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Absorption line shape of homogeneously broadened degenerate transition

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The effect of degeneracy in the magnetic quantum number M on the saturation of the absorption of a homogeneously broadened line is investigated. It is shown that the shape of the saturated contour depends on the polarization of the incident wave. The question of the limits of applicability of the approximation of spherical symmetry of the relaxation processes is discussed.

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1. INTRODUCTION

The angular-momentum selection rule causes at least one of the two levels between which a radiative transition is allowed to be degenerate. Moreover, in the case of light absorption by a molecule, both levels are as a rule strongly degenerate in the magnetic quantum number M. Therefore elastic-collision processes accompanied by reorientation of the angular momentum of an atom or a molecule make a discernible contribution to the broadening of the spectral line. The role of these processes in the formation of the linear-absorption line contour was taken into account in a large number of studies (see, e.g.,[1-5]), although not fully enough in most cases. Usually, owing to difficulties connected with the calculation of the collision S matrix, the shape of the contour was determined without taking into account the role of the interference between the transitions that connect various M-components of the lower and upper levels.[1,2]

In problems of nonlinear absorption (the so-called saturation effect) the role of interference of $M\to M'$ transitions, to our knowledge, has not been discussed at all. In this case it is customary to use for the absorbed power the formula derived for an isolated transition by Karplus and Schwinger back in 1948.[6]

In this paper we wish to discuss some qualitative effects that result from the interference of transitions that connect various M-components of the upper and lower levels. We assume here that the density of the perturbing particles is high enough so that the line contour can be regarded as homogeneously broadened and that the broadening due to the Doppler effect can be neglected.

2. EQUATIONS FOR THE DENSITY MATRIX

To describe the absorption line shape we start from a system of equations for the density matrix with a

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collision term in the form

$$\frac{d}{dt}[\rho_{ij}(\mathbf{v})]^{\text{col}}=-\sum_{\alpha\beta}[\Gamma_{ij}^{\alpha\beta}(\mathbf{v})+i\Delta_{ij}^{\alpha\beta}(\mathbf{v})]\rho_{\alpha\beta}(\mathbf{v}), \tag{2.1}$$

where ρ_{ij} are the density-matrix elements and $\mathbf{v}$ is the molecule velocity.

It is known that in spectral problems, in the equations for the density-matrix element that is not diagonal in ij, it is necessary to take into account in $d[\rho_{ji}(\mathbf{v})]^{\text{col}}/dt$ only the contributions from the transitions $\alpha\to\beta$ that differ in frequency from the transition $i\to j$ by an amount less than the homogeneous line width. Most frequently it is necessary to include in the sum over $\alpha\to\beta$ only the transitions that differ from the transition $i\to j$ by the angular-momentum projection M. In the equations for the matrix elements diagonal in ij it is necessary to include in the sum over $\alpha\beta$, generally speaking, all the elements diagonal in $\alpha\beta$. In most cases, however, it can be assumed that the populations of the levels that do not participate directly in the process of the interaction with the field are weakly deformed and preserve their equilibrium values. Therefore the contribution of these levels to the right-hand side of (2.1) is proportional to the Maxwellian velocity-distribution function, and the more complicated form of (2.1) must be retained only for degenerate states. We shall thus include in the sum over $\alpha\beta$ only the summation over the M-states of the degenerate level, and the density-matrix elements that depend on the projections M of the total angular momenta J_m and J_n of the levels m and n will be written in the form $\rho_{mn}(M_mM_n\mathbf{v})$.

It should be noted that the dependence of the quantities Γ and Δ on the velocity of the molecule makes it impossible, generally speaking, to represent the collision term in the simple form (2.1). Owing to this dependence, the collision term takes an integral form even at very high pressures. In the case of small-angle scattering, however (and this is precisely the case most frequently realized in practice), expression (2.1) becomes valid.

Following [7], we can express Γ and Δ in terms of the exact amplitudes of molecule scattering by perturbing particles:

$$\begin{aligned}&\Gamma_{mn}\left(M_mM_n, M_m'M_n', \mathbf{v}=\frac{\hbar\mathbf{k}}{m}\right)+i\Delta_{mn}\left(M_mM_n,\right.\\&\left.M_m'M_n', \mathbf{v}=\frac{\hbar\mathbf{k}}{m}\right)=-in_p\frac{2\pi\hbar}{\mu\mu_a^3}\int d\mathbf{q}\,W_p\left(\frac{\mu_p\mathbf{k}-\mathbf{q}}{\mu_a}\right)\\&\times[\delta_{M_mM_m'}f_n(M_n'\mathbf{q}, M_n\mathbf{q})-\delta_{M_nM_n'}f_m^*(M_m'\mathbf{q},\\&M_m\mathbf{q})]-n_p\frac{\hbar}{\mu\mu_a^3}\int d\varkappa d\mathbf{q}\,W_p\left(\frac{\mu_p\mathbf{k}-\mathbf{q}}{\mu_a}\right)\\&\times\frac{1}{q}\delta(|\varkappa-\mathbf{k}+\mathbf{q}|-q)f_m^*(M_m', \varkappa-\mathbf{k}+\mathbf{q}, M_m\mathbf{q})f_n(M_n', \varkappa-\mathbf{k}+\mathbf{q}, M_n\mathbf{q}).\end{aligned} \tag{2.2}$$

Here $\mathbf{k}$ is the wave vector of the molecule, n_p is the concentration of the perturbing particles, μ is the reduced mass of the molecule and of the perturbing particle, $\mu_a=\mu/m_p$, $\mu_p=\mu/m_a$, m_a and m_p are the masses of the molecule and of the perturbing particle, W_p is the distribution function of the perturbing particles over the wave vectors, $f_m(M_m'\mathbf{q}, M_m\lambda)$ are the molecule and perturbing-particle scattering amplitudes in the c.m.s., and $\hbar$ is Planck's constant.

If we disregard in (2.2) the degeneracy in the magnetic quantum number, i.e., we put $M=M'=0$, then Γ and Δ become functions of only the modulus of the molecule velocity.[7] In the presence of degeneracy, as seen from (2.2), the quantities Γ and Δ become functions of not only the magnitude but also of the direction of the velocity v, and only in the limiting case of very light perturbing particles $\mu_p\to 0$ does this dependence vanish.

It will be convenient henceforth, besides the representation $\rho_{mn}(M_mM_n\mathbf{v})$, to change over to the irreducible representation[8]

$$\rho_{LN}^{mn}(\mathbf{v})=\sum_{M_mM_n}(-1)^{J_n-M_n}(J_mJ_nLN|J_mM_mJ_n-M_n)\rho_{mn}(M_mM_n\mathbf{v}), \tag{2.3}$$

where $(J_mJ_nLN|J_mM_mJ_nM_n)$ is a Clebsch-Gordan coefficient. In this representation the collision term for the density matrix takes the form

$$\frac{d}{dt}[\rho_{LN}^{mn}(\mathbf{v})]^{\text{col}}=\sum_{L'N'}[\Gamma_{LN}^{L'N'}(\mathbf{v})+i\Delta_{LN}^{L'N'}(\mathbf{v})]\rho_{L'N'}^{mn}(\mathbf{v}). \tag{2.4}$$

The functions Γ and Δ are transformed in accordance with the usual formulas for the transformation of tensor quantities:

$$\begin{aligned}(T_{mn})_{LN}^{L'N'}=&\sum_{\substack{M_mM_m'\\M_nM_n'}}(-1)^{J_n-M_n+J_n-M_n'}(J_mJ_nLN|J_mM_mJ_n-M_n)\\&\times(J_mJ_nL'N'|J_mM_m'J_n-M_n')T_{mn}(M_mM_n, M_m'M_n').\end{aligned} \tag{2.5}$$

The convenience of changing over to the representation (2.3) consists in the following. If the quantities Γ and Δ do not depend on the direction of the vector $\mathbf{v}$ or generally do not depend on $\mathbf{v}$ (as is, e.g., the case for perturbation by light particles $\mu_p\to 0$), the equations for the density matrix with the collision term (2.4) should be invariant to rotations of the coordinate system, from which it follows that the constants Γ and Δ have in this case a diagonal form and do not depend on N[8,9]

$$(\Gamma_{mn}+i\Delta_{mn})_{LN}^{L'N'}=\delta_{LL'}\cdot\delta_{NN'}[\Gamma_{mn}(L)+i\Delta_{mn}(L)]. \tag{2.4a}$$

We shall hereafter assume, except in the last section, that Γ and Δ are independent of the direction of v, so that Eq. (2.4a) holds in the irreducible representation.

We consider the interaction between the degenerate transition $m\to n$ with natural frequency and the field of a traveling monochromatic wave $\mathbf{E}=\mathbf{E}_0\exp(i\mathbf{p}\cdot\mathbf{R}-i\omega t)+\text{c.c.}$, when the homogeneous line width $\Gamma\gg\Delta\omega_D$, so that the Doppler broadening can be neglected. We write down the equations for the density matrix with the collision term (2.1) in the form

$$\begin{aligned}&i(\omega-\omega_0)\rho_{12}(M_1M_2\mathbf{v})+\sum_{M_1'M_2'}[\Gamma_{12}(M_1M_2, M_1'M_2')\\&\quad+i\Delta_{12}(M_1M_2, M_1'M_2')]\rho_{12}(M_1'M_2'\mathbf{v})\\&\qquad=\frac{i}{\hbar}z_0W(\mathbf{v})\mathbf{d}_{12}(M_1M_2)E_0\end{aligned} \tag{2.6}$$

$$+\frac{i}{\hbar}\sum_{M_1'M_2'}[\mathbf{d}_{12}(M_1M_2')\mathbf{E}_0\Delta\rho_{22}(M_2'M_2\mathbf{v})-\Delta\rho_{11}(M_1M_1'\mathbf{v})\mathbf{d}_{12}(M_1'M_2)\mathbf{E}_0],$$

$$\sum_{MM'}\Gamma_{11}(M_1M_1',MM')\Delta\rho_{11}(MM'\mathbf{v})$$

$$=\frac{i}{\hbar}\sum_{M_2}[\mathbf{d}_{12}(M_1M_2)\mathbf{E}_0\rho_{12}^*(M_1'M_2\mathbf{v})-\rho_{12}(M_1M_2\mathbf{v})\mathbf{d}_{12}^*(M_1'M_2)\mathbf{E}_0^*],$$

$$(2.7)$$

$$\sum_{MM'}\Gamma_{22}(M_2'M_2,M'M)\Delta\rho_{22}(M'M\mathbf{v})$$

$$=\frac{i}{\hbar}\sum_{M_1}[\mathbf{d}_{12}^*(M_1M_2')\mathbf{E}_0^*\rho_{12}(M_1M_2\mathbf{v})-\rho_{12}^*(M_1M_2'\mathbf{v})\mathbf{d}_{12}(M_1M_2)\mathbf{E}_0].$$

$$(2.8)$$

Here $\rho_{12}(M_1M_2\mathbf{v})$ is the part of the density matrix independent of the time, $\rho_{12}(M_1M_2\mathbf{v},t)=\rho_{12}(M_1M_1\mathbf{v})e^{i\omega t}$, $z_0=z_2-z_1$, z_1 and z_2 are the equilibrium populations of the individual M components of levels 1 and 2 in the absence of the field, $\Delta\rho_{ii}(MM'\mathbf{v})=\rho_{ii}(MM'\mathbf{v})-z_i\delta_{MM'}W(\mathbf{v})$, $W(\mathbf{v})$ is the Maxwellian velocity distribution function, and $d_{12}(M_1,M_2)$ is the matrix element of the dipole moment of the $J_1M_1\to J_2M_2$ transition.

The absorbed power is expressed in terms of the density-matrix elements $\rho_{12}(M_1M_2\mathbf{v})$ in the following manner:

$$P(\omega)=2\hbar\omega_0\int d\mathbf{v}\cdot 2\,\mathrm{Re}\frac{i}{\hbar}\sum_{M_1M_2}\rho_{12}(M_1M_2\mathbf{v})\mathbf{d}_{12}^*(M_1M_2)\mathbf{E}_0^*. \qquad (2.9)$$

In the irreducible representation (2.3), Eqs. (2.6)–(2.8) take the form[10]

$$[i(\omega-\omega_0+\Delta_{12}(L))+\Gamma_{12}(L)]\rho_{LN}^{12}(\mathbf{v})=\frac{i}{\hbar}z_0W(\mathbf{v})\frac{E_0^N d_{12}}{\sqrt{3}}\delta_{L1}$$

$$+\sum_{lL'N'}\frac{i}{\hbar}\frac{E_0^l d_{12}}{\sqrt{3}}(-1)^{N'}[A_{LN,L'-N'}^l\Delta\rho_{L'N'}^{22}(\mathbf{v})-B_{L'-N',LN}^l\Delta\rho_{L'N'}^{11}(\mathbf{v})],$$

$$(2.10)$$

$$\Gamma_{22}(L')\Delta\rho_{L'N'}^{22}(\mathbf{v})=\frac{i}{\hbar}\frac{d_{12}^*}{\sqrt{3}}\sum_{lLN}E_0^{l*}(-1)^N A_{LN,L'-N'}^{-l}\rho_{LN}^{12}(\mathbf{v})$$

$$-\frac{i}{\hbar}\frac{d_{12}}{3^{1/2}}\sum_{lLN}E_0^l A_{L-N,L'N'}^l\rho_{LN}^{12*}(\mathbf{v}), \qquad (2.11)$$

$$\Gamma_{11}(L')\Delta\rho_{L'N'}^{11}(\mathbf{v})=\frac{i}{\hbar}\frac{d_{12}}{3^{1/2}}\sum_{lLN}B_{L'N',L-N}^l E_0^l\rho_{LN}^{12*}(\mathbf{v})$$

$$-\frac{i}{\hbar}\frac{d_{12}^*}{3^{1/2}}\sum_{lLN}E_0^{l*}(-1)^N B_{L'-N',LN}^{-l}\rho_{LN}^{12}(\mathbf{v}). \qquad (2.12)$$

Here

$$A_{LN,L'N'}^l=(-1)^{J_1+J_2+1}[(2L+1)(2L'+1)]^{1/2}\begin{Bmatrix}L & 1 & L'\\ J_2 & J_2 & J_1\end{Bmatrix}(LL'1l|LNL'N'),$$

$$B_{LN,L'N'}^l=(-1)^{J_1+J_2+1}[(2L+1)(2L'+1)]^{1/2}\begin{Bmatrix}L & 1 & L'\\ J_1 & J_1 & J_2\end{Bmatrix}(LL'1l|LNL'N'),$$

$$P(\omega)=2\hbar\omega_0\int d\mathbf{v}\cdot 2\,\mathrm{Re}\frac{i}{\hbar}\frac{d_{12}^*}{3^{1/2}}\sum_N(E_0^N)^*\rho_{1N}^{12}(\mathbf{v}), \qquad (2.13)$$

E^l are spherical contravariant components of the field vector[11]:

$$E^{-1}=\frac{1}{\sqrt{2}}(E_x+iE_y),\quad E^0=E_z,\quad E^1=-\frac{1}{\sqrt{2}}(E_x-iE_y),$$

d_{12} is the reduced matrix element of the $1\to 2$ transition:

$$(J_1M_1|d_l|J_2M_2)=d_{12}(J_21J_1M_1|J_2M_21l)(2J_1+1)^{-1/2}, \qquad (2.14)$$

d_l are spherical contravariant components of the vector $\mathbf{d}$[11]: $d_l=(-1)^l d^l$, and $\{\cdot\cdot\cdot\}$ is the Wigner $6j$-symbol.

3. SHAPE OF ABSORPTION CONTOUR

We start the analysis with the simplest case of linear absorption of the traveling-wave field. The linear-absorption contour can be easily found by using the equation for the irreducible representation of the density matrix (2.10) and retaining in its right-hand side only the term linear in the field

$$\rho_{1N}^{12}(\mathbf{v})=\frac{i}{\hbar}\frac{E_0^N d_{12}}{3^{1/2}}\frac{z_0W(\mathbf{v})}{i(\omega-\omega_0+\Delta_{12}(1))+\Gamma_{12}(1)}. \qquad (3.1)$$

Substituting (3.1) in (2.9) and (3.13) we get

$$P(\omega)=-\frac{4}{3}\hbar\omega_0\left|\frac{d_{12}E_0}{\hbar}\right|^2 z_0\frac{\Gamma_{12}(1)}{(\omega-\omega_0+\Delta_{12}(1))^2+\Gamma_{12}^2(1)}. \qquad (3.2)$$

Formula (3.2) duplicates the well-known result actually obtained already by Anderson[1] and subsequently formulated in the language of irreducible representations in a number of papers (see, e.g., [4,5]). It follows from (3.2) that the linear-absorption contour has a Lorentz profile with width $\Gamma_{12}(1)$ and shift $\Delta_{12}(1)$.

We proceed to consider the nonlinear problem. The system (2.10)–(2.12) is a chain of equations that interconnect density-matrix elements with neighboring indices L and L' such that $|L-L'|\leqslant 1$. As the first step, we break this chain of equations in the following manner: We assume that the only nonvanishing matrix elements ρ_{LN}^{12} are those with $L=1$, and the only nonzero elements $\Delta\rho_{LN}^{ii}$ are those with $L=0$. The physical meaning of this approximation will be discussed later. The truncated system of equations (2.10)–(2.12) takes the form[10]

$$[i(\omega-\omega_0+\Delta_{12}(1))+\Gamma_{12}(1)]\rho_{1N}^{12}(\mathbf{v})=\frac{i}{\hbar}z_0W(\mathbf{v})\frac{E_0^N d_{12}}{3^{1/2}}$$

$$+\frac{i}{\hbar}\frac{E_0^N d_{12}}{3^{1/2}}\left(\frac{1}{(2J_2+1)^{1/2}}\Delta\rho_{00}^{22}(\mathbf{v})-\frac{1}{(2J_1+1)^{1/2}}\Delta\rho_{00}^{11}(\mathbf{v})\right), \qquad (3.3a)$$

$$\Gamma_{22}(0)\Delta\rho_{00}^{22}(\mathbf{v})=2\,\mathrm{Re}\frac{i}{\hbar}\frac{d_{12}^*}{[3(2J_2+1)]^{1/2}}\sum_N(E_0^N)^*\rho_{1N}^{12}(\mathbf{v}), \qquad (3.3b)$$

$$\Gamma_{11}(0)\Delta\rho_{00}^{11}(\mathbf{v})=-2\,\mathrm{Re}\frac{i}{\hbar}\frac{d_{12}^*}{[3(2J_1+1)]^{1/2}}\sum_N(E_0^N)^*\rho_{1N}^{12}(\mathbf{v}). \qquad (3.3c)$$

Substituting $\rho_{00}^{ii}(\mathbf{v})$ from (3.3b) and (3.3c) in (3.3a), multiplying the left- and right-hand sides of the resultant equation by $(E_0^N)^*$, and summing over N we obtain an equation for

$$\rho^{12}=\sum_N(E_0^N)^*\rho_{1N}^{12}.$$

Solving this equation and substituting the result in (2.13) we obtain for the absorbed power

$$P(\omega)=-\hbar\omega_0 z_0\frac{4}{3}|d_{12}|^2|E_0|^2\hbar^{-2}\Gamma_{12}(1)\Big\{[\omega-\omega_0+\Delta_{12}(1)]^2$$
$$+\Gamma_{12}^2(1)+\frac{4}{3}|d_{12}|^2|E_0|^2\hbar^{-2}\Gamma_{12}(1)[(2J_1+1)^{-1}\Gamma_{11}^{-1}(0)+(2J_2+1)^{-1}\Gamma_{22}^{-1}(0)]\Big\}^{-1}. \tag{3.4}$$

Expression (3.4) coincides with the well-known result of Karplus and Schwinger[6] for the saturation of the absorption of an isolated transition. We note that this agreement can take place only if the truncated system (3.3) is used.

We now show that the assumptions made are satisfied in those cases when the relaxation constants $\Gamma_{ii}(1)$, $\Gamma_{ii}(2)$, ..., are much larger at $L\geqslant 1$ than the relaxation constants $\Gamma_{ii}(0)$, i.e., the scattering accompanied by angular momentum reorientation proceeds much more intensively than the scattering accompanied by inelastic departure of the molecules from the levels in question to all other levels. In fact, the right-hand sides of (2.11) and (2.12) are of the same order at $L=0$ and at $L=1$ or 2. Therefore $\rho_{LN}^{ii}\sim[\Gamma_{ii}(L)]^{-1}$ and consequently ρ_{1N}^{ii}, $\rho_{2N}^{ii}\ll\rho_{00}^{ii}$. As a result we need retain in the right-hand side of (2.10) at $L=1$ only ρ_{00}^{ii}, after which the equations take the form (3.3a)–(3.3c). We shall henceforth consider the case of transitions for which the inelastic scattering is much less than the elastic scattering, and consequently the assumptions made here are satisfied.

We consider now another limiting case, when the inelastic-scattering cross section is much larger than that of elastic scattering. Expression (3.4) for the absorbed power is then radically altered. To obtain this expression it is convenient to use the equations for the density matrix in the usual representation (2.6)–(2.8). In accordance with (2.1), the term $(d\rho/dt)^{\text{col}}$ is of the form

$$\frac{d}{dt}[\rho_{mn}(M_mM_n\mathbf{v})]^{\text{cr}}=-\Gamma_{mn}(M_mM_n,M_mM_n)\rho_{mn}(M_mM_n\mathbf{v})$$
$$-\sum_{M_m'M_n'}\Gamma_{mn}(M_mM_n,M_m'M_n')\rho_{mn}(M_m'M_n'\mathbf{v}). \tag{3.5}$$

The first term in the right-hand side of (3.5) reflects the role of the departure from the considered levels J_mM_m and J_nM_n to all the remaining levels, while the remaining terms included in the sum reflect the role of the transitions from the levels M' to M. The departure term includes all the inelastic transitions, and therefore this term makes the main contribution to the right-hand side of (3.5). The arrival terms are proportional to the cross section for the reorientation of the angular momentum without a change of the system energy (elastic channel of the reaction), and can be neglected in accord with the assumptions made. Next, using the spherical symmetry of the relaxation processes, we can show that all the relaxation constants Γ_{mn} do not depend on M, i.e., they are equal to one another. In fact, it follows from (2.4a) and (2.5) that

$$\Gamma_{mn}(M_mM_n,M_m'M_n')=\sum_{LM}(-1)^{J_n-M_n+J_n-M_n'}(J_mJ_nLN|J_mM_mJ_n-M_n)$$
$$\times\quad(J_mJ_nLN|J_mM_m'J_n-M_n')\Gamma_{mn}(L). \tag{3.6}$$

Recognizing that the foregoing implies $T_{mn}\propto\delta_{M_mM_m'}\delta_{M_nM_n'}$, we multiply the left- and right-hand sides of (3.6) by

$$(-1)^{J_n-M_n'}(J_mJ_nLN|J_mM_m'J_n-M_n')$$

and *um* over M_m' and M_n'. This yields

$$\Gamma_{mn}(M_mM_n,M_mM_n)=\Gamma_{mn}(L_1),$$

which proves the statement, since L_1 is arbitrary.

Let us find the shape of the absorption contour of a linearly polarized wave. We direct the atom quantization axis along the field polarization. Equations (2.6)–(2.9) take the form

$$[i(\omega-\omega_0+\Delta_{12})+\Gamma_{12}]\rho_{12}(MM\mathbf{v})=\frac{i}{\hbar}z_0W(\mathbf{v})E_0d_{12}(MM)$$
$$+\frac{i}{\hbar}d_{12}(MM)E_0[\Delta\rho_{22}(MM\mathbf{v})-\Delta\rho_{11}(MM\mathbf{v})], \tag{3.7}$$

From (3.7) we readily obtain an expression for the absorbed power:

$$P(\omega)=-\hbar\omega_0z_0\sum_M\frac{\hbar^{-2}|2E_0d_{12}(MM)|^2\Gamma_{12}}{(\omega-\omega_0+\Delta_{12})^2+\Gamma_{12}^2+\hbar^{-2}|2E_0d_{12}(MM)|^2\Gamma_{12}\beta^{-1}}$$
$$1/\beta=1/\Gamma_{11}+1/\Gamma_{22}. \tag{3.8}$$

From (3.8), as well as from (3.7), it is seen that all the $M\to M$ transitions are saturated independently, as if they were isolated. In each $M\to M$ transition the power absorbed is described by an expression of the Karplus-Schwinger type (3.4). The field broadening is proportional to the dipole moment and, in accord with (2.14), with changing M is changes from zero to a value on the order of $\hbar^{-1}|d_{12}E_0|\Gamma_{12}^{1/2}(\beta J)^{-1/2}$. Thus, instead of one Lorentz contour of the line (3.4) we obtain in this case a superposition of Lorentz contours, each of which has its own field-induced width.

At large values of J we can change in (3.8) from summation to integration. As a result, for the two cases $J_1=J_2$ and $|J_1-J_2|=1$ we obtain respectively $(J_1\approx J_2=J)$

$$P(\omega)=-2\beta J\hbar\omega_0z_0\left[1-\frac{1}{2^{1/2}x}\operatorname{arctg}(2^{1/2}x)\right],\quad J_1=J_2, \tag{3.9}$$

$$P(\omega)=-2\beta J\hbar\omega_0z_0\left[1-\frac{1}{2x(1+x^2)^{1/2}}\ln\left(\frac{(1+x^2)^{1/2}+x}{(1+x^2)^{1/2}-x}\right)\right],$$
$$|J_1-J_2|=1, \tag{3.10}$$

$$x^2=\lambda^2\frac{\Gamma_{12}^2}{(\omega-\omega_0+\Delta_{12})^2+\Gamma_{12}^2},\quad\lambda^2=\frac{1}{J}\left|\frac{d_{12}E_0}{\hbar}\right|^2\frac{1}{\beta\Gamma_{12}}, \tag{3.11}$$

where λ is the saturation parameter.

In the case of circular magnetization of the light wave, the only nonvanishing matrix elements are $d_{12}(M,\ M+1)$ (the quantization axis is best chosen in this case along the vector p). Therefore Eqs. (3.7) retain the same form apart from the substitutions $\rho_{12}(MM\mathbf{v})\to\rho_{12}(M,M\pm 1,\mathbf{v})$, $\rho_{22}(MM\mathbf{v})\to\rho_{22}(M\pm 1,M\pm 1,\mathbf{v})$, $d_{12}(MM)\to d_{12}(M,M\pm 1)$. As a result, the absorbed power also retains the form (3.8), with the substitution $d_{12}(MM)\to d_{12}(M,M\pm 1)$. At large J we can again go over to integration with respect to M, as a result of which we obtain expression (3.10) for the case $J_1 = J_2$, and formula (3.9) for the case $J_1 = J_2 \pm 1$. Thus, if the inelastic-collision cross sections exceed greatly the elastic ones, the fields with linear and circular polarizations are absorbed in different manners.

Let us make a more detailed comparison of (3.4) with formulas (3.8)–(3.10). We note first that at small values of the saturation parameter λ, when the field term in the denominator can be neglected, all the expressions, (3.4) and (3.8)–(3.10), lead to the same result, in full agreement with (3.2). The same statement remains valid also at large values of the parameter of the saturation in the line wing—in the line wing the absorption is always linear. Near the line center, formulas (3.4) and (3.8)–(3.10) lead in general to different results. The only exception is the case of total saturation at $J_1 = J_2$, i.e., the immediate vicinity of the line center, when the field-induced broadening is large: $(\omega - \omega_0 + \Delta_{12})^2 \ll \lambda^2\Gamma(1)/\beta$. A numerical comparison of (3.4) with the exact expressions (3.8) and (3.11) is made difficult by the presence of the summation over M, although their qualitative difference is obvious. The comparison is much smaller at large J, for which it is convenient to rewrite (3.4) in the notation of (3.10):

$$P(\omega) = -2\beta J\hbar\omega_0 z_0\left[1 - \frac{1}{1+{}^2/{}_3x^2}\right]. \tag{3.4a}$$

Figure 1 shows the absorbed power $P(\omega)$ as a function of the parameter $\Delta\omega/\Gamma_{12}(1)$ at different values of the saturation parameter λ, plotted from the formulas (3.4a), (3.9), and (3.10). It is seen from the figure that in this case, when the inelastic scattering greatly exceeds the elastic one (formulas (3.9) and (3.10)), the dependence of the absorbed power on the polarization of the light wave is quite discernible. This makes it possible to deduce, from the observation of such a dependence, which of the relaxation mechanism prevails. If the absorbed power is practically independent of the polarization of the wave, then it can be stated that the main contribution to the relaxation of the system is made by elastic-scattering processes. In this case, vigorous relaxation over the M components leads to equalization of their populations, so that the entire transition can be regarded as nondegenerate with a single saturation parameter λ, in full agreement with formula (3.4a).

The question of the possibility of neglecting degeneracy for molecular transitions with large J has been discussed in the literature in connection with the problem of the propagation of coherent 2π pulses. It was assumed in [12] that vigorous relaxation in M takes place in the system but makes no contribution to the broadening of the transition, so that the total transition relaxation time $1/\Gamma$ may turn out to be less than the duration of the light pulse. At the same time, the populations of all M components manage to become equalized during the pulse, and the transition can be regarded as nondegenerate with a transition dipole-moment matrix element averaged over M. We wish to make a few stipulations in this connection.

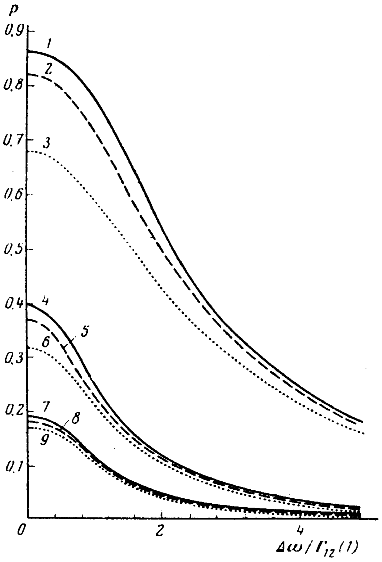

FIG. 1. Dependence of the absorbed power, in units of $2\hbar\omega_0\beta Jz_0$ on the parameter $\Delta\omega/\Gamma_{12}(1)$ at different values of the saturation parameter λ. The solid lines show the absorption-contour shape described by formula (3.4a); dashed—by formula (3.10); dotted—by formula (3.9). Curves 1, 2, and 3 were plotted for saturation-parameter values $\lambda = 3$; curves 3, 5, and 6—for $\lambda = 1$; 8 and 9 for $\lambda = 0.6$.

The possibility of describing a transition that is degenerate in M as nondegenerate is entirely connected with the neglect, in the right-hand side of (2.10), of the matrix elements ρ^{ii}_{LN} at $L \geqslant 1$. In the case of a stationary field it suffices for this purpose to satisfy the condition $\Gamma_{ii}(0) \ll \Gamma_{ii}(L)$, $L \geqslant 1$. In the case of propagation of a short light pulse it is seen from a system of equations such as (2.10)–(2.12), but in which the time derivatives $\dot{\rho}$ are retained, that to be able to neglect these matrix elements it is necessary also to satisfy the condition $\Gamma_{12}(1) \ll \Gamma_{ii}(L)$, $L \geqslant 1$. By suitably choosing the pulse duration τ it is possible to satisfy the conditions

$$\Gamma_{ii}(0) \ll \frac{1}{\tau},\ \Gamma_{12}(1) \ll \frac{1}{\tau},\ \Gamma_{ii}(L) \gg \frac{1}{\tau},\ L \geqslant 1. \tag{3.12}$$

The conditions (3.12) are the complete set of conditions that must be satisfied in order to regard the transition as nondegenerate. We find it difficult, however, to cite a concrete example wherein the condition $\Gamma_{12}(1) \ll \Gamma_{ii}(1)$, $\Gamma_{ii}(2)$, which is needed for the inequalities (3.12) to be compatible, is satisfied.

4. SINGULARITIES OF BROADENING OF VIBRATIONAL-ROTATIONAL TRANSITIONS IN MOLECULES

We consider first the question of the applicability of the results expressed by formulas (3.4), (3.9) and (3.10) to real molecular transitions. We recall that formulas (3.4), (3.9), and (3.10) describe only two limiting cases: when the inelastic-scattering cross section is much larger than the elastic-scattering cross section, and the converse condition. In most real molecular transitions the intermediate case seems to be realized, wherein the inelastic- and elastic-scattering cross sections are of the same order. We can point, however, to molecular transitions to which the approximations considered in the preceding section are applicable with good approximation.

We point first to vibrational-rotational transitions in diatomic molecules containing light atoms such as HCl, HBr, and others. The energy spacing between the rotational levels of these molecules is relatively large, so that the channel of inelastic departure is suppressed to a considerable degree, and with increasing angular momentum of the molecule J the probability of the inelastic departure decreases. In this case we can state that the main contribution to the broadening is made by the reorientation of the angular momentum, i.e., $\Gamma_{ii}(0) \ll \Gamma_{ii}(1)$, $\Gamma_{ii}(2)$. Formulas (3.4) and (3.4a) are therefore valid.

As a second example, we consider the broadening of vibrational-rotational transitions in molecules of the spherical-top type, such as CH_4, SF_6, etc. The Coriolis interaction leads to a relatively small splitting of the rotational components of such molecules, so that inelastic transitions between such components remain practically unchanged with increasing J. At small values of the angular momentum, the cross section of the inelastic transition with reorientation of the angular momentum are generally speaking of the same order. It can however be stated that with increasing angular momentum the contribution made to the broadening by collisions with spin flip decreases. To explain this circumstance we note that the Van der Waals constant depends little on J, as a result of which the value of the angular momentum transferred in the collision remains bounded at $\Delta M \sim (1-10)\hbar$ with increasing J. Therefore the relaxation constant $\Gamma_{mn}(M_m M_n,\ M'_m M'_m)$ at large J is a sharp function of $M_i - M'_i$, as compared with the smooth dependence of $\rho_{mn}(M'_m M'_n \mathbf{v})$ on M'_i. As a result, the matrix $\rho_{mn}(M'_m M'_n \mathbf{v})$ can be taken outside the summation sign at $M'_i = M_i$. After this, the relaxation term takes the form

$$\frac{d}{dt}[\rho_{mn}(M_m M_n \mathbf{v})]^{\mathrm{col}} = -\rho_{mn}(M_m M_n \mathbf{v}) \sum_{M_m' M_n'} \Gamma_{mn}(M_m M_n, M_m' M_n'). \qquad (4.1)$$

This form of the relaxation term denotes in fact neglect of the arrival terms in the equation for the density matrix, i.e., a transition to the approximation (3.7). As shown in the preceding section, in this approximation the sum in (4.1) is independent of M_m or M_n. At first glance, this statement seems quite strange, and we shall therefore dwell on it in somewhat greater detail.

It follows from (3.6) that the constant Γ differs from zero only when $M_m - M_n = M'_m - M'_n$. Therefore the sum in the right-hand side of (4.1) takes for the diagonal density-matrix element $\rho_{ii}(MM)$ the form

$$\sum_{M'} \Gamma_{ii}(MM, M'M') = \Gamma_{ii}(0),$$

i.e., it is equal to the total probability of inelastic departure from the level i. Thus, in the case of a diagonal matrix element collisions with spin flip make no contribution to the right-hand side of (4.1).

In the case of the off-diagonal matrix element $\rho_{12}(M_1 M_2 \mathbf{v})$ we consider the sum

$$\begin{aligned} &\sum_{M_1' M_2'} (J_1 1 J_2 M_2' | J_1 M_1' 1 N) \Gamma_{12}(M_1 M_2, M_1' M_2') \\ &\approx (J_1 1 J_2 M_2 | J_1 M_1 1 N) \sum_{M_1' M_2'} \Gamma_{12}(M_1 M_2, M_1' M_2'). \end{aligned} \qquad (4.2)$$

On going over from the left-hand side of (4.2) to the right one we have used the smoothness of the dependence of the Clebsch-Gordan coefficient on M'_i and M'_2, and have taken it outside the summation sign. Using now Eq. (3.6), we can easily show that the sum (4.2) is equal to $(J_1 1 J_2 M_2 | J_1 M_1 1 N)\Gamma_{12}(1)$, i.e., the sum in the right-hand side of (4.1) is equal to $\Gamma_{12}(1)$ and actually does not depend on M_1 and M_2.

We can now make more precise the meaning of the approximation made on changing over to Eqs. (7). In the example considered here there is no need to state that the inelastic scattering is much larger than the elastic one. Since elastic scattering is accompanied only by transitions to neighboring M components, it follows that at sufficiently large J it ceases to contribute to the broadening.

It is interesting to estimate the accuracy with which relation (4.1) is satisfied. To this end we subtract from (4.1) the exact expression for the relaxation term, and making use of the fact that at large J the quantities $\Gamma_{12}(M_1 M_2,\ M'_1 M'_2)$ are even functions of the difference $M_1 - M_2 = M'_1 - M'_2$, we obtain

$$\begin{aligned} &\sum_{M_1' M_2'} \Gamma_{12}(M_1 M_2, M_1' M_2') [\rho_{12}(M_1 M_2) - \rho_{12}(M_1' M_2')] \\ &\qquad \sim \left(\frac{\Delta M}{J}\right)^2 \Gamma_{12}(M_1 M_2, M_1 M_2) \rho_{12}(M_1 M_2). \end{aligned}$$

Thus, the accuracy of the approximation increases with increasing J. The same estimate is applicable also to diatomic molecules. Therefore in those cases when the inelastic scattering channel plays no role, and there is no randomization of the phase (the Van der Waals constants for the upper and lower levels are close to one another), it can be stated that the line width of the vibrational-rotational transition decreases with increasing J in proportion to $(\Delta M/J)^2$.

5. DEVIATIONS FROM SPHERICAL SYMMETRY

Let us examine the applicability of the spherical-symmetry approximation of relaxation processes. As already noted, the assumption of spherical symmetry holds well in the case of broadening by light particles (e.g., electrons). In other situations, such as, for example, broadening by intrinsic pressure, this question calls for a more detailed examination. By way of example we consider the contour of the linear absorption of the transition $J_1 = 0 \to J_2 = 1$ at an arbitrary ratio of the masses of the investigated and perturbing particles. In this case the collision term in (2.10) no longer has the diagonal form (2.4a) (the relaxation constants $\Gamma^{1N'}_{1N} + i\Delta^{1N'}_{1N}$ differ from zero at $N \neq N'$). Therefore the problem reduces to a system of three coupled equations for the quantities $\rho_{1N}^{12}(N=0,\pm 1)$. It is possible, however, to simplify the problem by a special choice of the quantization axis. We direct the z axis along the velocity of the investigated molecule. It is then obvious from axial-symmetry considerations that only the relaxation constants $\Gamma_{1N}^{1N}+i\Delta_{1N}^{1N}\equiv\Gamma_N+i\Delta_N$ differ from zero, with $\Gamma_{-1}+i\Delta_{-1}=\Gamma_1+i\Delta_1$, and all the constants depend only on the modulus of the velocity.[1)]

The equations for the density matrix take the form

$$[i(\omega-\omega_0+\Delta_N)+\Gamma_N]\rho_{1N}^{12}=\frac{i}{\hbar}z_0W(\mathrm{v})\frac{1}{3^{1/2}}E_0^N d_{12},\quad N=0,\pm1. \tag{5.1}$$

From (5.1) we obtain an expression for the absorbed power:

$$P(\omega)=-\frac{4}{3}\hbar\omega_0z_0\sum_N\int\left|\frac{d_{12}E_0^N}{\hbar}\right|^2W(\mathrm{v})\frac{\Gamma_N(v)\,d\mathrm{v}}{[\omega-\omega_0+\Delta_N(v)]^2+\Gamma_N^2(v)} \tag{5.2}$$

With the aid of the rotation matrices we express $|E_0^N|^2$ in terms of the components of the vector $\mathbf{E}_0$ in an immobile coordinate system:

$$|E_0^N|^2=\sum_{ij}E_{0i}E_{0j}^{*}D_{iM}(\alpha,\beta,0)D_{jM}^{*}(\alpha,\beta,0),$$

where $\beta=\theta$, $\alpha=\varphi-\pi/2$, and θ and φ are the angles of the vector $\mathbf{v}$ in the immobile coordinate system. Substituting this expression in (5.2) and integrating with respect to do_v, we obtain

$$P=-\frac{4}{3}\hbar\omega_0z_0\left|\frac{d_{12}E_0}{\hbar}\right|^2\left\{\frac{1}{3}\int_0^\infty v^2W(v)\frac{\Gamma_0(v)}{[\omega-\omega_0+\Delta_0(v)]^2+\Gamma_0(v)}dv\right.$$
$$\left.+\frac{2}{3}\int_0^\infty v^2W(v)\frac{\Gamma_1(v)}{[\omega-\omega_0+\Delta_1(v)]^2+\Gamma_1^2(v)}dv\right\}$$
$$W(v)=\frac{4}{\pi^{1/2}v_0^3}e^{-v^2/v_0^2}. \tag{5.3}$$

It is seen from this formula that there are two reasons why the absorption line contour differs from a Lorentzian: the dependence of the relaxation constants on v, and the presence, at a given v, of two contours with different relaxation constants. The first of these causes is not connected with degeneracy in the magnetic number M and has already been noted in an investigation[7] of the broadening of a nondegenerate transition. The second sets in only when account is taken of the degeneracy and is connected with the deviation of the relaxation processes from spherical symmetry. It is easily seen that these two causes are closely related. At $v=0$ we have spherical symmetry, and therefore $\Gamma_0(v)=\Gamma_1(0)$. If the relaxation constants do not depend on v, or if the dependence is very weak, then this equality remains in force for all v, so that both causes cease to play a role simultaneously, and the line contour becomes Lorentzian. These arguments, as well as a concrete calculation of the constants Γ_0 and Γ_1, carried out in [14], show that the difference between $\Gamma_0(v)$ and $\Gamma_1(v)$ is of the same order as the difference between $\Gamma_0(v)$ and $\Gamma_0(0)$. The dependence of Γ_0 on v changes little with changing form of the interaction. In the case of a Van der Waals interaction we can describe the $\Gamma(v)$ dependence by using the result of [5]:

$$\Gamma(y)=\Gamma(0)e^{-y^2}\Phi\left(\frac{9}{5},\frac{3}{2},y^2\right),\quad y^2=\frac{m_p}{m_a}\frac{v^2}{v_0^2}. \tag{5.4}$$

Here Φ is a confluent hypergeometric function and v_0 is the mean thermal velocity of the molecule.

At small values of y we can use the expansion $\Gamma(y)=\Gamma(0)(1+0.2y^2)$, which can be used with good accuracy up to values $y\leq 1$. At $m_a=m_p$ (broadening by intrinsic pressure), $\Gamma(v)$ changes by only 20% when v changes from zero to v_0, so that the effect of deviation from spherical symmetry can hardly be noted. This indicates that a substantial difference between the contour (5.3) and a Lorentzian takes place only if $m_p/m_a\gg 1$; if $m_p/m_a\leq 1$ the effects of deviation from spherical symmetry are of little importance. If the case of an arbitrary $J_1\to J_2$ transition, and also for nonlinear absorption, the arguments presented above become somewhat more complicated, but the result remains qualitatively the same as before.

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[1)] In the usual MM' representation this statement is equivalent to asserting that the density-matrix elements ρM_1M_2 and $\rho(M_1', M_2')$, for which $M_1-M_2=M_1'-M_2'$, are connected with the relaxation.

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