2 \gg K^2$. If the field is sufficiently strong, we can easily see that the characteristic equation for the matrix **Q** is

$$p_n(\varepsilon)=\begin{vmatrix} 2+2\varepsilon & 1 & 0 & \dots & 0 \\ 1 & 2+2\varepsilon & 1 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & 1 & 2+2\varepsilon \end{vmatrix}=0,$$

where $\epsilon = 4q/\alpha_0F^2$, and q are the eigenvalues of **Q**.

The following recurrence relationship can be obtained for the polynomials $p_n(\epsilon)$:

$$p_n(\varepsilon)=2(1+\varepsilon)p_{n-1}(\varepsilon)-p_{n-2}(\varepsilon),$$

which is identical with the recurrence relationship for the Chebyshev polynomials with the argument $1 + \epsilon$. Using the explicit form of these polynomials for n = 1 and 2, [9] we find that p_n are the related Chebyshev polynomials of the second kind:

$$p_n(\varepsilon)=U_n(1+\varepsilon),\quad U_n(x)=\sin[(n+1)\arccos x]/\sin x.$$

Thus, the spectrum of a rotator in a strong field is given by the roots of the Chebyshev polynomials of the second kind:

$$x_n^{(k)}=\cos\frac{k\pi}{n+1};\quad k=1,2,\dots,n. \tag{9}$$

It is natural to expect the behavior of lower levels in the field to be stable when new high-J states are added to a mixed set, i.e., when the order of polynomials p_n is increased. It follows from Eq. (9) that these stable roots may be either the roots with numbers $k \ll n$ approximately equal to 1, or the roots with numbers $k \sim n$, approximately equal to -1. In the former case we have $\epsilon \sim 0$ and the center of gravity of the terms is not shifted, whereas in the latter case $\epsilon \sim -2$, $q \approx -\alpha_0F^2/2$, and the center of gravity shifts twice as fast as predicted by the perturbation theory which ignores the rotational state mixing by the field. We shall show in the next section that in the special case of K = 0 these two possibilities are obtained for the negative and positive polarizabilities, respectively.

Figure 1 shows the behavior of the lower levels in the spectrum of a rotator in a field, obtained for several values of M. The range of values of the parameter $g^2 = \alpha_0F^2/4B < 0$ corresponds to the negative polarizability (see below).

3. THREE-DIMENSIONAL ROTATOR WITH AN INDUCED DIPOLE MOMENT IN A STATIC FIELD

In this section we shall show that the equation describing the influence of an alternating field on a symmetric top molecule with one longitudinal polarizability in the K = 0 state is identical with the equation for a three-dimensional rotator in a static field whose interaction with this field is represented by its polarizability β provided we make the substitution $\beta \to \alpha_0/2$.

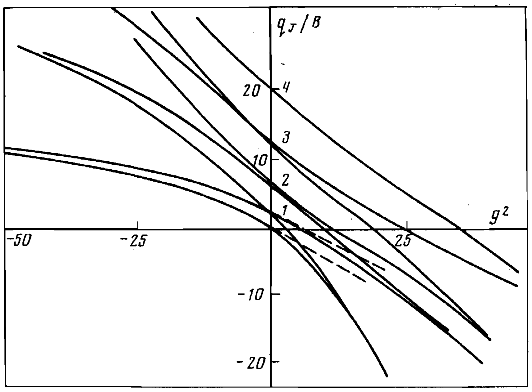

FIG. 1. Dependences of the eigenvalues q_{MJ} on the field intensity (in units of q_J/B and $g^2=\alpha_0F^2/4B$) plotted for several values of J, given on the right of the ordinate and several values of M. The dashed curves show the result of (8) obtained from the perturbation theory for levels with J=0, M=0, and J=1, M=0.

The Schrödinger equation for a rotator in a static field is

$$(BL^2-{}^1/_2\beta F^2\cos^2\theta)\psi=E\psi, \tag{10}$$

where θ is the angle between the rotator axis and the z axis selected to be parallel to the field. We can show that nonzero matrix elements of the operator describing the interaction with the field, calculated in terms of spherical functions $Y_{JM}(\theta, \varphi)$ representing the wave functions in the unperturbed state

$$Q_{JJ'}=-{}^1/_2\beta F^2\langle Y_{JM}|\cos^2\theta|Y_{J'M}\rangle,$$

are identical with the matrix elements of Eq. (7) if we substitute K = 0 and $\beta = \alpha_0/2$.

This result can be explained as follows. The Schrödinger equation for a rotator in an alternating field is of the form

$$i\frac{\partial\psi}{\partial t}=\left(BL^2-\frac{\alpha_0F^2}{2}\cos^2\theta\cos^2\omega t\right)\psi,$$

where α_0 is the dynamic polarizability of the rotator at a frequency ω. If we replace the rapidly oscillating term $\cos^2 \omega t$ by its average value, we obtain Eq. (10) where β is replaced with $\alpha_0/2$. The error due to this replacement is of the order of α_0F^2/ω.

The substitution of the variable $\xi = \cos\theta$ reduces Eq. (10) to

$$\left[\frac{d}{d\xi}(1-\xi^2)\frac{d}{d\xi}+g^2\xi^2-\frac{M^2}{1-\xi^2}+q\right]\psi=0, \tag{11}$$

where q = E/B and $g^2 = \beta F^2/2B$. This equation is satisfied by spheroidal functions. [10] In our case we have $|\xi| \le 1$ and the solutions of Eq. (11) are angular spheroidal functions. Depending on the sign of g^2, we can distinguish prolate spheroidal functions $S_{MJ}(|g|, \xi)$ when $g^2 < 0$ and oblate functions $S_{MJ}(-ig, \xi)$ when $g^2 > 0$.[1)] The sign of g^2 is governed by the sign of the polarizability α_0. Since, in contrast to a static field, the polarizability can be positive or negative in an alternating field, we can have both signs of g^2.

If g^2 is low, expansion of q_{MJ} as a power series gives

$$q_{MJ}=\sum_{k=0}^{\infty} l_{2k}^{MJ}g^{2k},$$

$$l_0^{MJ}=J(J+1), \quad l_2^{MJ}=\frac{2J^2+2J-1-2M^2}{(2J-1)(2J+3)},\dots$$

This formula is identical with Eq. (8) if we make the substitution $\beta \rightarrow \alpha_0/2$. The tables in[10] give the dependence $q_{MJ}(g)$ for several values of M and J (compared with Fig. 1).

We shall now consider the case of strong fields ($|g^2| \rightarrow \infty$). The asymptotics of the spheroidal functions of the parameter g is different for the prolate and oblate functions. If the polarizability is positive, the solutions are the oblate functions. In the limit $g^2 \rightarrow \infty$, the first term of the asymptotic series for q_{MJ} is

$$q_{MJ}=-g^2+2g(M+2\nu+1)$$

or in the notation of Sec. 2:

$$E_{JM}=-{}^1/_4\alpha_0F^2+F(\alpha_0B)^{1/2}(M+2\nu+1); \tag{12}$$

$$\nu=\begin{cases} {}^1/_2(J-M), & J-M \text{ even} \\ {}^1/_2(J-M-1), & J-M \text{ odd} \end{cases}.$$

The asymptotic forms of the spheroidal functions S_{MJ} are given by the Laguerre polynomials:

$$S_{MJ}(-ig,\xi)\sim(1-\xi^2)^{M/2}e^{-g(1-|\xi|)}L_\nu^M[2g(1-|\xi|)]. \tag{13}$$

The physical meaning of the asymptotic forms in strong fields can be understood on the basis of the classical motion of a rotator in a strong static field (compare with[2,3]), which represents small oscillations of the rotator axis about the direction of the field. The greatest contribution to the wave function is then made by the points $\theta = 0$ and $\theta = \pi$, $\xi = \pm 1$. Expanding the Schrödinger equation as a series in θ near these values to terms of the order of θ^2 inclusive, we obtain

$$\left[\frac{d^2}{d\theta^2}-\frac{M^2-{}^1/_4}{\theta^2}-g^2\theta^2+g^2-q\right]\chi=0,$$

$$\chi=(1-\xi^2)^{1/2}e^{-iM\varphi}\psi.$$

This is the equation for a two-dimensional oscillator of frequency $F(2\beta B)^{1/2}$, whose solutions are given in terms of the Laguerre polynomials (13) with arguments limited to terms of the order of θ^2.

The spectrum of an oscillator is equidistant and governed by the quantum number $N = M + 2\nu$; it is described by Eq. (12) and has a characteristic oscillation degeneracy. Thus, the complete spectrum of a molecule as a whole shifts in a strong field proportionally to F^2, which is twice as fast as the shift predicted by the perturbation theory (8). The separation between the levels, which eventually become equidistant, rises proportionally to F. An additional double degeneracy follows from the equivalence of the angles $\theta = 0$ and $\theta = \pi$ for a rotator with an induced dipole moment. In accordance with Eq. (12), the levels with even and odd values of J form separate oscillation spectra corresponding to $\theta = 0$ and $\theta = \pi$.

The correspondence between the rotator levels and the oscillator levels (12) can be obtained by applying the Wigner-Neumann theorem which predicts that in this case the terms with identical values of M and $(-1)^J$ do not intersect. This is shown schematically in Fig. 2.

We shall now consider the case of negative polarizability ($g^2 < 0$), which is possible only in an alternating field. Here, we have to use the prolate spheroidal functions. The asymptotic forms of these functions are

$$S_{MJ}(|g|,\xi)\approx(1-\xi^2)^{1/2}\sum_r h_r^{(N)}(-1)^{N+r}\exp\left(-\frac{|g|}{2}\xi^2\right)H_{n+r}(\xi|g|^{1/2}), \tag{14}$$

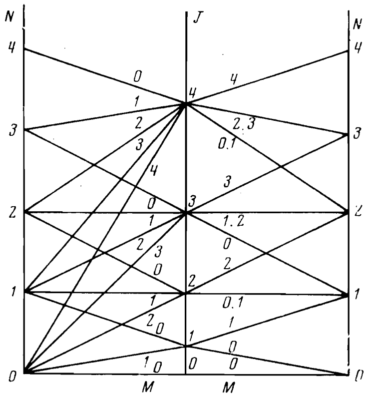

FIG. 2. Correspondence between the spectrum of a rotator and the limiting spectra of two-dimensional ($\alpha_0 > 0$) and one-dimensional ($\alpha_0 < 0$) oscillators.

where H are Hermitian polynomials, h are known coefficients,[10] and

$$N=J-M; \quad r=0,1,\dots; \quad q_{MJ}=2|g|(N+{}^1/_2).$$

The corresponding spectrum is

$$E_{JM}=F(|\alpha_0|B)^{1/2}(N+{}^1/_2). \tag{15}$$

As in the preceding case, the spectrum is equidistant with an asymptotic separation between the levels equal to $F(|\alpha_0|B)^{1/2}$. This corresponds to the case when the rotator with a negative polarizability is oriented perpendicularly to an alternating field. The main contribution to the wave function is given by the values of θ close to $\pi/2$. Following the treatment described above, we obtain

$$\left[-\frac{d^2}{d\tau^2}+M^2-\frac{1}{2}-g^2\tau^2-q\right]\chi=0, \tag{16}$$

where $\tau = \pi/2 - \theta$ and in the limit $|g^2| \rightarrow \infty$, we have

$$\left(\frac{d^2}{d\tau^2}+g^2\tau^2+q\right)\chi=0.$$

This is the equation for a one-dimensional oscillator of frequency $F(|\alpha_0|B)^{1/2}$. Its spectrum is given by Eq. (15) and the wave functions are expressed in terms of the Hermitian polynomials (14). Thus, the motion of a rotator can be represented by the motion in a plane perpendicular to the direction of the field and by harmonic oscillations relative to this plane. The rejected term $M^2 - 1/2$ in Eq. (16) is small compared with g^2 and it gives the spectrum of a two-dimensional rotator. In this limit the energy of the rotator oscillations is independent of M. This corresponds to an infinite order of the degeneracy of each oscillator level (15), namely a level of energy E_N corresponds to an infinite set $\{JM\}$ with $J = M + N$.

Figure 2 shows schematically the correspondence between the rotator and oscillator levels for a negative polarizability in a strong field and, as in the preceding case, this correspondence can be obtained with the aid of the Wigner-Neumann theorem.

4. ROTATIONAL SPECTRUM OF A DIATOMIC MOLECULE IN AN ELLIPTICALLY POLARIZED FIELD

In this section we shall obtain general formulas describing the perturbation of the rotational spectrum of a diatomic molecule by a strong optical field. We shall not restrict our discussion to a linearly polarized field. The polarization structure of quasistationary states of a molecule in an alternating field is in many respects similar to the structure of such states of an atom, discussed in[11]. If the polarization of the radiation field is elliptic, there is no special direction in space and the projection of the total momentum is not conserved. Quasistationary states of a molecule in such a field are obtained by constructing the correct combinations of unperturbed states of the molecule even for weak fields in the absence of mixing of states with the different values of J. The mixing of states with different values of M is then allowed for and it corresponds to inclusion of the influence of the stimulated scattering of light by a molecule, accompanied by a reorientation of its total momentum in space, on the formation of quasistationary molecular states. It is evident that such a reorientation does not occur in the linear and circular polarizations because of conservation of the projection of the total momentum on the direction of polarization in the former case and on the direction of propagation of radiation in the latter case.

The most important forms of the coupling between the orbital and spin momenta of a diatomic molecule are the Hund cases a and b, which we shall now consider in turn.[2]

Case a. In this type of coupling the interaction between the electron spin and the orbital momentum is stronger than the separate interaction of each of these momenta with the molecular axis. The wave functions of a free molecule are described by the quantum number $\Omega = \Lambda + \Sigma$, where Σ is the projection of the spin on the axis. This number is identical with the projection of the total angular momentum on the molecular axis.

In the case of arbitrary polarization of the incident radiation the quantization axis z can conveniently be the direction of propagation of the radiation. The electric vector of the incident wave can be expressed in the form

$$\mathbf{E}(t)=\mathrm{Re}\,(\mathbf{F}e^{-i\omega t}),$$

where $\mathbf{F}$ is the complex amplitude and $F_z = 0$. The equations for the coefficients a_{JM} in the expansion of the wave function of a molecule in a field

$$\psi_{n\Omega}(t)=\sum_{JM} a_{JM}(t)\exp(-iE_{n\Omega}t)\,|n\Omega JM\rangle$$

are analogous to the equations in the system (3):

$$i\dot{\mathrm{a}}=\mathrm{Qa};\quad Q_{JM,J'M'}=BJ(J+1)\delta_{JJ'}\delta_{MM'}-\frac{1}{4}\sum_{ik}F_i^*F_k(c_{ik})_{J\Omega M,J'\Omega M'},\qquad(17)$$

where c_{ik} is the light scattering tensor of Eq. (4). The number K is now replaced with the number Ω, but the mixing of states with different values of Ω is ignored because it corresponds to a change in the electron function of the molecule by the field.

It follows from the above formula that the equations for M = M′ are governed by the coherent (M ≠ M′) and noncoherent (J = J′) matrix elements of the unshifted-scattering tensor (J = J′). The coherent and noncoherent channels make the same contribution to a_{JM} for any field intensity but at high radiation frequencies the noncoherent matrix elements tend to zero faster than the coherent elements.[7] At high field intensities we must bear in mind, as has been done in Sec. 2, the scattering channel involving a change in the frequency (J ≠ J′).

In subsequent transformation we shall replace the Cartesian components F with spherical components and we introduce polarization tensors of an electromagnetic wave:

$$P_{jm}(F)=\frac{1}{I}\sum_{pq}C^{jm}_{1q\,1p}F_pF_q^*,\qquad(18)$$

where I = FF* is the radiation intensity.

The tensors P can be expressed in terms of the Stokes parameters ξ_i:[12][3]

$$\xi_1=l\sin 2\varphi,\quad \xi_2=A,\quad \xi_3=l\cos 2\varphi,$$

where l and A are the degrees of linear and circular polarization, and φ is the angle made by the direction of maximum linear polarization with the x axis. This angle can be reduced to zero by a suitable rotation of the coordinate system and then the components of P become real:

$$P_{00}=-3^{-1/2},\quad P_{10}=2^{-1/2}A,\quad P_{2,\pm2}=l/2,\quad P_{20}=-6^{-1/2}.$$

We shall assume that such a rotation has already been made.

Using the well-known formulas for the matrix elements of the dipole moment operator,[7] we shall transform **Q** to

$$Q_{JM,J'M'}=BJ(J+1)\delta_{JJ'}\delta_{MM'}-\frac{I}{4}\left(\frac{2J+1}{2J'+1}\right)^{1/2}\sum_{J_1jmp\Omega'}[(2J_1+1)(2j+1)]^{1/2}$$
$$\times W(J1J'1;J_1j)C^{J'M'}_{JMjm}C^{J_1\Omega'}_{J\Omega\,1-p}C^{J'\Omega}_{J_1\Omega'1p}\alpha_p^jP_{jm}(F);\qquad(19)$$
$$\alpha_p^j=\sum_{n'\Lambda'}\frac{(\omega_{n'\Omega',n\Omega}-\omega)+(-1)^j(\omega_{n'\Omega',n\Omega}+\omega)}{\omega^2_{n'\Omega',n\Omega}-\omega^2}\langle n\Lambda|\bar{d}_p|n'\Lambda'\rangle\langle n'\Lambda'|\bar{d}_{-p}|n\Lambda\rangle.$$

The formula (19) can be simplified considerably by ignoring the dependences of the energy factors in α_p^j on the quantum number Ω', which is possible far from the resonance frequencies of a molecule. Simple calculations yield

$$Q_{JM,J'M'}=BJ(J+1)\delta_{JJ'}\delta_{MM'}-\frac{I}{4}\left(\frac{2J+1}{2J'+1}\right)^{1/2}\sum_{jmp}C^{J'M'}_{JMjm}C^{j0}_{1-p\,1p}C^{J'\Omega}_{J\Omega j0}P_{jm}\alpha_p^j.\qquad(20)$$

The rotational spectrum of a molecule in a field is governed by the spectrum of the matrix **Q**. Since $P_{jm} = 0$ for m = ±1, the field mixes only the magnetic sublevels which differ in respect of the values of M by ±2, ±4, ... If $l = 0$, we find that $P_{jm} \sim \delta_{m0}$ and the value of M is conserved because a definite direction appears in space (the direction of propagation of the incident wave). The magnetic quantum number is conserved also for A = 0 if the quantization axis is selected to be the x axis but it is difficult to deduce this directly from Eqs. (19) and (20).

A reversal of the sign of the pseudoscalar quantity A reduces the matrix elements $Q_{JM,J'M'}$ to the matrix elements $Q_{J-M,J'-M'}$. If J is an integer, the matrix elements which differ in respect of the sign of the magnetic quantum numbers belong to the same set of mixed states because 2M is an even number. If J is a half-integer, which is possible if the number of electrons in a molecule is odd, these matrix elements occur in different sets. Therefore, if A = 0, the two sets are identical and the spectrum of a molecule is at least doubly degenerate, in agreement with the Kramers theorem.

Case b. In this type of coupling the interaction between the orbital momentum of electrons with the axis is stronger than the LS interaction. This is always true, particularly for the singlet terms. The integral of motion of a free molecule is then **N**, which is the momentum of the molecule apart from its spin, and the projection of **N** on the molecular axis is Λ.

The rotational part of the energy of an unperturbed molecule is[1]

$$E_{NJ}=BN(N+1)+C\Lambda(J-S)(J+S+1)/2N(N+1),$$

where S is the spin of the molecule; $\mathbf{J}=\mathbf{N}+\mathbf{S}$; B and C are the rotational constants.

The equations for the coefficients a_{NJM} in the expansion of the wave function of a molecule in a field in terms of the $|n\Lambda NJM\rangle$ states are

$$i\dot{\mathbf{a}}=\mathbf{Q}\mathbf{a},\quad Q_{NJM,\,N'J'M'}=E_{NJ}\delta_{NN'}\delta_{JJ'}\delta_{MM'}$$

$$-\frac{I}{4}\sum_{N_1pjm}(-1)^{N+N'+j}[(2N+1)(2N_1+1)(2J+1)(2j+1)]^{1/2}C^{J'M'}_{jmJM}C^{N_1\Lambda-p}_{N\Lambda\,1-p}$$

$$\times C^{N'\Lambda}_{N_1\Lambda-p1p}W(N1N'1;\,N_1j)W(jNJ'S;\,N'J)P_{jm}(\mathbf{F})\alpha_p^j, \qquad (21)$$

where the quantities α_p^j differ from the corresponding quantities in (19) by the substitution $\Omega,\ \Omega'\to\Lambda,\ \Lambda'$.

The properties of the eigenvalues of the matrix **Q** mentioned above in case a apply also to case b.

5. SCATTERING OF INTENSE RADIATION BY A MOLECULE

In discussing the scattering of high-intensity optical radiation by a molecule we shall employ, as is usual in problems of this kind, the "strong + weak field" scheme. In the present case a strong classical field modifies the spectrum of a molecule and one of the photons of this field (a quantum of a weakly quantized field) undergoes spontaneous scattering. For simplicity, we shall assume that before this scattering a molecule is in a definite state, which is typical of steady-state conditions when the intensity of an exciting light pulse is much longer than the rotational relaxation time of a molecule (this time usually does not exceed 10^{-11} sec). Otherwise, the scattering amplitude should be quantum-mechanically averaged over the distribution of states.

When a photon of frequency ω is scattered by a state $|n_i\nu_i\rangle$ causing a molecule to undergo a transition to a state $|n_f\nu_f\rangle$, a photon of frequency $\omega'=(E_{n_i}+q_{\nu_i}+\omega)-(E_{n_f}+q_{\nu_f})$ is emitted. Here, q_ν are the eigenvalues of the matrix **Q** for the term $|n\rangle$; ν is the number of a quasistationary state in this term;

$$|n\nu\rangle=\sum_{\varkappa}f_{\varkappa}^{(\nu)}|n\varkappa\rangle,$$

where **f** is the eigenvector of **Q** and κ is the set of quantum numbers representing the state of a free molecule. For a symmetric top we have $\kappa=\{JKM\}$, whereas for a diatomic molecule we have $\kappa=\{JM\}$ in case a and $\kappa=\{NJM\}$ in case b.

The scattering amplitude is expressed in terms of the scattering tensor of a free molecule:

$$A_{\nu_i\nu_f}=\sum_{\varkappa_i\varkappa_f pq}(-1)^{p+q}e'^{*}_{-p}e_{-q}(c_{pq})_{\varkappa_f\varkappa_i}f_{\varkappa_f}^{(\nu_f)*}f_{\varkappa_i}^{(\nu_i)},$$

where $\mathbf{e}'$ is the polarization vector of a photon ω' and $\mathbf{e}$ is a unit vector of the polarization of the incident wave.

The scattering of weak radiation by a free molecule cannot alter its momentum by more than ±2. This gives rise to, in particular, five branches in the Raman and Rayleigh scattering spectra corresponding to changes in the momenta by 0, ±1, and ±2. In a strong field the momentum selection rules no longer apply and a large number of scattering lines may be observed. Moreover, the relative intensities of the scattering in these five branches then depend also on the intensity of the strong incident radiation.

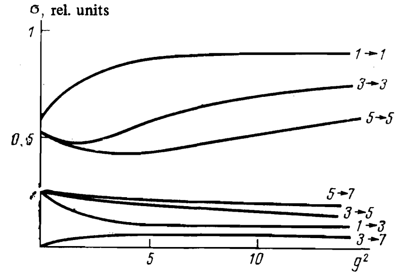

FIG. 3. Field dependences of the light scattering cross sections for M=M′=1; the change in J is given alongside each curve.

Figure 3 gives the field dependences of the cross section for the scattering of intense radiation by a rotator. In weak fields the transition 3—7 and similar transitions are forbidden. It is clear from Fig. 3 that the forbidden lines can appear only if the interaction of a molecule with the field is comparable with the rotational constant.

In the estimates we can use the fact that the theoretical parameter g^2 governing the appearance of new scattering branches becomes of the order of unity for heavy molecules such as CsI with $B\sim10^3$ MHz in fields $F\sim10^4$ V/cm. It is assumed that the polarizabilities governed by the resonance term for which the dipole moment of the transition to the ground term is of the order of 0.1 D when the detuning from resonance is $\Delta\sim10$ cm^{-1}. Experimental observation of the forbidden branches may be difficult because the states with low values of J are weakly populated at room temperature.

Another manifestation of the perturbation of the rotational spectrum may be an induced broadening of the nonresonance scattering line. The field splitting of the various M sublevels, which is a linear function of the field intensity, should result in a linear intensity dependence of the scattering accompanied by a change in M if the field is polarized linearly or circularly. In the elliptic polarization case an increase in the field intensity gives rise to scattering lines corresponding to transitions with $|\Delta M|>2$, which again causes line broadening. However, in reality the intensity dependence of the line width is more complex and is governed by the specific situation.

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[1)] Here M and J are nonnegative integers and J⩾M. The notation is related to the circumstance that $S_{MJ}(0,\xi)\sim Y_{JM}(\theta,0)$, but in the presence of a field the quantity J no longer represents the momentum of a level.

[2)] This treatment is inapplicable to Π terms because of the Λ degeneracy.

[3)] Introduction of the Stokes parameters is also very convenient in the case of totally polarized radiation, which is discussed here.

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