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General features of collision narrowing of spectral lines in gases

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A theoretical description is presented of the narrowing of the Doppler contour of spectral lines and of the narrowing of the Q branch of the Raman-scattering spectrum of molecules. The description is based on the exact properties of the collision integral. This reveals a number of new features of the phenomenon, some of which had been observed in experiment and found to have no theoretical explanation. The identity of the mathematical formalism used in the investigation of spectral structures of different origin emphasizes the common interference origin of the phenomenon.

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In the overwhelming majority of cases, collisions of a molecule with surrounding particles lead to a broadening of the spectral line. We consider below two deviations from this rule: the relatively rarely observed narrowing of the Doppler line contour by collisions, which was predicted by Dicke,[1] and the narrowing of the Q-branch of Raman scattering of simple molecules (see, e.g., Refs. 2–4 and the literature cited therein).

Model solutions were constructed for the theoretical description of these effects.[3,5–8] It is shown in the present article that the main qualitative features of the line-narrowing effects can be described without invoking model solutions, within the framework of a theory based only on the exact properties of the collision integral. In addition to an overall survey of the spectral-line narrowing process, this approach reveals new features, not contained in the model solutions, of the described phenomenon.

1. NARROWING OF THE DOPPLER CONTOUR OF A SPECTRAL LINE BY COLLISIONS

1. To facilitate the subsequent comparison with experiment, we consider the specific case of broadening of an isolated vibrational-rotational component of the Raman-scattering spectrum of a molecule. With simple and obvious change of the coefficients of the right-hand sides of the equations, all the formulas presented below are equally applicable to ordinary linear or two-photon absorption.

The line shape of an isolated vibrational-rotational component of the Raman-scattering spectrum of a molecule is described by the density-matrix element

$$\rho(q=0j_1m_1,\ q=1j_2m_2,\ \mathbf{v},\ t)=e^{i(\omega_1-\omega_2)t}\rho(m_1m_2\mathbf{v}),$$

where q is the vibrational quantum number, j is the rotational number, m is the projection of the angular momentum on the z axis, and ω_1 and ω_2 are the frequencies of the incident and scattered waves. The matrix elements $\rho(m_1m_2v)$ satisfy the equation (see, e.g., Ref. 9)

$$i(\Delta\omega-\mathbf{pv})\rho(m_1m_2\mathbf{v})+\sum_{m_1'm_2'}\nu(m_1m_2,\ m_1'm_2',\ \mathbf{v})\rho(m_1'm_2'\mathbf{v})$$
$$-\sum_{m_1'm_2'}\int A(m_1m_2\mathbf{v},\ m_1'm_2'\mathbf{v}')\rho(m_1'm_2'\mathbf{v}')\,d\mathbf{v}'=DQ(m_1m_2)W(\mathbf{v}),\qquad(1.1)$$
$$D=\frac{i}{\hbar}(N_{m_1}-N_{m_2});\ Q(m_1m_2)=\sum_{ks}E_{1k}E_{2s}^{*}(\alpha_{ks})_{m_1m_2}.$$

Here $\Delta\omega=\omega_{12}-\omega_1+\omega_2$, $\mathbf{p}=\mathbf{p}_1-\mathbf{p}_2$, ω_{12} is the frequency of the molecular transition $1\to 2$; $\mathbf{p}_{1,2}$ and $\mathbf{E}_{1,2}$ are the wave vectors and the complex amplitudes of the incident and scattered fields, $N_{mi}=n_i/(2j_i+1)$ is the equilibrium population, m_i are the components of the level with angular momentum j_i, $W(\mathbf{v})$ is the Maxwellian velocity distribution function, α_{ks} is the molecule scattering tensor, and $\hbar$ is Planck's constant.

The intensity of the Raman-scattering line is given by

$$I(\omega)=-2Re\,i\omega_2\sum_{m_1m_2}Q^{*}(m_1m_2)\int\rho(m_1m_2\mathbf{v})\,d\mathbf{v}.\qquad(1.2)$$

In the case of linear absorption, the transition density matrix is

$$\rho(q=0j_1m_1,\ q=1j_2m_2,\ \mathbf{v},\ t)\equiv e^{i\omega t}\rho(m_1m_2\mathbf{v}),$$

where ω is the frequency of the absorbed wave, and Eq. (1.1) remains unchanged if it is kept in mind that in this case $\Delta\omega=\omega_{12}-\omega$, $\mathbf{p}$ and $\mathbf{E}$ are the wave vector and amplitude of the absorbed wave, $Q=\mathbf{E}\cdot\mathbf{d}_{j_1m_1,j_2m_2}$, and $\mathbf{d}$ is the dipole moment of the transition. Expression (1.2) for the intensity likewise remains unchanged.

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The collision term in (1.1) is written in the impact approximation; the quantities ν and A can be expressed in terms of the scattering amplitudes f_1 and f_2 of the molecule in the states $1 \equiv (q_1 j_1)$ and $2 \equiv (q_2 j_2)$ by the molecules of the exciting gas[10]:

$$A\left(m_1m_2\mathbf{v}=\frac{\hbar}{M_a}\mathbf{k},\ m_1'm_2'\mathbf{v}'=\frac{\hbar}{M_a}\mathbf{k}'\right)$$
$$=\frac{N_p\hbar}{\mu\mu_a^3}\left(\frac{M_a}{\hbar}\right)^3\int d\mathbf{q}W_p\left(\frac{\mathbf{k}-\mu_a\mathbf{k}'-\mathbf{q}}{\mu_a}\right)$$
$$\times\delta(|\mathbf{k}'-\mathbf{k}+\mathbf{q}|-q)\frac{1}{q}f_1(m_1,\mathbf{q}+\mathbf{k}'-\mathbf{k};\ m_1'\mathbf{q})$$
$$\times f_2^*(m_2,\mathbf{k}'-\mathbf{k}+\mathbf{q};\ m_2'\mathbf{q});\qquad(1.3)$$
$$\nu(m_1m_2,m_1'm_2',\mathbf{v})=\frac{N_p\hbar}{\mu\mu_a^3}\int d\mathbf{q}$$
$$\times W_p\left(\frac{\mu_p\mathbf{k}-\mathbf{q}}{\mu_a}\right)q\sigma(m_1m_2,m_1'm_2',\mathbf{q});$$
$$\sigma(m_1m_2,m_1'm_2',\mathbf{q})=-\frac{2\pi i}{q}$$
$$\times[\delta_{m_2m_2'}f_1(m_1\mathbf{q},\ m_1'\mathbf{q})-\delta_{m_1m_1'}f_2(m_2\mathbf{q},\ m_2'\mathbf{q})].$$

Here $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{q}$ are wave vectors; M_a and M_p are the masses of the perturbed particles,

$$\mu_p=M_p/(M_a+M_p),\quad \mu_a=M_a/(M_a+M_p),$$
$$\mu=M_aM_p/(M_a+M_p);$$

W_p is the Maxwellian distribution function of the wave vectors of the perturbing particles and N_p is the density of the perturbing particles. The presence of a δ-function under the integral sign in (1.3) and the symmetry of the scattering process with respect to inversion of the coordinate system and of the time lead to an important property of the kernel of the collision integral

$$A(m_1m_2\mathbf{v},\ m_1'm_2'\mathbf{v}')W(\mathbf{v}')$$
$$=A(m_1'm_2'\mathbf{v}',\ m_1m_2\mathbf{v})W(\mathbf{v}).\qquad(1.4)$$

If the molecule scattering amplitudes in states 1 and 2 coincide, the angular momentum is not reoriented by the collisions, and there is no inelastic scattering, then the optical theorem leads to the relation

$$\nu(\mathbf{v})=\int A(\mathbf{v}',\mathbf{v})d\mathbf{v}'.\qquad(1.5)$$

In this case the line contour becomes monotonically narrower with increasing density. In a real situation the relation (1.5) can be satisfied only approximately and, as will be shown later on, this relation is more accurate the more strongly pronounced the narrowing of the Doppler line contour by the collisions. Bearing this in mind, we represent the amplitudes of molecule scattering by the perturbing particles in the form of the sum

$$f_i(m,\ m')=f_0\delta_{mm'}+\Delta f_i(m,\ m'),\qquad(1.6)$$

in which the first term describes elastic scattering, and the second the reorientation with respect to the magnetic moment. It follows from the foregoing that to obtain narrowing of the Doppler line contour by collision it suffices to satisfy the relation $|\Delta f| \ll |f_0|$; this relation will subsequently be made more precise.

From (1.6) follows an analogous subdivision of the kernel of the collision integral:

$$A(m_1m_2\mathbf{v},\ m_1'm_2'\mathbf{v}')=A_0(\mathbf{v},\mathbf{v}')\delta_{m_1m_1'}\delta_{m_2m_2'}$$
$$+\Delta A(m_1m_2\mathbf{v},\ m_1'm_2'\mathbf{v}'),\qquad(1.7)$$
$$A_0(\mathbf{v},\mathbf{v}')\propto|f_0|^2,\quad \Delta A\propto f_0\Delta f_1+f_0\Delta f_2^*+\Delta f_1\Delta f_2^*$$

and of the parameter ν, which we represent as a sum of three terms:

$$\nu(m_1m_2,\ m_1'm_2',\ \mathbf{v})=\nu_0(\mathbf{v})\delta_{m_1m_1'}\delta_{m_2m_2'}$$
$$+\Delta_1\nu(\mathbf{v})\delta_{m_1m_1'}\delta_{m_2m_2'}+\Delta_2\nu(m_1m_2,\ m_1'm_2',\ \mathbf{v}).\qquad(1.8)$$

The parameter $\Delta_2\nu$ is obtained from (1.3) by substituting for f_1 and f_2 the quantities Δf_1 and Δf_2; $\nu_0+\Delta\nu_1$ are obtained from (1.3) by the substitution $f_1=f_2=f_0$, while ν_0 is determined by (1.5) with $A=A_0$. The quantity $\Delta_1\nu$ reflects the role of the inelastic scattering channel and vanishes in the absence of the latter. The quantity ΔA satisfies a relation similar to (1.4). From the inequality $|\Delta f| \ll |f_0|$ and from the additional assumption that the inelastic-scattering cross section is small, an assumption needed for the line narrowing, it follows that $|\Delta A| \ll |A_0|$, and $|\Delta\nu_1|$ and $|\Delta\nu_2| \ll |\nu_0|$.

It is convenient to change from the representation $\rho(m_1m_2\mathbf{v})$ to the irreducible representation $\rho(LM\mathbf{v})$ (Ref. 11):

$$\rho(LM\mathbf{v})=\sum_{m_1m_2}(-1)^{j_2-m_2}C^{LM}_{j_1m_1,j_2-m_2}\cdot\rho(m_1m_2\mathbf{v}),\qquad(1.9)$$

where C are Clebsch-Gordan coefficients.[12] In this representation, Eq. (1.1) and the expression for the intensity (1.2) take the form

$$i(\Delta\omega-\mathbf{pv})\rho(LM\mathbf{v})+(\nu_0+\Delta_1\nu)\rho(LM\mathbf{v})$$
$$+\sum_{L'M'}\Delta_2\nu(LM,L'M',\mathbf{v})\rho(L'M'\mathbf{v})$$
$$-\int A_0(\mathbf{v},\mathbf{v}')\rho(LM\mathbf{v}')d\mathbf{v}'-\sum_{L'M'}\int\Delta A(LM\mathbf{v},L'M'\mathbf{v}')$$
$$\times\rho(L'M'\mathbf{v}')d\mathbf{v}'=DW(\mathbf{v})B_{LM}(2j+1)^{1/2},\qquad(1.10)$$
$$I(\omega)=-2\,\mathrm{Re}\,i\omega_2\sum_{LM}B_{LM}^*(2j+1)^{1/2}\int\rho(LM\mathbf{v})d\mathbf{v}.\qquad(1.11)$$

The kernel of the collision integral $\Delta A(LM\mathbf{v}, L'M'\mathbf{v}')$ is connected here with the kernel in the m_1, m_2 representation by the relation

$$\Delta A(LM\mathbf{v},\ L'M'\mathbf{v}')=\sum_{m_{1,2}m'_{1,2}}(-1)^{2j_2-m_2-m_2'}$$
$$\times C^{LM}_{j_1m_1,\ j_2-m_2}C^{L'M'}_{j_1m_1',\ j_2-m_2'}\Delta A(m_1m_2\mathbf{v},\ m_1'm_2'\mathbf{v}');$$

a similar relation makes it possible to calculate the coefficient $\Delta_2\nu(LM, L'M', \mathbf{v})$ in the new representation. The quantity B_{LM} is given by

$$B_{LM}=(2L+1)^{-1/2}\mathscr{E}(\mathbf{E}_1\mathbf{E}_2^*)\delta_{L,0}\delta_{M,0}$$
$$-\left(\frac{3}{5}\right)^{1/2}\delta_{L,2}\sum_{q\lambda}\begin{pmatrix}2&1&1\\M&\lambda&-q\end{pmatrix}E_{1\lambda}(E_2^*)_{-q}\cdot(j\|S\|j),$$

where $\mathscr{E}$ and S are respectively the scalar part and the symmetrical part with zero trace of the scattering tensor α, E_λ are the spherical components of the vectors, $\begin{pmatrix}j_1&j_2&j_3\\m_1&m_2&m_3\end{pmatrix}$ is the Wigner $3j$-symbol, and $(j\|S\|j)$ is the reduced matrix element.[12]

At a low density of the perturbing particles ($\nu_0 \ll p\cdot v$) the collision term in (1.10) can be neglected, the equations for each LM component of the density matrix become independent and can be easily solved. In this case the intensity $I(\omega)$ is represented as a sum of two Doppler contours corresponding to the values $L=0$ (scalar scattering) and $L=2$ (symmetrical scattering).

With increasing pressure of the perturbing gas, the parameters ν_0, $\Delta_1\nu$, $\Delta_2\nu$, A_0, and ΔA increase in pro-

portion to the density, and Eqs. (1.10) are made more complicated not only because it contains an integral term, but also because the density matrix elements with different L and M become coupled. Naturally, it is impossible to solve such a system of integral equations in general form. It turns out, however, that under the assumptions made concerning the relative smallness of the quantities $\Delta_1\nu$, $\Delta_2\nu$, and ΔA this system can be investigated by perturbation theory, which yields a solution in the form of an expansion in the parameter $\Delta\omega_D/\nu_0$, where $\Delta\omega_D$ is the Doppler line width, and no model assumptions need be made concerning the form of the kernel of the collision integral.

2. We change over in (1.10) to a new function $\tilde{\rho}(LM\mathbf{v}) = [W(\mathbf{v})]^{-1/2}\rho(LM\mathbf{v})$, and introduce the notation

$$\begin{aligned}
&\tilde{A}_0(\mathbf{v},\mathbf{v}') = [W(\mathbf{v}')/W(\mathbf{v})]^{1/2}A_0(\mathbf{v},\mathbf{v}'),\\
&\hat{K}\varphi = \nu_0\varphi - \int \tilde{A}_0(\mathbf{v},\mathbf{v}')\cdot\varphi(\mathbf{v}')\,d\mathbf{v}',\\
&\Delta\tilde{A}(LM\mathbf{v}, L'M'\mathbf{v}') = [W(\mathbf{v}')/W(\mathbf{v})]^{1/2}\Delta A(LM\mathbf{v}, L'M'\mathbf{v}'),\\
&\hat{U}(LM, L'M')\varphi = \Delta_1\nu\delta_{LL'}\cdot\delta_{MM'}\cdot\varphi + \Delta_2\nu(LM, L'M', \mathbf{v})\varphi\\
&\quad - \int \Delta\tilde{A}(LM\mathbf{v}, L'M'\mathbf{v}')\varphi(\mathbf{v}')\,d\mathbf{v}';\\
&\hat{V}(LM, L'M') = i\mathbf{p}\mathbf{v}\delta_{LL'}\cdot\delta_{MM'} + \hat{U}(LM, L'M').
\end{aligned} \tag{1.13}$$

In this notation, Eq. (1.1) takes the form

$$i\Delta\omega\tilde{\rho}(LM\mathbf{v}) + \sum_{L'M'}\hat{V}(LM, L'M')\tilde{\rho}(L'M'\mathbf{v}) + \hat{K}\rho(LM\mathbf{v}) = D[W(\mathbf{v})]^{1/2}B_{LM}(2j+1)^{1/2}. \tag{1.14}$$

Using (1.13) and (1.4), it is easy to verify that the kernel $\tilde{A}_0(\mathbf{v},\mathbf{v}')$ is a symmetrical function with respect to the permutation of $\mathbf{v}$ and $\mathbf{v}'$. It is also seen from (1.5) that the following relation holds for the kernel $\tilde{A}_0(\mathbf{v},\mathbf{v}')$

$$\nu_0(\mathbf{v})[W(\mathbf{v})]^{1/2} - \int A_0(\mathbf{v},\mathbf{v}')[W(\mathbf{v}')]^{1/2}d\mathbf{v}' = 0. \tag{1.15}$$

At high densities, besides the customarily employed inequality $\|\hat{K}\| \gg \|\hat{U}\|$, the relation $\|\hat{K}\| \gg |\mathbf{p}\cdot\mathbf{v}|$ also becomes valid, and consequently $\|\hat{K}\| \gg \|\hat{V}\|$. In this case it is natural to seek the solution of (1.14) in the form of an expansion in the eigenfunctions of the operator $\hat{K}$. Let us note some of the properties of the eigenfunctions of this operator.

Since the function $\tilde{A}_0(\mathbf{v},\mathbf{v}')$ is symmetrical in the variables $\mathbf{v}$ and $\mathbf{v}'$, all the eigenvalues of the operator $\hat{K}$ are real. The equality (1.15) shows that the function $[W(\mathbf{v})]^{1/2}$ is the eigenfunction of the operator $\hat{K}$ corresponding to the eigenvalue $\lambda_0 = 0$. It can be shown that all the remaining eigenvalues of the operator K are positive, $\lambda_n > 0$. Indeed, using the Cauchy inequality and relation (1.15), we obtain for an arbitrary function $\varphi(\mathbf{v})$

$$\begin{aligned}
&\left(\int \varphi(\mathbf{v})[W(\mathbf{v})]^{1/2}\tilde{A}_0(\mathbf{v},\mathbf{v}')[W(\mathbf{v}')]^{1/2}\varphi(\mathbf{v}')\,d\mathbf{v}d\mathbf{v}'\right)^2\\
&\leqslant \int \varphi^2(\mathbf{v})[W(\mathbf{v})]^{1/2}\tilde{A}_0(\mathbf{v},\mathbf{v}')[W(\mathbf{v}')]^{1/2}d\mathbf{v}d\mathbf{v}' \int \varphi^2(\mathbf{v}')[W(\mathbf{v})]^{1/2}\tilde{A}_0(\mathbf{v},\mathbf{v}')\\
&\quad\times[W(\mathbf{v}')]^{1/2}d\mathbf{v}d\mathbf{v}' = \left(\int \varphi^2(\mathbf{v})\nu_0 W(\mathbf{v})\,d\mathbf{v}\right)^2,
\end{aligned}$$

or, introducing a new arbitrary function $\chi(\mathbf{v}) = [W(\mathbf{v})]^{1/2}\varphi(\mathbf{v})$, we obtain

$$\int \chi(\mathbf{v})[\nu_0(\mathbf{v})\chi(\mathbf{v}) - \int \tilde{A}_0(\mathbf{v},\mathbf{v}')\chi(\mathbf{v}')\,d\mathbf{v}']\,d\mathbf{v} \geqslant 0,$$

from which it follows in fact that all the eigenvalues are nonnegative. With respect to the minimum nonzero eigenvalue λ_1 we assume, as is customary, that it does not differ from ν_0 by an order of magnitude, so that when the inequality $\|\hat{K}\| \gg \|\hat{V}\|$ is satisfied we also have $\lambda_n \gg \|\hat{V}\|$ at $n \neq 0$.

We proceed now to solve Eqs. (1.14). During the first stage of the solution of the problem we assume that the operator $\hat{U}$ is diagonal in the indices LM and $L'M'$. In this case the system (1.14) breaks up into separate integral equations for the quantities $\tilde{\rho}(LM\mathbf{v})$. We shall seek the solutions of these equations in the form of expansions in the eigenfunctions of the operator $\hat{K}$:

$$\tilde{\rho}(LM\mathbf{v}) = \sum_n a_n\varphi_n(\mathbf{v}).$$

Substituting this expansion in (1.14), multiplying by $\varphi_k(\mathbf{v})$, and integrating with respect to $\mathbf{v}$, we obtain

$$i\Delta\omega a_0 + V_{00}a_0 + \sum_{n\neq 0} V_{0n}a_n = DB_{LM}(2j+1)^{1/2}, \tag{1.16a}$$

$$(i\Delta\omega + \lambda_k)a_k + V_{k0}a_0 + \sum_{n\neq 0} V_{kn}a_n = 0. \tag{1.16b}$$

A direct solution of (1.16) by perturbation theory is made difficult by the smallness of the coefficient of a_0. We therefore proceed as follows. We express formally a_k in terms of a_0 and a_n, using (1.16b), and substitute in (1.16a). As a result, we get

$$(i\Delta\omega + V_{00} - \Phi_{00})a_0 = DB_{LM}\sqrt{2j+1} + \sum_{s\neq 0}\Phi_{0s}a_s, \tag{1.17}$$

where

$$\Phi_{0s} = \sum_{n\neq 0}(i\Delta\omega + \lambda_n)^{-1}V_{0n}V_{ns}. \tag{1.18}$$

Expressing a_0 from (1.17) in terms of a_s and substituting in (1.16b), we obtain

$$\begin{aligned}
&(i\Delta\omega + \lambda_k)a_k + V_{k0}(i\Delta\omega + V_{00} - \Phi_{00})^{-1}\sum_{s\neq 0}\Phi_{0s}a_s\\
&+ \sum_{s\neq 0}V_{ks}a_s = -DB_{LM}(2j+1)^{1/2}V_{k0}(i\Delta\omega + V_{00} - \Phi_{00})^{-1}.
\end{aligned} \tag{1.19}$$

In the vicinity of the line center $|\Delta\omega - \mathrm{Im}\,V_{00}| \ll \Phi_{00}$ the last two terms in the left-hand side of (1.19) are of the order of Va_k, whereas the first term $\sim\lambda_k a_k$, so that the solution can be sought in the form of a perturbation-theory series in the small parameter V/λ. The first term of the series is of the form

$$a_k^{(0)} = -DB_{LM}(2j+1)^{1/2}(i\Delta\omega + \lambda_k)^{-1}V_{k0}(i\Delta\omega + V_{00} - \Phi_{00})^{-1}.$$

Substituting this expression in (1.17) for a_0, we obtain

$$\begin{aligned}
a_0 &= DB_{LM}(2j+1)^{1/2}(i\Delta\omega + V_{00} - \Phi_{00})^{-1}\\
&\times\left[1 - (i\Delta\omega + V_{00} - \Phi_{00})^{-1}\sum_{s\neq 0}(i\Delta\omega + \lambda_s)^{-1}\Phi_{0s}V_{s0}\right].
\end{aligned} \tag{1.20}$$

Changing now again to the function

$$\rho(LM\mathbf{v}) = [W(\mathbf{v})]^{1/2}\sum_n a_n\varphi_n,$$

substituting it in the expression (1.11) for the intensity, and integrating with respect to $\mathbf{v}$ (the function $[W(\mathbf{v})]^{1/2}$ is orthogonal to φ_n at $n \neq 0$), we obtain

$$I(\omega) = -2\omega_2\,\mathrm{Re}\,iB_{LM}^*a_0(2j+1)^{1/2}. \tag{1.21}$$

Thus, formulas (1.20) and (1.21) enable us to investigate the line contour.

3. We stop first to discuss the expression for the intensity near the line center. In first-order approximation in V/λ we can retain in (1.20) only unity in the square brackets, after which the expression for the intensity becomes

$$I_0(\omega)=J\,\mathrm{Re}[i\Delta\omega+V_{00}-\Phi_{00}]^{-1},\quad J=2\omega_2|D||B_{LM}|^2(2j+1). \tag{1.22}$$

The matrix element $(\mathbf{p}\cdot\mathbf{v})_{00}=0$. Therefore the quantity

$$V_{00}=\int [W(\mathbf{v})]^{1/2}(\Delta_1\nu+\Delta_2\nu+\hat{U})[W(\mathbf{v})]^{1/2}\,d\mathbf{v}=\gamma_{00}+i\delta_{00} \tag{1.23}$$

yields the impact width and the line shift, which differ from their ordinary-impact-theory values in that $\Delta_1\nu$ and $\Delta_2\nu$ depend on the velocity $\mathbf{v}$, and in that an integral operator is present.

It is necessary next to calculate the matrix elements of the operator Φ, which according to (1.18) is expressed in terms of the off-diagonal elements of the operator $\hat{V}$ at $n\neq 0$:

$$V_{0n}\equiv i(\mathbf{pv})_{0n}+\gamma_{0n}+i\delta_{0n}=i\int [W(\mathbf{v})]^{1/2}(\mathbf{pv})\varphi_n(\mathbf{v})\,d\mathbf{v} + \int [W(\mathbf{v})]^{1/2}(\Delta_1\nu+\Delta_2\nu-\hat{U})\varphi_n(\mathbf{v})\,d\mathbf{v}. \tag{1.24}$$

Using (1.24) and (1.18) and neglecting $\Delta\omega$ compared with λ_n, we obtain

$$\Phi_{00}=\sum_{n\neq 0}\lambda_n^{-1}[-(\mathbf{pv})_{0n}^2-2(\mathbf{pv})_{0n}\delta_{0n} +\gamma_{0n}^2-\delta_{0n}^2+2i(pv)_{0n}\gamma_{0n}+2i\gamma_{0n}\delta_{0n}]. \tag{1.25}$$

We now substitute (1.25) in (1.22), retaining only the terms of order $(\mathbf{p}\cdot\mathbf{v})^2/\lambda$, $\mathbf{p}\cdot\mathbf{v}\delta/\lambda$, $\mathbf{p}\cdot\mathbf{v}\gamma/\lambda$. As a result we get

$$I_0(\omega)=J\frac{\gamma_{00}+\Gamma'}{(\Delta\omega+\delta_{00}+\Gamma'')^2+(\gamma_{00}+\Gamma')^2}, \tag{1.26}$$

$$\Gamma'=\sum_{n\neq 0}[\lambda_n^{-1}(\mathbf{pv})_{0n}^2+2\lambda_n^{-1}(\mathbf{pv})_{0n}\delta_{0n}],\quad \Gamma''=\sum_{n\neq 0}2\lambda_n^{-1}(\mathbf{pv})_{0n}\gamma_{0n}. \tag{1.27}$$

We can now refine the condition $|\Delta f|\ll|f_0|$ used to justify the applicability of perturbation theory in (1.16). It is seen from the system (1.16) that actually the condition $|V_{0n}|\ll\lambda_n$ could be satisfied at $n\neq 0$. In the case $L\neq 0$ (linear absorption $L=1$ and depolarization scattering $L=2$), the inequality $|\Delta f|\ll|f_0|$ and the smallness of the inelastic scattering $|\Delta_1\nu|\ll|\nu_0|$ are the necessary and sufficient conditions for the satisfaction of $|V_{0n}|\ll\lambda_n$. In scalar scattering $L=0$, however, this condition may be relaxed. In this case there is no need for requiring the cross section for the reorientation of the angular momentum to be small, and it suffices to have the amplitudes of the scattering accompanied by reorientation to differ little in the upper and lower states. In fact, if, e.g., these amplitudes coincide exactly and there is no inelastic scattering, then by virtue of the optical theorem there follows from (1.3) and (1.12) the relation $\Delta_2\nu=\int\Delta A(\mathbf{v}',\mathbf{v})d\mathbf{v}'$, which ensures the vanishing of all the matrix elements γ_{0n} and δ_{0n}.

Equation (1.26) describes the narrowing of the line contour by collisions. At low densities, when $\lambda^{-1}(\mathbf{p}\cdot\mathbf{v})^2\gg\gamma_{00}$, we have $\Gamma'\gg\gamma_{00}$, so that the width of the Lorentz contour (1.26) decreases monotonically with increasing density ($\lambda\propto N_p$). At a certain perturbing-gas density these quantities become comparable ($\gamma_{00}\propto N_p$), and the line width reaches a maximum. With further increase of the density, γ_{00} increases and the inequality $\gamma_{00}\gg\Gamma'$ begins to be satisfied. In this region the line width Γ and the shift Δ are given by

$$\Gamma=\gamma_{00}+\sum_{n\neq 0}2\lambda_n^{-1}(\mathbf{pv})_{0n}\delta_{0n},\quad \Delta=\delta_{00}+\sum_{n\neq 0}2\lambda_n^{-1}(\mathbf{pv})_{0n}\gamma_{0n}. \tag{1.28}$$

This equation takes into account the density-independent width and line-shift increments that are preserved at high densities of the perturbing gas far beyond the narrowing region. We emphasize that it is precisely these terms which distinguish qualitatively expression (1.28) from the analogous expression obtained with the aid of the model collision integral. Their appearance is due to the dependence of the quantities $\Delta_1\nu$ and $\Delta_2\nu$ on the velocity of the investigated molecule and to the presence of the integral operator in (1.24). Even though at very high pressures these terms result in small additions to the quantities Γ and Δ, it is important that they depend on the geometry of the experiment and take on different values, e.g., in the case of forward and backward Raman scattering. This fact, experimentally observed in Ref. 13, cannot be explained within the framework of the model solutions.

The next term of the expansion (1.20), while much smaller than the first, does lead to a new qualitative effect—the line contour becomes asymmetrical. Since the general expression for the density is very complicated, we confine ourselves to the limiting case of high densities, when $\lambda^{-1}(\mathbf{p}\cdot\mathbf{v})^2\ll\gamma,\delta$. In the calculation of the matrix elements Φ_{0s} and V_{0s} we can neglect the quantity $\mathbf{p}\cdot\mathbf{v}$ and retain only the term $\gamma_{0n}+i\delta_{0n}$. We can simultaneously neglect the quantities Γ' and Γ'', after which we get

$$I(\omega)=J\frac{\gamma_{00}}{(\Delta\omega+\delta_{00})^2+\gamma_{00}^2}\times\left\{1+\frac{1}{\gamma_{00}}\frac{a[\gamma_{00}^2-(\Delta\omega+\delta_{00})^2]+b\gamma_{00}(\Delta\omega+\delta_{00})}{(\Delta\omega+\delta_{00})^2+\gamma_{00}^2}\right\}$$

$$a+ib=\sum_{n,s\neq 0}(\lambda_n\lambda_s)^{-1}V_{0n}V_{ns}V_{s0},\quad V_{ns}=\gamma_{ns}+i\delta_{ns}. \tag{1.29}$$

Expression (1.29) is of interest because it leads to the asymmetry of the line in the pure impact region of the broadening, and the asymmetrical increment is of the order of $(\gamma/\lambda)^2$, and is consequently independent of the gas density. We recall that this distinguishing feature of the broadening of the impact contour is due entirely to the dependence of $\Delta_1\nu$ and $\Delta_2\nu$ on the velocity $\mathbf{v}$ and to the integral term $\hat{U}$ in the operator $\hat{V}$. If the integral term $\hat{U}$ is neglected and $\Delta_1\nu$ and $\Delta_2\nu$ are assumed to be constant, then the coefficients a and b vanish and (1.29) goes over into the usual Lorentz contour. In those cases when a substantial narrowing of the Doppler contour of the investigated line is observed, it is certainly obvious that the parameter $(\gamma/\lambda)^2$ is very small and the deviations of the contour (1.9) from a Lorentz shape could hardly be observed in experiment. However, if the narrowing is small or not observed at all, and all the more if γ is several times

smaller than the parameter λ, then these deviations can be substantial. The fact that the expansion at high densities is actually carried out with respect to the parameter $(\gamma/\lambda)^2$ ensures the validity of (1.29) in this case.

Equation (1.27) for the quantity $\Gamma = \Gamma' + i\Gamma''$ is valid in the region $\Delta\omega \ll \lambda_n$. In the far wing of the line $\Delta\omega \gg \lambda_n$ it is possible to retain $\Delta\omega$ in the calculation of Φ_{00} and neglect the quantities λ_n. As a result, the real and imaginary parts of the parameter Γ change place, so to speak, in the line wing, and the intensity takes the form

$$I(\omega) = J\frac{1}{\Delta\omega^2}\left(\gamma_{00} + \frac{2}{\Delta\omega}\sum_{n\neq 0}(\mathbf{pv})_{0n}\gamma_{0n}\right). \tag{1.30}$$

It is seen from this formula that the asymmetry of the line is preserved also in quite remote wings. It is of interest to note that if γ_{00} and γ_{0n} are equal to zero, then the right-hand side of (1.30) vanishes. This means that in this case the intensity in the wings decreases like the fourth power of $\Delta\omega$.

4. In the entire preceding investigation of the line contour we started from the assumption that the operator $\hat{U}(LM, L'M')$ is diagonal in LM and $L'M'$ or, equivalently, that the different irreducible representations of the density matrix $\rho(LM\mathbf{v})$ are not intermixed by the relaxation processes. Let us examine how the line contour is altered if we disregard this assumption.

We seek the solution of the system (1.14) in the form

$$\delta_\alpha(\mathbf{v}) = \sum_n a_n^\alpha \varphi_n,$$

where α stands for the pair of indices LM. For the coefficients a_n^α we obtain

$$i\Delta\omega a_0^\alpha + \sum_{\alpha'}(V_{\alpha\alpha'})_{00}a_0^{\alpha'} + \sum_{\alpha',n\neq 0}(V_{\alpha\alpha'})_{0n}a_n^{\alpha'} = DB_\alpha(2j+1)^{1/2}, \tag{1.31a}$$

$$(i\Delta\omega+\lambda_k)a_k^\alpha + \sum_{\alpha'}(V_{\alpha\alpha'})_{k0}a_0^{\alpha'} + \sum_{\alpha',n\neq 0}(V_{\alpha\alpha'})_{kn}a_n^{\alpha'} = 0, \quad k\neq 0. \tag{1.31b}$$

We solve (1.31b) formally with respect to $a_k^{\alpha'}$ and substitute in (1.31a). As a result we get

$$i\Delta\omega a_0^\alpha + \sum_{\alpha'}[(V_{\alpha\alpha'})_{00} - (\Phi_{\alpha\alpha'})_{00}]a_0^{\alpha'} - \sum_{\alpha',s\neq 0}(\Phi_{\alpha\alpha'})_{0s}a_s^{\alpha'} = DB_\alpha(2j+1)^{1/2}, \tag{1.32}$$

$$(\Phi_{\alpha\alpha'})_{0s} = \sum_{\alpha'',n\neq 0}(i\Delta\omega+\lambda_n)^{-1}(V_{\alpha\alpha''})_{0n}(V_{\alpha''\alpha'})_{n0}.$$

In the zeroth order in V/λ we can put in (1.32) $a_s^\alpha = 0$ at $s\neq 0$. If the operator $U_{\alpha\alpha'}$, and with it also $V_{\alpha\alpha'}$, are then assumed to be diagonal, we obtain from (1.32) for a_0^α a solution that coincides with the first term of (1.20). On the other hand, if the operator $U_{\alpha\alpha'}$ is not diagonal, then to find a_0^α it is necessary to solve a system of linear equations already in the zeroth order in V/λ. Naturally, this procedure can be carried through to conclusion only by considering a concrete molecular transition. Without dwelling on this question here, we note the following.

The complex operators $U_{\alpha\alpha'}$ and $\Phi_{\alpha\alpha'}$ are symmetrical with respect to permutation of the indices α and α', so that the matrix of the coefficients of (1.32) is not Hermitian. Therefore neither a Lorentz contour, nor even a superposition of Lorentz contours, can represent the solution for a_0^α, and hence also the line intensity. It is obvious, however, that the width of the resultant contour is as before of the order of $U + (\mathbf{p}\cdot\mathbf{v})^2/\lambda$, first increasing and then decreasing with increasing density. Other qualitative features of the broadening are also preserved, including the line-width increment that does not depend on the density.

The form of Eqs. (1.32) allows us to refine the meaning of the approximation wherein the operator $U_{\alpha\alpha'}$ is assumed to be diagonal. It is seen from (1.32) that in the zeroth order in V/λ only a connection between the coefficients a_0^α is produced. For this reason, the coefficients of the equation likewise contain only matrix elements of the form $(U_{\alpha\alpha'})_{n0}$. The detailed expression for the matrix element of the integral part of this operator is

$$\int \varphi_n(\mathbf{v})\Delta\tilde{A}(LM\mathbf{v}, L'M'\mathbf{v}')[W(\mathbf{v}')]^{1/2}\,d\mathbf{v}\,d\mathbf{v}'$$
$$= \int \varphi_n(\mathbf{v})[W(\mathbf{v})]^{1/2}\Delta A(L'M'\mathbf{v}', LM\mathbf{v})\,d\mathbf{v}\,d\mathbf{v}'.$$

Thus, the diagonality of the operator U follows automatically from the assumption that the coefficients $\Delta\nu(LM, L'M', \mathbf{v})$ and $\int \Delta A(LM\mathbf{v}, L'M'\mathbf{v}')d\mathbf{v}$ are diagonal. The last assumption is fully equivalent to the approximation of spherical symmetry of the relaxation processes, which is traditionally used to describe the broadening of a degenerate transition without allowance for collisions with change of velocity.[11,14] Although in most cases the applicability of this approximation cannot be strictly corroborated,[14,15] one can expect the off-diagonal parts of the operator $(U_{\alpha\alpha'})_{n0}$ to be relatively small and not to lead to qualitative deviations from the broadening picture described above.

5. Murray and Javan[13] measured carefully the line width of the Q-branch of Raman scattering by hydrogen molecules. The line width as a function of the density, for forward and backward scattering, is shown in Fig. 1 by the dark and light circles, respectively. In backward scattering one observes a strong collision narrowing of the Doppler line, $\Delta\omega_D = 0.34\ \text{cm}^{-1}$. In the case of forward scattering, the Doppler width is much smaller, $\Delta\omega_D \approx 0.035\ \text{cm}^{-1}$, the line narrowing sets in at low density, and the line width in the narrowing region becomes comparable with the experimental error; this region is not shown in Fig. 1. The measurements results are compared in Ref. 13 with the linewidth calculations used in the strong and weak collision models. It turns out that to reconcile the calculations with experiment it must be assumed that the plot of the impact

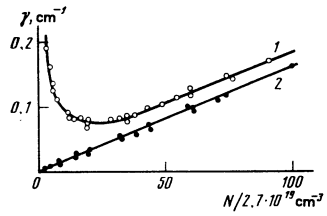

FIG. 1. Experimentally measured[3] backward-scattering line width (○). Curves 1—theoretical dependence of the backward-scattering line width on the density; 2—experimental dependence[3] of the forward scattering line width on the density.

line width against the gas density has different slopes for forward and backward scattering. The actual reason is that, as seen from Fig. 1, the difference between the forward and backward scattering line widths in the density region[1)] from 40 to 100 amagat remains constant at approximately 0.02 cm^{-1}, whereas within the framework of the models of both strong and weak collisions these widths should come close together with increasing density. Naturally, the different dependence of the pure impact line width on the density for forward and backward scattering does not agree with the premises of the impact theory.

Formula (1.27) resolves this contradiction completely. As already noted, owing to the dependence of the parameters of the broadening on the velocity v and owing to the presence of an integral term in the operator $\hat{V}$, a density-independent increment appears in the parameter Γ', equal in order of magnitude to the difference between the experimentally measured forward and backward scattering line widths. We assume for our estimate that

$$2\sum_{n\neq 0}\frac{(\mathbf{pv})_{0n}}{\lambda_n}\delta_{0n}\approx 2\frac{\Delta\omega_D}{\lambda}\delta,$$

where $\Delta\omega_D$ is the Doppler width. For the backward scattering $\Delta\omega_D\approx 0.34$ cm^{-1} we assume the shift to be $\delta = 1.5\times 10^{-3}[cm^{-1}/amagat]\cdot N_p$, where N_p is the gas density, and we estimate $\Delta\omega_D/\lambda$ from the equation $\Delta\omega_D^2/\lambda = \gamma_{00}$, which holds true at the density $N_0 = 20$ amagat at which the width is a minimum. In the case of backward scattering we obtain

$$2\Delta\omega_D\delta/\lambda\approx 2\Delta\omega_D^{-1}\gamma_{00}(N_0)\,\delta(N_0)\approx 6\cdot 10^{-3}\ cm^{-1}.$$

For forward scattering $\Delta\omega_D\approx 0.035$ cm^{-1}, so that the corresponding increment is decreased to approximately one-tenth. We thus obtain that the difference between the line widths in forward and backward scattering is approximately 6×10^{-3} cm^{-1}, which differs by only a factor of three from the experimentally observed value. Naturally, it is difficult to expect from the foregoing estimate a better agreement. It follows from (1.28) that a similar density-independent increment appears also in the line shift. This fact, however, cannot be compared with experiment, inasmuch as the line shift was measured in Ref. 13 only for backward scattering.

The values of λ_n and δ_{0n} in (1.27) are proportional to the gas density N_p. It follows therefore from (1.26) that the total line width is $\Gamma = A_1/N_p + A_2 + A_3N_p$, where $A_3N_p = \gamma_{00}$ and $A_3 = 1.5\times 10^{-3}$ cm^{-1}/amagat [the experimentally measured slope of the $\gamma_{00}(N_p)$ curve], and

$$A_2 = 2\sum_{n\neq 0}\lambda_n^{-1}(\mathbf{pv})_{0n}\delta_{0n} = 14\cdot 10^{-3}\ cm^{-1}$$

is also the experimentally measured difference between the forward and backward scattering line widths at high densities.

The only remaining unknown is A_1, which can be determined, e.g., by requiring that the minimum of the width be reached at the experimentally obtained value $N_0 = 20$ amagat. From this we get $A_1 = A_3\cdot(20)^2 = 6\times 10^{-1}$ $cm^{-1}\cdot$amagat. The $\Gamma(N_p)$ curve plotted with these parameters is shown in Fig. 1. The agreement is within the limits of the experimental error.

6. It is of interest to compare the foregoing approach to the description of the broadening with the extensively used models of weak and strong collisions.

In the strong-collision model $\Delta A(\mathbf{v}, v') = 0$ and $A_0(\mathbf{v}, \mathbf{v}') = \nu_0 W(\mathbf{v})$. From Eq. (1.4), which takes the form

$$\nu_0(\mathbf{v})W(\mathbf{v})W(\mathbf{v}') = \nu_0(\mathbf{v}')W(\mathbf{v}')W(\mathbf{v}),$$

it follows that $\nu_0(\mathbf{v}) = \nu_0(\mathbf{v}')$, i.e., the parameter ν_0 does not depend on the velocity. It would therefore be inconsistent to retain in this model the dependences of $\Delta_1\nu$ and $\Delta_2\nu$ on v, and as a result the sum $\Delta_1\nu + \Delta_2\nu$ must be set equal to velocity-independent parameter $\gamma + i\delta$ that describes the impact broadening. The equation for the eigenfunctions of the kernel

$$\tilde{A}_0(\mathbf{v}, \mathbf{v}') = \nu_0[W(\mathbf{v})W(\mathbf{v}')]^{1/2}$$

takes the form

$$\nu_0\varphi_n(\mathbf{v}) - \nu_0[W(\mathbf{v})]^{1/2}\int[W(\mathbf{v}')]^{1/2}\varphi_n(\mathbf{v}')\,d\mathbf{v}' = \lambda_n\varphi_n(\mathbf{v}).$$

This equation has one eigenvalue $\lambda_0 = 0$ and an eigenfunction $\varphi_0 = [W(v)]^{1/2}$. All the remaining eigenvalues are the same and equal to $\lambda_n = \nu_0$, $n\neq 0$. All the matrix elements γ_{0n} and δ_{0n} in (1.27) vanish, and Γ takes the form

$$\Gamma' = \nu_0^{-1}\sum_{n\neq 0}(\mathbf{pv})_{0n}^2 = \nu_0^{-1}\{[(\mathbf{pv})^2]_{00} - [(\mathbf{pv})_{00}]^2\}$$
$$= \nu_0^{-1}\int W(\mathbf{v})(\mathbf{pv})^2\,d\mathbf{v}, \quad \Gamma'' = 0.$$

If, despite the inconsistency of this step, we retain the dependence of γ and δ on v in the strong-collision model, the density-independent increments to Γ' and Γ'' still vanish because the functions δ and γ are even. For this reason, e.g.,

$$\nu_0^{-1}\sum_{n\neq 0}(\mathbf{pv})_{0n}\delta_{n0} = \int W(\mathbf{v})(\mathbf{pv})\delta(\mathbf{v})\,d\mathbf{v} = 0.$$

Thus, the strong-collision model is by its very nature a two-parameter model and does not yield in principle the density-independent increments to the line width.

In the weak-collision model, a transition is made, after assuming the kernel $\tilde{A}_0(v, v')$ to be narrow, from integral equations of the type (1.14) in their diagonal variant to an equation of the Fokker-Planck type.[5] The two coefficients that appear in this equation are assumed to be constant parameters, inasmuch as only in this case does the equation admit of an analytic solution that leads to the same qualitative results as the strong-collision model. If we retain in the equation the velocity dependence of the coefficients, a procedure permissible in principle, the problem becomes no less complicated than the analysis of the initial integral equation in general form.

2. NARROWING OF THE *Q*-BRANCH OF THE VIBRATIONAL BAND OF THE RAMAN-SCATTERING SPECTRUM IN A GAS

1. In the preceding section we considered the broadening of an isolated j component of the Q branch.

Naturally it was assumed here that the frequencies of the different j components differ quite strongly and that they do not overlap in the entire considered range of pressures. The splitting of the j components is determined by the interaction between the vibration and rotation

$$\omega_0-\omega_j=\Delta_j=2\pi c\alpha_e j(j+1),$$

where ω_0 is the frequency of the vibrational transition, c is the speed of light, and α_e is the constant of the interaction between the vibration and rotation. The splitting Δ_j for the light molecules H_2, D_2 and HD is large, so that the j components broaden independently up to very high pressures. For all the remaining molecules the constant α_e is small, and the different j components of the Q branch begin to overlap even at pressures of several atmospheres. Starting from this stage, the broadening of the entire structure as a whole depends essentially on the interference of the overlapping components. In the case of depolarized scattering, this interference, while restructuring the broadening picture as a whole, does not lead to qualitative singularities, since contributions to the line width are made only by collisions accompanied by a reorientation of the angular momentum. The situation is different in the case of the scalar part of the Q branch. In this case the collisions accompanied by reorientation of the angular momentum do not influence the broadening, as a result of which the scalar part of the Q branch of simple molecules (such as, e.g., N_2 and O_2) begins to narrow with increasing density. This phenomenon was considered theoretically in Refs. 3, 7, and 8, where model representations were used concerning the collision integral, and was observed experimentally numerous times.[2,4,16]

It will be shown below that the narrowing of the Q branch is similar in many respects to the collision narrowing of the Doppler line contour. The main qualitative features of this phenomenon follow from the law of conservation of the number of particles (unitarity of the collision S matrix), and can be described within the framework of a theory based only on the exact properties of the collision integral.

2. At those densities at which narrowing of the Q branch takes place, the impact width of the line exceeds substantially the Doppler width, so that the Doppler broadening can be neglected. As a result one can neglect also the change of the velocity of the molecules in collisions, and it can be assumed that the colliding particles move along classical linear trajectories. Nonetheless, the dependence of the relaxation constants on the relative particle velocity is subsequently preserved.[14,15] This dependence, however, is of no principal significance in our problem and will also be neglected. Within the framework of this approximation, the relaxation processes have spherical symmetry and interrelate only density matrix elements with identical L and M.

The system of equations for the elements of the density matrix $\rho(L=0,M=0,j)\equiv\rho(j)$, which describe the broadening of the scalar part of the Q branch, is easiest to obtain formally from (1.10) by replacing the parameter $\mathbf{p}\cdot\mathbf{v}$ by Δ_j, the molecule velocity $\mathbf{v}$ by the discrete index j, and the function $W(\mathbf{v})$ in the right-hand side of (1.10) by unity, and by introducing a new relaxation matrix $A(j,j')$ that describes transitions of the molecule from the level j' to j in collisions. After this we obtain for the density matrix $\rho(j)\equiv\rho(L=0,M=0,j)$, which is connected by relation (1.9) with the matrix elements $\rho(q_1=0jm_1,q_2=1jm_2)$ in the jm representation, the system of equations

$$i(\Delta\omega+\Delta_j)\rho(j)+\sum_{j'}A(j,j')\rho(j')=D_jB_{L=0,M=0}(2j+1)^{1/2}. \qquad (2.1)$$

In Eqs. (2.1) is retained only the connection between the matrix elements that are at resonance at close frequencies, i.e., that correspond to radiative transitions without change of the rotational quantum number. The expression for the line intensity is analogous to (1.11):

$$I(\omega)=-2\omega_2\,\mathrm{Re}\left\{iB^*_{L=0,M=0}(2j+1)^{1/2}\sum_j\rho(j)\right\}. \qquad (2.2)$$

The relaxation constants $A(j,j')$ are connected by a relation similar to (1.12) with the relaxation constants $\Gamma(q_1jm_1,q_2jm_2;q_1j'm'_1,q_2j'm'_2)$ in the jm representation. In the case of interest to us $L=L'=M=M'=0$, taking into account the explicit form of the coefficients[12]

$$C^{L=0,M=0}_{jm_1,j-m_2}=(-1)^{j_2-m_2}\frac{\delta_{m_1m_2}}{(2j+1)^{1/2}},$$

we obtain

$$A(j,j')=(2j+1)^{-1/2}(2j'+1)^{-1/2}\sum_{mm'}\Gamma(q_1jm,q_2jm;\,q_1j'm',q_2j'm'). \qquad (2.3)$$

Thus, to investigate the shape of the Q-branch contour it is necessary to solve the system of coupled equations (2.1) for the quantities $\rho(j)$. In general form, naturally, this problem cannot be solved. In the particular case of broadening of the Q branches of simple molecules, however, the relaxation matrix Γ has certain distinguishing properties that make it possible to establish a number of qualitative properties of the broadening picture.

In the quasiclassical molecule-trajectory representation the coefficients Γ are of the form[17]

$$\Gamma(q_1jm,q_2jm;\,q_1j'm',q_2j'm')$$
$$=-\int[\delta_{jj'}\delta_{mm'}-S(q_1jm,q_1j'm',\mathbf{b})S^*(q_2jm,q_2j'm',\mathbf{b})]F(\mathbf{b})\,d\mathbf{b}. \qquad (2.4)$$

The elements of the S matrix for the scattering of the investigated molecule by the perturbing particles depend on the vibrational quantum number and on a number of other collision parameters, designated by the collective symbol $\mathbf{b}$, with respect to which the averaging is performed. It is very important in what follows that all the Γ are proportional to the density N_p of the perturbing gas. Reference 3 contains detailed arguments in favor of the statement that in our case the S matrix depends very little on the vibrational quantum number and that the probabilities of transitions between different vibrational states are small. Bearing this in mind, we represent the S matrix as a sum of two terms

$$S(qjm,qj'm',\mathbf{b})=S_0(jm,j'm',\mathbf{b})+\Delta S(qjm,qj'm',\mathbf{b}),$$

the first of which is independent of the vibrational state

of the molecule, whereas the second takes into account the small difference between the scattering matrices in the upper and lower states of the molecule as well as the possible presence of transitions with change of q (quenching of the oscillations). Naturally, $|\Delta S| \ll |S_0|$. Equations (2.4) and (2.3) can be represented in the form of a similar sum:

$$\begin{aligned}&\Gamma(q_1jm,\ q_2jm;\ q_1j'm',\ q_2j'm')\\&=\Gamma_0(jm;\ j'm')+\Delta\Gamma(q_1jm,\ q_2jm;\ q_1j'm',\ q_2j'm');\\&A(j,j')=A_0(j,j')+\Delta A(j,j').\end{aligned}\tag{2.5}$$

The quantity Γ_0 is expressed in terms of the transition probability. Therefore, by virtue of the unitarity of the S matrix (the particle-number conservation law) we have

$$\sum_{j'm'}\Gamma_0(jm;\ j'm')=0,\quad \sum_{j'}A_0(j,j')\,(2j'+1)^{1/2}=0.\tag{2.6}$$

The succeeding transformation, as well as the subdivision in (2.5), are completely analogous to the transformations of the preceding section. The values of Γ_0, just as the probabilities of the $j'm'\to jm$ transitions per unit time, satisfy the detailed-balancing condition

$$N_j(2j+1)^{-1}\Gamma_0(j'm';\ jm)=N_{j'}(2j'+1)^{-1}\Gamma_0(jm;\ j'm'),$$

from which it follows that

$$A_0(j',j)=\frac{N_{j'}}{N_j}\frac{2j+1}{2j'+1}A_0(j,j').$$

A transition to new functions

$$\tilde\rho(j)=\left(\frac{2j+1}{N_j}\right)^{1/2}\rho(j)$$

symmetrizes the relaxation matrix

$$i(\Delta\omega+\Delta_j)\tilde\rho(j)+\sum_{j'}\tilde A_0(j,j')\tilde\rho(j')+\sum_{j'}\Delta\tilde A(j,j')\tilde\rho(j')$$

$$=\left(\frac{2j+1}{N_j}\right)^{1/2}D_jB(2j+1)^{1/2},\quad \tilde A_0(j,j')=A_0(j,j')\left(\frac{2j'+1}{2j+1}\right)^{1/2}\left(\frac{N_j}{N_{j'}}\right)^{1/2}.\tag{2.7}$$

The matrix $\tilde A_0(j,j')$ is symmetrical and, as seen from (2.6), satisfies the relation

$$\sum_{j'}\tilde A_0(j,j')\,(N_{j'})^{1/2}=0,\tag{2.8}$$

i.e., the vector $(N_j)^{1/2}$ is an eigenvector of the matrix $\tilde A_0$ and corresponds to the eigenvalue $\lambda_0=0$.

3. At low pressures, the $\tilde A_0$ are small, $\tilde A_0\ll\Delta_j$. Therefore each of the functions $\tilde\rho(j)$ has a resonance at the natural frequency $\Delta\omega\approx-\Delta_j$, so that the contours of the lines corresponding to different j transitions do not overlap. As a result, the system (2.7) breaks up into independent equations for the quantities $\tilde\rho(j)$, with trivial solutions. For the intensity of the entire Q branch we obtain from (2.2) in this case

$$\begin{aligned}&I(\omega)=2\omega_2\sum_j\gamma_j|D_j||B_j|^2(2j+1)\,[(\Delta\omega+\Delta_j+\delta_j)^2+\gamma_j^2]^{-1},\\&\gamma_j+i\delta_j=\tilde A_0(j,j)+\Delta\tilde A'(j,j)+i\Delta\tilde A''(j,j),\\&\Delta\tilde A(j,j)=\Delta\tilde A'+i\Delta\tilde A''.\end{aligned}\tag{2.9}$$

Thus, at low density of the perturbing gas the intensity $I(\omega)$ of the Q branch is a superposition of Lorentz contours. Equation (2.9) is valid so long as these contours do not overlap. With increasing density, the components begin to overlap and to find $I(\omega)$ it is necessary to solve the complete system (2.7). In the intermediate pressure region, when the shifts Δ_j and the relaxation coefficients $\tilde A_0$ are of the same order, it is necessary to specify for such a solution the explicit form of the matrix $\tilde A_0$, after which the problem can be solved numerically. At high pressures, however, when the relaxation terms in Eqs. (2.7) become dominant, i.e., $|\tilde A_0(j,j')|\gg\Delta_j$, the problem can again be solved analytically.

In this case it is natural to seek the solution in the form of the eigenvectors χ_{nj} of the matrix $\tilde A_0$:

$$\tilde\rho(j)=\sum_n a_n\chi_{nj},\quad \sum_{j'}\tilde A_0(j,j')\chi_{nj'}=\lambda_n\chi_{nj}.\tag{2.10}$$

The following is known concerning the eigenvectors and eigenvalues of the matrix. Since the matrix $\tilde A_0$ is symmetrical, all its eigenvalues are real, and the eigenvectors corresponding to these eigenvalues are orthogonal. Next, it follows from (2.8) that one of the eigenvalues is equal to zero, $\lambda_0=0$, and corresponding to this eigenvalue is the vector

$$\chi_{0j}=(\sigma)^{-1/2}(N_j)^{1/2},\quad \sigma=\sum_s N_s.\tag{2.11}$$

Using the property (2.6) and the inequality $\tilde A_0(j,j')>0$ at $j\neq j'$, which follows from (2.4), it can be shown that all the remaining eigenvalues are larger than zero, $\lambda_n>0$. The relative magnitudes of these eigenvalues depend on the explicit form of the relaxation matrix A_0. It is obvious, however, that all are proportional to the perturbing-gas density N_p, and we shall also assume that they do not condense towards zero.

Substituting the expansion (2.10) in (2.7) and introducing the symbol $V_{jj'}=i\Delta_j\delta_{jj'}+\Delta\tilde A(j,j')$, we obtain for the coefficients a_n by the standard method the system of equations

$$(i\Delta\omega+V_{00})a_0+\sum_{n\neq0}V_{0n}a_n=\frac{t}{\hbar}B\sigma^{1/2},\tag{2.12a}$$

$$(i\Delta\omega+\lambda_k)a_k+V_{k0}a_0+\sum_{n\neq0}V_{kn}a_n=0,\tag{2.12b}$$

which differs from (1.16) only in the right-hand side. At high pressures $\lambda_k\gg V$ at $k\neq0$, so that the solution of this system is similar to (1.16), and a_0 differs from (1.20) only by a coefficient.

4. Changing back from the functions $\tilde\rho(j)$ to $\rho(j)$ and substituting in (2.2), we obtain

$$I(\omega)=-2\omega_2\,\mathrm{Re}\left[iB\sum_{jn}(N_j)^{1/2}a_n\chi_{nj}\right]=-2\omega_2\,\mathrm{Re}[iBa_0\sigma^{1/2}].\tag{2.13}$$

We have taken into account here (2.11) and the orthogonality of the eigenvectors

$$\sum_j(N_j)^{1/2}\chi_{nj}=\delta_{n0}\sigma^{1/2}.$$

Substituting a_0 in (2.13) we obtain in the zeroth order in V/λ

$$\begin{aligned}&I(\omega)=2\frac{\omega_2}{\hbar}|B|^2\sigma\Gamma'[(\Delta\omega+\Gamma'')^2+(\Gamma')^2]^{-1},\\&\Gamma'+i\Gamma''=V_{00}-\Phi_{00}.\end{aligned}\tag{2.14}$$

Taking into account the explicit form of the operator V,

we obtain the expression

$$V_{0n}=\sigma^{-1/2}\left[i\sum_j (N_j)^{1/2}\Delta_j\chi_{nj}+\sum_{jj'}(N_j)^{1/2}\Delta\tilde{A}_0(j,j')\chi_{nj'}\right]=i\Delta_{0n}+\gamma_{0n},$$

from which it is seen that the quantities Δ_{0n} are real and do not depend on the density N_p, while

$$\Delta_{00}=\sigma^{-1}\sum_j N_j\Delta_j$$

coincides with the center of gravity of the structure (2.9) as $N_p\to 0$, and the parameters $\gamma_{0n}=\gamma'_{0n}+i\gamma''_{0n}$ are generally speaking complex and proportional to N_p. At $\Delta\omega\ll\lambda_k$ we can neglect $\Delta\omega$ in the denominator of (1.18). The line intensity (2.14) then takes the form of a Lorentz contour of width Γ' and with the maximum shifted by Γ'', given by

$$\Gamma'=\left[\gamma_{00}'+\sum_{n\neq 0}\frac{1}{\lambda_n}((\gamma_{0n}'')^2-(\gamma_{0n}')^2)\right]+\left[\sum_{n\neq 0}\frac{2}{\lambda_n}\gamma_{0n}''\right]+\left[\sum_{n\neq 0}\frac{\Delta_{0n}^2}{\lambda_n}\right],\qquad(2.15)$$

$$\Gamma''=\left[\gamma_{00}''-\sum_{n\neq 0}\frac{1}{\lambda_n}2\gamma_{0n}''\gamma_{0n}'\right]+\left[\Delta_{00}-\sum_{n\neq 0}\frac{1}{\lambda_n}2\Delta_{0n}\gamma_{0n}'\right].$$

In the square brackets of (2.15) are combined terms having the same dependence on the gas density N_p: the first term is proportional to N_p, the second is independent of N_p, and the third is inversely proportional to N_p. It is therefore clear that the line width can be represented in the form $\Gamma'(N_p)=C_1N_p+c_2+c_3/N_p$, where c_i are coefficients independent of the density. The line width Γ' first decreases with increasing N_p, reaches at a density $N_0=(c_3/c_1)^{1/2}$ a minimum equal to $\Gamma'(N_0)=c_2+2(c_1c_3)^{1/2}$, and increases with further increase of density. Since $\gamma_{0n}/\lambda_n\ll 1$, the second term in the first square bracket of (2.15) is much smaller than the first, so that $c_1N_p\approx\gamma'_{00}$. The order of magnitude of c_2 is $\Delta\gamma''/\lambda$. The parameter γ''/λ is small, $\gamma''/\lambda\ll 1$, but since it may turn out that $\Delta\gg\gamma'_{00}$, the first and second terms of (2.15) can be of the same order. Moreover, we shall present below reasons why the inequality $\gamma''\gg\gamma'$ may be valid. In this case the second term can be much larger than the first in the entire range of pressures accessible to experiment.

It appears that the line shift can always be represented with high accuracy as $\Gamma''=\gamma''_{00}+\Delta_{00}$, since $\gamma'/\lambda\ll 1$. We recall that Eqs. (2.14) and (2.15) were obtained in zeroth order in the parameter V/λ. Without dwelling on the investigation of the next terms of the expansion, we note that allowance for these terms, just as in the case of the narrowing of a Doppler contour, leads to asymmetry of the line.

5. It is of interest to compare the formulas obtained above with the results to which the strong-collision model leads. In this model

$$A_0(j,j')=-\nu[(2j'+1)/(2j+1)]^{1/2}N_j\sigma^{-1}\ \text{at}\ j\neq j',\quad A_0(j,j)=\nu(\sigma-N_j)\sigma^{-1}$$

and consequently

$$\tilde{A}_0(j,j')=-\nu(N_jN_{j'})^{1/2}\sigma^{-1}\ \text{at}\ j\neq j',\quad \tilde{A}_0(j,j)=\nu(\sigma-N_j)\sigma^{-1}.$$

It is seen directly from the eigenvalue equation that $\lambda_0=0$, and all the remaining values λ_n are the same and equal to $\lambda_n=\nu$. The last term in (2.15a) takes in this case a particularly simple form

$$(\nu)^{-1}\sum_{n\neq 0}\Delta_{0n}\Delta_{n0}=(\nu)^{-1}[(\Delta^2)_{00}-\Delta_{00}^2].$$

All the qualitative features of (2.15) are preserved. However, besides the assumption concerning the form of the matrix $\tilde{A}_0(j,j')$, in the strong-interaction model it is actually assumed that the matrix $\Delta\tilde{A}(j,j')$ is diagonal and does not depend on j or j'. In this case all the $\gamma_{0n}=0$ at $n\neq 0$, and (2.15) becomes a two-parameter formula

$$\Gamma'+i\Gamma''=\gamma_{00}'+(\nu)^{-1}[(\Delta^2)_{00}-\Delta_{00}^2]+i(\gamma_{00}''+\Delta_{00}).$$

6. We discuss now the possible relative values of γ'_{0n} and γ''_{0n}. As seen from (2.4) and (2.5), the quantities γ_{0n} are proportional to the difference between the collision S matrix in the upper and lower states, $\gamma_{0n}\propto S\Delta S$. We express the S matrix in the upper state S_1 in terms of the S matrix in the lower state S_0 in the form

$$S_1(b)=S_0(b)\exp[i\varphi(b)-\Gamma(b)],$$

emphasizing by the same token the role of change of the phase shift $\varphi(b)$ in collisions because of the differences between the Van der Waals constants in the vibrational states $q=0$ and $q=1$, and the role of the damping of the oscillation. Since $\varphi(b)$ and $\Gamma(b)$ are small, the exponential can be expanded in a series, after which we get

$$\Delta A(j,j')\propto-\int|S_0(b)|^2\left[i\varphi(b)-\frac{1}{2}\varphi^2(b)-\Gamma(b)\right]F(b)\,db.\qquad(2.16)$$

If there is no phase change in the collisions, $\varphi=0$, then the $\Delta A(j,j')$ are real and only in this case can the Q branch width at high pressures γ_{00} (in the region where the width increases with increasing density) be identified with the vibration-damping rate averaged over j. If, on the contrary, $\varphi^2(b)>\Gamma(b)$, the width of the Q branch at high pressures is determined by the loss of phase. In this case, as seen from (2.16), the imaginary part of γ_{0n} is much larger than the real part, $\gamma''_{0n}\gg\gamma'_{0n}$, thus justifying the retention of the second term in (2.15a).

7. Smirnov and Fabelinskiĭ[16] investigated experimentally the narrowing of the Q branch of acetylene C_2H_2 by pressure of nitrogen N_2. The dependence of the width and of the shift of the Q branch on the nitrogen pressure p_1 was measured at different acetylene pressures p_2, and in the region of effective narrowing of the Q branch ($p_1=70-120$ atm) the nitrogen pressure exceeded substantially the acetylene pressure ($p_2=0.55-3.7$ atm). Under these conditions it can be assumed that the matrix A_0 and its eigenvalues are determined by the collisions of the acetylene molecules with the nitrogen molecules, and consequently, the values of λ in (2.15) are proportional to p_1.

The line broadening of acetylene by its own pressure can be treated as a perturbation, by including the results of the actions of these collisions and the quantities γ_{0n}. In this case the quantities γ_{0n} are linear functions of both the nitrogen density and of the acetylene densi-

ty: $\gamma_{0n} = c_1 p_1 + c_2 p_2$. Substituting these values of γ_{0n} in (2.15) we can easily verify that the dependence of the Q-branch width on the density takes the form

$$\Gamma'(p_1, p_2) = A_1 p_1 + A_2 p_2 + B_1 + B_2 p_2/p_1 + c/p_2,$$

where A, B, and c are constants independent of the density. At constant nitrogen pressure and with increasing acetylene density, the width of the Q branch increases in proportion to p_2 with a proportionality coefficient $A_2 + B_2/p_1$ that depends on the nitrogen pressure. Therefore, with increasing nitrogen pressure the $\Gamma'(p_1)$ curves corresponding to different acetylene pressures come closer together, as is qualitatively confirmed by experiment.[16] Similar increments appear also in the line shift $\Gamma''(p_1, p_2)$, so that the shift becomes a nonlinear function of the nitrogen density p_1. This nonlinearity is also quite noticeable on the experimental $\Gamma''(p_1)$ curve obtained in Ref. 16.

CONCLUSION

From the physical point of view, the two considered phenomena have a common property, which is apparently typical of all the cases in which a narrowing of collision lines can be observed. In both the lower and the upper states there is a level substructure (connected in the former case with the kinetic energy of the molecules and in the latter with the rotational energy), and the quantum numbers characterizing the substructure do not change in radiative transitions. At the same time, the collisions of the molecules in a gas lead mainly to transitions between states of only one and the same substructure and are identical in the initial and final states that are connected by the radiative transition. The narrowing is the result of interference between the spectral components that make up the transition.

[1)] One amagat equals 2.69×10^{19} cm^{-3}.

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