

# Rotational spectrum and collision broadening of rotational lines of molecules in a strong light field

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It is shown that the rotational spectrum and the collision characteristics of molecules are significantly altered in a strong electromagnetic field. The cross section for the phase mismatch and for the excitation of the rotational levels are calculated and it is shown that they decrease with increasing field intensity.

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An electromagnetic field of sufficient intensity alters significantly the energy spectrum and the relaxation characteristics of a quantum system. This leads to the appearance of distinctive nonlinear optical effects connected with the influence of the field on the cross sections of the inelastic processes. A number of papers have recently been published on this topic (see, e.g., [1-4]). In the present article we consider collisions of molecules in a strong electromagnetic field. The field frequency  $\omega$  is assumed to be far from all the resonances, i.e.,  $\omega_e \gg \omega \gg \omega_v, \omega_r$ , where  $\omega_e, \omega_v, \omega_r$  are the corresponding electron, vibrational, and rotational frequencies of the molecule. The ratio  $\omega_e/\omega$  can also be noticeably larger than unity, since the electron frequencies of many molecules correspond to the ultraviolet band, and for the existing high-power lasers  $\omega$  lies in the red band.

The energy of the interaction of the molecules with the electromagnetic field, averaged over the electron variables, can be represented in the form of a series in power of the electric field of the wave:

$$V = -dE \cos \omega t - \frac{1}{2} \alpha_{ie} e_i E^2 \cos^2 \omega t + \dots \quad (1)$$

Here  $d$  and  $\alpha_{ie}$  are respectively the dipole moment and the electron polarization of the molecule at the frequency  $\omega$  in the electronic ground state,  $E$  and  $e_i$  are respectively the amplitude and components of the polarization vector of the electromagnetic field. The next terms of the expansion take into account the dependence of the polarizability on the field, and can be neglected in our situation, since the field is assumed to be much weaker than atomic.

Assuming the inequalities  $dE \ll \omega$  and  $\alpha E^2 \ll \omega$  to be satisfied, we can also disregard the rapidly oscillating terms in (1). Thus, Eq. (1) takes the form

$$V = -\frac{1}{2} \alpha_{ie} e_i E^2.$$

This expression corresponds to the interaction energy in the case of immobile nuclei, i.e., it pertains to a non-vibrating and non-rotating molecule. Therefore  $\alpha_{ie}$  depends on the orientation angles of the molecule relative to the immobile axes and on the internal vibrational coordinates. Since the displacements of the nuclei in the vibrations are relatively small, we can in the principal order assume the nuclei to be at rest in

an equilibrium position and solve at this stage the problem of rotation of the molecule in the presence of an electromagnetic field. Subsequent allowance for the dependence of  $\alpha$  on the vibrational coordinates leads to small corrections that are well known from molecule theory: the non-rigidity of the rotator, the interaction of the vibration and the rotation, etc. If no degenerate vibrations are excited in the molecule, then these effects are of no particular interest and will not be considered from now on. Thus, it can be assumed that the symmetry of the tensor  $\alpha_{ik}$  coincides with the symmetry of the equilibrium configuration of the molecule.

We consider a linear molecule in the state  $^1\Sigma$  in a linearly polarized electromagnetic field. In this case we easily obtain

$$V = -\frac{1}{2} \alpha_{\parallel} E^2 + A \sin^2 \theta, \quad A = \frac{1}{4} (\alpha_{\parallel} - \alpha_{\perp}) E^2, \quad (2)$$

where  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are the principal values of the polarizability tensor in the directions parallel and perpendicular to the molecule axes, respectively, and  $\theta$  is the angle between the molecule axes and the electric vector of the wave. We see that in the presence of an electromagnetic field the free rotation of the rotator is replaced by a motion in the potential (2). If  $\alpha_{\parallel} > \alpha_{\perp}$ , then there are two stable equilibrium positions,  $\theta = 0$  and  $\theta = \pi$ . If  $\alpha_{\parallel} < \alpha_{\perp}$  there is one stable equilibrium position,  $\theta = \pi/2$ .

The Schrödinger equation, which describes the motion of the rotator in the potential (2), was investigated in [5], where scattering of high-power light by a molecule was considered. We are interested in fields so strong that the condition  $A \gg B$  is satisfied, when  $B$  is the rotational constant of the molecule (we assume for the sake of argument that  $\alpha_{\parallel} > \alpha_{\perp}$ , i.e.,  $A > 0$ ). Then only a small region of angles  $\theta$  near zero or  $\pi$  is of importance, and the Schrödinger reduces to the equation for a two-dimensional isotropic oscillator of frequency  $\omega_0 = 2(AB)^{1/2}$ . The energy levels are given, accurate to terms of order  $B$ , by

$$W(N, M) = -\frac{1}{2} \alpha_{\parallel} E^2 + (2AB)^{1/2} B [N + \frac{1}{2} B [(N-1)^2 - M^2]]. \quad (3)$$

where  $N = 1, 2, \dots$  is the principal quantum number of the two-dimensional oscillator,  $M$  is the quantum number of the projection of the angular momentum on the field direction;  $M = 0, \pm 2, \pm 4, \dots \pm (N-1)$  if  $N$  is odd and

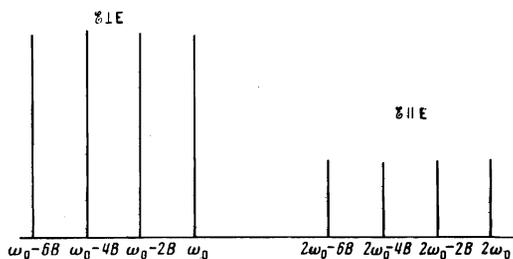


FIG. 1.

$N$ ,  $M = \pm 1, \pm 3, \dots \pm (N-1)$  if  $N$  is even.

Formula (3) pertains to the initial section of the rotational spectrum, where the influence of the strong electromagnetic field is the most appreciable. The number of levels that are correctly described by formula (3) is determined from the relation  $N_{\max} \sim (A/B)^{1/2}$ . The presence of two equivalent minima of the potential energy at  $\theta = 0$  and  $\theta = \pi$  leads to a tunnel splitting of the levels (3), analogous to the inversion doubling. The magnitude of this splitting for the first level ( $N=1$ ,  $M=0$ ) is

$$\Delta E = \frac{32}{\pi\sqrt{5}} A \exp[-2(A/B)^{1/2} + \arctg(\sqrt{5}+2) - \pi(\sqrt{5}/2+1)].$$

If the molecule has an intrinsic dipole moment, then optical transitions between the obtained levels are possible (the analog of the infrared rotational spectrum). The selection rules for these transitions depend on the direction of the electric vector  $\mathcal{E}$  of the emitted or absorbed wave (of the weak field). At  $\mathcal{E} \parallel \mathbf{E}$ , transitions with  $\Delta M = 0$  and  $\Delta N = \pm 2$  are possible. The frequencies of the successive lines of this series are equal to  $2\omega_0 - 2Bn$ ,  $n = 0, 1, 2, \dots$ , and their intensities are proportional to  $\omega_0^3 c^{-3} (\mathcal{E}d)^2 B/A$ . In the case  $\mathcal{E} \perp \mathbf{E}$ ,  $\Delta M = \pm 1$ ,  $\Delta N = \pm 1$  the frequencies are equal to  $\omega_0 - 2Bn$  and the line intensities are proportional to  $\omega_0^3 c^{-3} (\mathcal{E}d)^2 (B/A)^{1/2}$ . The structure of the spectrum is qualitatively illustrated in Fig. 1. The appearance of the small factors  $B/A$  and  $(B/A)^{1/2}$  in the expressions for the intensities means that the dipole moment of the optical transition decreases in the electromagnetic field. The physical reason is that the rotation of the molecule subtends over only a small solid angle near  $\theta = 0$  or  $\theta = \pi$ . This circumstance plays an important role also in the calculation of the cross sections of the elastic and inelastic collisions that determine the width of the rotational line.

It is known<sup>[6]</sup> that rotational lines of dipole molecules are characterized by large collision widths: the corresponding cross sections are of the order of  $(1-3) \times 10^{-4} \text{ cm}^2$ . This is due to the long-range dipole interaction.

We consider collisions of dipole molecules in a strong electromagnetic field. The principal part of the potential, which describes the interaction of the dipole molecules in pair collisions, is of the form

$$U = -\frac{d_1 d_2}{R^3} + 3 \frac{(\mathbf{d}_1 \mathbf{R})(\mathbf{d}_2 \mathbf{R})}{R^5}, \quad (4)$$

where  $\mathbf{R}$  is the relative molecule-positive vector. We assume the translational motion of the molecule to be classical and along straight lines, so that  $\mathbf{R} = \boldsymbol{\rho} + \mathbf{v}t$  ( $\boldsymbol{\rho}$  is the impact parameter and  $\mathbf{v}$  is the relative collision velocity).

Inasmuch as in a strong electromagnetic field an important role is played by small deviations of the molecule axes from the direction  $\mathbf{E}$ , the potential (4) must be expanded in  $\theta$  (or  $\pi - \theta$ ). It is convenient to change over to Cartesian coordinates:  $q_{1,2} = \theta_{1,2} \cos \varphi_{1,2}$ ,  $p_{1,2} = \theta_{1,2} \sin \varphi_{1,2}$ . In first-order approximation in the parameter  $B/A$  expression (4) becomes

$$U = -\frac{d^2}{R^3} + 3 \frac{d^2}{R^5} z^2 + 3 \frac{d^2}{R^5} z [x(q_1 + q_2) + y(p_1 + p_2)]. \quad (5)$$

$x$ ,  $y$ , and  $z$  are the Cartesian components of  $\mathbf{R}$ . Thus, the problem of the collision of two dipole molecules in a strong electromagnetic field reduces to the following: there are two two-dimensional oscillators, which are subjected to a time-dependent perturbation in the form (5).

The quantum transitions induced by this perturbation in the oscillator determine the rotational relaxation of the molecules in the collisions. As seen from (5), in this situation the variables are fully separable and we arrive at the problem of transitions in an oscillator under the influence of an alternating external force. This problem admits of an exact solution (see, e.g.,<sup>[7]</sup>). Consequently, the probabilities of the inelastic transitions can be obtained without using the traditional approximations of collision theory such as the Born, impulse, or adiabatic approximation. The only assumption is smallness of the parameter  $B/A$ .

In the general case the expressions for the transition probabilities are quite cumbersome (see<sup>[7]</sup>). We are interested in the dependence of the cross section on the velocity and on the EMF intensity. We therefore present by way of illustration an expression for the total cross section for the departure from the ground state. The probability of this event is

$$w = 1 - \exp\{-v_x - v_y\},$$

$$v_{x,y} = \frac{1}{2} \left(\frac{B}{A}\right)^{1/2} \left| \int_{-\infty}^{+\infty} F_{x,y}(t) e^{i\omega t} dt \right|^2, \quad (6)$$

$$F_x = 3d^2 z x / R^5, \quad F_y = 3d^2 z y / R^5.$$

To find the cross section  $\sigma$  it is necessary to integrate the probability (6) over the vector  $\boldsymbol{\rho}$  and to average over the orientations of the vector  $\mathbf{v}$  relative to  $\mathbf{E}$ , recognizing the fact that  $\boldsymbol{\rho} \perp \mathbf{v}$ . In the two limiting cases we obtain ( $\bar{w} = 1$ ): at  $v^3 \gg d^2 A^{3/4} B^{5/4}$

$$\sigma = 2\sqrt{\pi} \left(\frac{B}{A}\right)^{1/2} \frac{d^2}{v} \int_0^{\pi/2} E(\cos \theta) \cos^2 \theta d\theta = 3,6 \left(\frac{B}{A}\right)^{1/2} \frac{d^2}{v}, \quad (7a)$$

where  $E$  is a complete elliptic integral of the second kind; at  $v^3 \ll d^2 A^{3/4} B^{5/4}$

$$\sigma = \frac{\pi}{8} \frac{v^2}{AB} L^2 \left[ 1 + o\left(\frac{1}{L}\right) \right], \quad L = \ln \frac{64d^2 B^{3/4} A^{1/4}}{v^6}. \quad (7b)$$

We obtain now the cross section for phase mismatching in elastic collisions. This effect is connected with those terms of the expansion of the interaction (4) which are quadratic in  $q_{1,2}$  and  $p_{1,2}$ . Indeed, in the principal order in  $B/A$  it is precisely these terms which determine the renormalization of the oscillator frequency, and since their coefficients depend on the time, it is with them that the phase mismatching is connected in an adiabatic collision.<sup>1)</sup>

Without allowance for the interaction (4), the system in question has a quadrupole frequency  $\omega_0$  (two identical two-dimensional isotropic oscillators). The interaction lifts this degeneracy, and after diagonalization of the quadratic form resulting from the expansion (4) we obtain the values of the instantaneous frequencies:

$$\omega_s^2 = \omega_0^2 + 2Bd^2\lambda_s/R^2, \quad s=1, 2, 3, 4; \\ \lambda_1 = -1, \quad \lambda_2 = 3(1-2z^2/R^2), \quad \lambda_3 = 2-3z^2/R^2, \quad \lambda_4 = -3z^2/R^2. \quad (8)$$

As seen from (8), it is meaningful to speak of an adiabatic phase mismatching only if the following condition

$$Bd^2/R^2\omega_0^2 \sim d^2/R^2A \ll 1 \quad (9)$$

is satisfied, for in the opposite case the interaction between the molecules exceeds the interaction of the molecules with the electromagnetic field in the collision, and the energy spectrum obtained above becomes significantly distorted.<sup>2)</sup> Assuming (9) to be satisfied, we can obtain the mismatch phase  $\eta_s(\rho)$  for the impact-parameter region  $\rho^3 \gg d^2/A$  by means of the known formula

$$\eta_s = \int_{-\infty}^{+\infty} [\omega_s(t) - \omega_0] dt.$$

The line contour of the rotational transition is formed by superposition of four dispersion contours, the widths and positions of which are determined by the broadening and shift cross sections  $\sigma'$  and  $\sigma''$  (see<sup>[8]</sup>). The presence of two equivalent equilibrium positions at  $\theta=0$  and  $\theta=\pi$  results in an equal probability of molecule collisions in parallel and antiparallel dipole orientations. Since the sign of the interaction (4) is determined by the sign of the product  $d_1d_2$ , the average frequency shift vanishes. For  $\sigma'$  we obtain

$$\sigma_1' = \frac{\pi^2}{2} \left( \frac{B}{A} \right)^{1/2} \frac{d^2}{v}. \quad (10)$$

(At other values of  $s$  the result differs only in a factor on the order of unity.) The contribution of the impact-parameter region in which (9) is violated does not exceed  $\pi(d^2/A)^{2/3}$ . Therefore (10) yields the principal part of the cross section in the velocity region  $v \ll (B/A)^{1/2}(dA)^{2/3}$ .

As seen from (7a), (7b), and (10), the collision width of the rotational lines decreases with increasing electromagnetic-field intensity. This is due to the action of two factors: first, narrowing of the region of essential angles  $\theta$  leads to an effective decrease of the

matrix elements of the interaction between the molecules; second, the increase of the distance between levels by a factor  $(A/B)^{1/2}$  broadens the velocity region in which the adiabatic approximation is valid, thereby decreasing the probabilities of the inelastic transitions.

For an oblate molecule ( $\alpha_{||} < \alpha_{\perp}$ ,  $A < 0$ ) the influence of a strong electromagnetic field on the rotational relaxation is not so significant. In this case, the motion of the molecule reduces to small oscillations about  $\theta = \pi/2$  and to free rotation in the angle  $\varphi$ .<sup>[5]</sup> In other words, in the asymptotic limit  $|A|/B \rightarrow \infty$  a strong electromagnetic field converts a three-dimensional rotator into a plane rotator. It is easily understood that in this case the entire region of angles between the dipole moments of the colliding molecules is effective. Therefore the matrix elements of the interaction (4) has the same characteristic value as in the absence of the electromagnetic field, and are independent of the field intensity in the principal order in  $B/A$ . The spectrum of a plane rotator (in the dipole approximation) consists of equidistant lines with spacing  $2B$ , i.e., is also independent of  $E$ . Thus, in our case the collision broadening does not depend on the electromagnetic-field intensity and has the same order of magnitude as in the absence of a field.

In conclusion we present some numerical estimates. For the HCN molecules,  $B = 4.4 \times 10^{10}$  Hz,  $\alpha_{||} - \alpha_{\perp} = 16$  at. un.,  $d = 2.9 D$ , and the parameter  $A/B$  becomes comparable with unity in fields  $E \sim 10^{-3}$  at. un. We have used here the static values of  $\alpha_{||}$  and  $\alpha_{\perp}$ , i.e., we have obviously overestimated  $E$ , inasmuch as at  $\omega < \omega_0$  the polarizability increases with increasing  $\omega$ . Choosing the value  $A/B \sim 10^2$ , we obtain for the velocity that separates the regions (7a) and (7b) the estimate  $v_0 \approx 2.2 \times 10^5$  cm/sec, and in formula (10) we should put  $v < 10^5$  cm/sec.

<sup>1)</sup> It is easy to see that the terms linear in  $q$  and  $p$  in the perturbation (5) do not lead to a change in the frequency, since they correspond to a shift of the suspension point of the oscillator.

<sup>2)</sup> This manifests itself formally in the fact that  $\omega_s^2$  becomes negative.

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