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INFLUENCE OF COLLISIONS ON STIMULATED RANDOM SCATTERING IN GASES

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We investigate the influence of collisions on the structure of the Q branch of random scattering in gases. We show that according to the experimental data the total width of the Q branch remains constant in a wide range of pressures.

INTRODUCTION

FOR stimulated random scattering (SRS) on vibrational transitions of diatomic molecules such as O_2, N_2, and particularly for the magnitude and the pressure dependence of the gain, principal interest attaches to the Q-branch structure made up of the transitions $\Delta v = 1$, $\Delta J = 0$ (v and J are the vibrational and rotational quantum numbers). At low pressure, the distribution of the intensity in the Q branch is determined by the splitting of the frequencies of the $J \rightarrow J'$ transition as a result of interaction of the vibration and rotation. The frequencies of the Q-branch components are described by the formula (see[1,2])

$$\omega(J) = \omega_0 - 2\pi c\alpha_e J(J+1), \tag{1}$$

where α_e is the interaction constant. This constant is small ($\alpha_e = 0.0171\ \text{cm}^{-1}$ for N_2 and $\alpha_e = 0.016\ \text{cm}^{-1}$ for S_2), so that even at relatively low pressures, on the order of several atmospheres, the Q-branch components overlap completely. One might expect a further increase of the pressure to lead to an increase in the width of the Q branch. The experimental data, however, yield an entirely different result. For example, in the case of O_2 and N_2 the widths $\Delta\omega_Q$ ($\approx 3\ \text{cm}^{-1}$ at $T \approx 300°\text{K}$) remain constant in the pressure region 15–125 atm[2,3]. In the same pressure interval, the widths of the individual components of the purely rotational band of the Raman scattering $\Delta v = 0$, $\Delta J = \pm 2$ increase in proportion to the concentration, and at $p \approx 100$ atm they exceed the total width of the entire Q branch by almost two times. These experimental results have not been explained in the theory to this day (a qualitative discussion is contained in[4,5]).

At the same time, in recent years, in connection with the great interest in SRS in gases and in connection with a number of applied problems, this problem has acquired considerable significance. It suffices to indicate that the SRS gain in gases of the type under consideration is $k \propto N/\Delta\omega_Q$, where N is the molecule concentration.

In this paper we construct a theory of the broadening of the Q branch of Raman scattering in gases. It is shown that with increasing pressure the growth of the width of the Q branch is stopped as a result of specific interference effects. Moreover, under certain conditions and in a certain pressure interval, we can expect a decrease in the value of $\Delta\omega_Q$, and consequently a nonmonotonic dependence of the gain k on the pressure.

GENERAL THEORY OF IMPACT BROADENING

We first formulate the theory of impact broadening in a form most convenient for the description of the interference effects of interest to us. We start from the following formulas for the calculation of the spectrum of the radiative transition of an arbitrary quantum system, an atom or a molecule, experiencing collisions with the surrounding particles:

$$I(\omega) = \frac{1}{\pi}\operatorname{Re}\int_0^\infty e^{-i\omega\tau}\Phi(\tau)\,d\tau, \tag{2}$$

$$\Phi(\tau) = \sum_{\alpha\beta\alpha'\beta'} W_\alpha \rho^{(\alpha\beta)}_{\alpha'\beta'}(\tau) f_{\alpha'\beta'} f_{\beta\alpha}. \tag{3}$$

The correlation function $\Phi(\tau)$ is written here in the form of a sum over all possible states of the system, $W_\alpha \propto \exp[-E_\alpha/kT]$ is the population of the state α, $f_{\alpha\beta}$ are the unperturbed matrix elements of the considered radiative transition, and $\rho^{(\alpha\beta)}_{\alpha'\beta'}(\tau)$ is the element of the system density matrix. The superscripts ($\alpha\beta$) denote that these matrix elements satisfy the initial conditions

$$\rho^{(\alpha\beta)}_{\alpha'\beta'}(0) = \delta_{\alpha\alpha'}\delta_{\beta\beta'}. \tag{4}$$

Using (2) and (3), we have

$$I(\omega) = \frac{1}{\pi}\operatorname{Re}\sum_{\alpha\beta\alpha'\beta'} W_\alpha \rho^{(\alpha\beta)}_{\alpha'\beta'}(\omega) f_{\alpha'\beta'} f_{\beta\alpha}, \tag{5}$$

$$\rho(\omega) = \int_0^\infty e^{-i\omega\tau}\rho(\tau)\,d\tau. \tag{6}$$

Assuming that the perturbation experienced by the system reduces to binary collisions, and assuming these collisions to be instantaneous, we write for $\rho(\tau)$ the following equation:

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[H_0\rho] + \left(\frac{\partial\rho}{\partial t}\right)_{\text{coll}} \tag{7}$$

Here H_0 is the Hamiltonian of the unperturbed system, and $[H_0\rho] = (H_0\rho - \rho H_0)$.

We denote the set of parameters characterizing the collision by g. Let the number of collisions per second with parameters in the interval g, g + dg be equal to P(g) dg, and let the increment of the density matrix ρ as a result of one collision be $\Delta\rho(g)$. Then

$$\left(\frac{d\rho}{dt}\right)_{\text{coll}} = \int P(g)\,\Delta\rho(g)\,dg = \int P(g)[S^{+}\rho S-\rho]dg, \tag{8}$$

where S = S(g) is the exact S-matrix of the collision.

Substituting (8) in (7), taking the Fourier transform (6), and taking the initial conditions (4) into account, we obtain a system of equations for the determination of $\rho_{\alpha'\beta'}^{(\alpha\beta)}(\omega)$:

$$\sum_{\alpha''\beta''} G_{\alpha'\beta',\alpha''\beta''}\rho_{\alpha''\beta''}^{(\alpha\beta)}(\omega) = \delta_{\alpha\alpha'}\delta_{\beta\beta'}, \tag{9}$$

$$G_{\alpha'\beta',\alpha''\beta''} = i(\omega-\omega_{\alpha'\beta'})\delta_{\alpha'\alpha''}\delta_{\beta'\beta''} + \int (\delta_{\alpha'\alpha''}\delta_{\beta'\beta''} - S_{\alpha'\alpha''}^{+}S_{\beta''\beta'})P(g)\,dg. \tag{10}$$

Using the linearity of the system (9), we can carry out the summation over α and β in (5) in general form. We introduce the notation

$$F_{\alpha'\beta'} = \sum_{\alpha\beta} W_{\alpha}f_{\beta\alpha}\rho_{\alpha'\beta'}^{(\alpha\beta)}(\omega) \tag{11}$$

Multiplying (9) by $W_{\alpha}f_{\beta\alpha}$ and summing over α and β, we obtain a system of equations for the quantities $F_{\alpha'\beta'}$, which differs from (9) only in the form of the right-hand side:

$$\sum_{\alpha''\beta''} G_{\alpha'\beta',\alpha''\beta''}F_{\alpha''\beta''} = W_{\alpha'}f^{*}_{\alpha'\beta'}. \tag{12}$$

Now

$$I(\omega) = \frac{1}{\pi}\operatorname{Re}\sum_{\alpha'\beta'} f_{\alpha'\beta'}F_{\alpha'\beta'}. \tag{13}$$

The system (12) is a system of linear algebraic equations, the solution of which in each concrete case entails no fundamental difficulties.

Formally, the summation in (12) and (13) extends over all the states of the system. In practice, however, it is necessary to take into account only those transitions which make an appreciable contribution to the considered region of the spectrum, i.e., transitions with $\omega_{\alpha'\beta'} \approx \omega$ and $\omega_{\alpha''\beta''} \approx \omega$.

We emphasize specially that our formulation of the problem of calculating I(ω) does not differ at all in principle from the general theory of broadening of overlapping spectral lines, developed in[6,7]. Its convenience lies in the fact that it is possible to investigate with the aid of (12) and (13) the character of the spectrum I(ω) as a function of the form of the exact S-matrix of the collisions.

Q-BRANCH STRUCTURE

As already mentioned, the Q branch of the vibrational band of Raman scattering of diatomic molecules is the result of ΔJ = 0 transitions between the vibrational-rotational levels of the molecule. The corresponding levels and transitions are shown in Fig. 1a. Since under ordinary experimental conditions $kT \ll \hbar\Omega$, where Ω is the collision frequency, we can confine ourselves to allowance for transitions with v = 0, J → v = 1, J. The frequencies of the Q-branch components are described by formula (1).

Let us consider the influence of collisions on the vJ levels. It is well known that the effective cross sections of collisions accompanied by a change of the rotational state of the molecule vJ → vJ′ are equal in order of magnitude to the gas-kinetic cross sections σ_{gk}. On the other hand, the change of the vibrational state is characterized by much smaller cross sections, $\sim(10^{-3}\text{--}10^{-4})\sigma_{\text{gk}}$ (see, for example,[8]). We shall therefore assume that the collision S-matrix elements are diagonal in v. It can also be assumed that the matrix elements $S_{vJ,vJ'}$ are the same at v = 0 and v = 1. In any case, it is difficult to expect the cross sections of the J → J′ transitions for the ground and first excited vibrational states to differ significantly. We therefore have

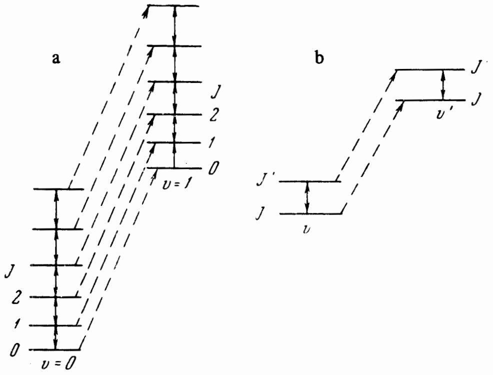

FIG. 1. Vibrational-rotational level scheme of diatomic molecule. The solid arrows show the transitions due to collisions, and the dashed arrows the radiative transitions.

$$S_{vJ,\,v'J'} \approx S_{JJ'}\delta_{vv'}. \tag{14}$$

For the radiative transitions ΔJ = 0, in the approximation (14) for the S-matrix of the collisions, the problem of interest to us, that of calculating the spectrum, can be formulated as follows. There are two interacting subsystems, the molecule vibrations (I) and the molecule rotations (II); the subsystem II is perturbed by the collisions, but the collisions do not affect the subsystem I. It is required to ascertain how and under what conditions the relaxation transitions J → J′ in the second subsystem (i.e., transitions due to collisions) can influence the spectrum of the radiative transition v → v′ of the subsystem I.

We consider first the simplest case, when the subsystem II has only two levels, J and J′. The system, as a whole, obviously has four levels, namely vJ, vJ′, v′J, and v′J′, as shown in Fig. 1b. The radiative transition v → v′ corresponds to two transitions vJ → v′J and vJ′ → v′J′ in this figure. If the interaction between the subsystems I and II is small, then we can assume, with sufficiently good approximation, that it leads to a frequency difference $\Delta = 2\pi c\alpha_e[J(J+1) - J'(J'+1)]$ [cm^{-1}], but does not affect the magnitude of the corresponding matrix element in (11)–(13). Obviously, the frequencies of all other possible transitions in Fig. 1b lie in an entirely different region of the spectrum. They can therefore be disregarded.

To simplify the notation, we designate the transition vJ → v′J by the index 1, the transition vJ′ → v′J′ by the index 2, W_{vJ} by W_1, and $W_{vJ'}$ by W_2. We then get from (12) and (13) (in accordance with the statements made above, $f_1 = f_2 = f$)

$$I(\omega) = \pi^{-1}\operatorname{Re}[F_1+F_2]f, \tag{15}$$

$$G_{11}F_1 + G_{12}F_2 = W_1 f^{*}, \tag{16}$$

$$G_{21}F_1 + G_{22}F_2 = W_2 f^{*}. \tag{17}$$

Using further (10) and (14) and taking into account the conditions of the unitarity of the S matrix, we obtain

$$G_{11} = i(\omega - \omega_1) + \gamma_1/2, \qquad G_{12} = -\gamma_2/2,$$
$$G_{21} = -\gamma_1/2, \qquad G_{22} = i(\omega - \omega_2) + \gamma_2/2, \tag{18}$$

where

$$\frac{\gamma_1}{2} = N\langle v\sigma_{JJ'}\rangle = \int |S_{JJ'}|^2 P(g)\,dg,$$
$$\frac{\gamma_2}{2} = N\langle v\sigma_{J'J}\rangle = \int |S_{J'J}|^2 P(g)\,dg, \tag{19}$$

N is the concentration of the perturbing particles, v is the relative velocity, σ is the effective cross section of the corresponding transition, and the angle brackets denote averaging over the velocities. Under stationary conditions the populations of the levels W and the probabilities of the transitions should be connected by the relations $W_{vJ} < v\sigma_{JJ'}\rangle = W_{vJ'}\langle v\sigma_{J'J}\rangle$. Therefore

$$W_1\gamma_1 = W_2\gamma_2. \tag{20}$$

We introduce the notation

$$\omega_1 = \omega_0 - \delta; \quad \omega_2 = \omega_0 + \delta; \quad 2\delta = \Delta \tag{21}$$

and reckon the frequency ω from ω_0. It then follows from (15) that

$$I(\omega) = \frac{1}{\pi} \frac{2\delta^2(W_1\gamma_1 + W_2\gamma_2)|f|^2}{(\omega+\delta)^2(\omega-\delta)^2 + [\gamma_1(\omega-\delta) + \gamma_2(\omega+\delta)]^2}. \tag{22}$$

Let us consider first the two limiting cases $\delta/\gamma_{1,2} \gg 1$ and $\delta/\gamma_{1,2} \ll 1$. When $\delta/\gamma_{1,2} \gg 1$, the distribution $I(\omega)$ has two maxima at the points $\omega = \pm\delta$, and can be written in the form

$$I(\omega) \approx \frac{1}{\pi}\left[\frac{W_1\gamma_1}{(\omega+\delta)^2 + \gamma_1^2} + \frac{W_2\gamma_2}{(\omega-\delta)^2 + \gamma_2^2}\right]|f|^2. \tag{23}$$

In the second limiting case, $\delta/\gamma_{1,2} \ll 1$, expression (22) has one sharp maximum at

$$\omega \approx \omega_{max} = (\gamma_1 - \gamma_2)\delta/(\gamma_1 + \gamma_2). \tag{23'}$$

In this region

$$I(\omega) \approx \frac{1}{\pi}\frac{\Gamma}{(\omega - \omega_{max})^2 + \Gamma^2}\frac{(W_1\gamma_1 + W_2\gamma_2)(\gamma_1 + \gamma_2)}{2\gamma_1\gamma_2}|f|^2, \tag{24}$$

$$\Gamma = 4\gamma_1\gamma_2\delta^2/(\gamma_1 + \gamma_2)^3. \tag{25}$$

Formulas (24) and (25) describe a dispersion contour of width $\Gamma \infty 1/N$.

Thus, at low pressures ($\delta/\gamma_{1,2} \gg 1$), both components of the line broaden independently, and their widths γ, and γ are proportional to N.

With further increase of pressure, when overlap of the components begins, the character of the broadening changes, and in the limiting case $\delta/\gamma_{1,2} \ll 1$ both components contract into one dispersion contour, the width of which decreases with increasing pressure in proportion to $1/N$[1)].

Similar effects of the narrowing of the spectral lines were considered earlier in the theory of magnetic resonance (see, for example,[9,10]). The possible appearance of such effects in the optical region of the spectrum was first indicated by Burshtein and Naberukhin[11]. They, however, confined themselves to the particular case of equally-populated states α. Their entire analysis is based on an equation of the type (7) for the time-dependent operator of the radiative transition f(t).

Such an approach is possible in the case of equal populations W_α, but in the general case of different W_α it leads to incorrect results.

Let us return to the structure of the Q branch. The problem of interest to us differs from the considered example only in the large number of the J-sublevels, which must be taken into account in the calculation. We can therefore expect the following picture of broadening of the Q branch with increasing pressure. At small pressures, when the characteristic dimensionless parameter is

$$\xi = 2\pi c\alpha_e J_{max}^2/\gamma \gg 1, \tag{26}$$

where J_{max} is the angular momentum corresponding to the maximally populated (at a given temperature) rotational sublevel and γ is the relaxation width, each component of the Q branch broadens independently in proportion to N. When $\xi \sim 1$ and the Q-branch components overlap, the interference effects, which we considered above with the two J-sublevels as an example, may come into play. For the molecules N_2 and O_2 at room temperature, $J_{max}^2 \approx 50$ and $\gamma = N\langle v\sigma\rangle \approx N \times 10^{10}$. Therefore ξ reaches values ~ 1 at $N \sim 10^{21}$ cm^{-3}.

The performed calculation confirms these qualitative considerations. By way of an example, Fig. 2 shows the results of a calculation of the structure of the Q branch of the molecule N_2 at different values of the density N. In this calculation we assumed that kT = 200 cm^{-1} and took into account 20 components of the Q branch. To simplify the picture, we took into account transitions due to the collisions only between neighboring sublevels (such a simplification does not change the qualitative picture). We assumed that the transition probability $N\langle v\sigma_{J,J-1}\rangle$ is equal to

$$N\langle v\sigma_{J,\,J-1}\rangle = 4{,}5 \cdot 10^{-10}\,N.$$

The probability of the inverse processes were determined from the detailed-balancing condition

$$\begin{aligned}(2J'+1)\exp[-BJ'(J'+1)/kT]\langle v\sigma_{J',\,J}\rangle &= \\ = (2J+1)\exp[-BJ(J+1)/kT]\langle v\sigma_{J,\,J'}\rangle&.\end{aligned} \tag{27}$$

Such a choice of the transition probabilities ensures approximately the same broadening of all the rotational

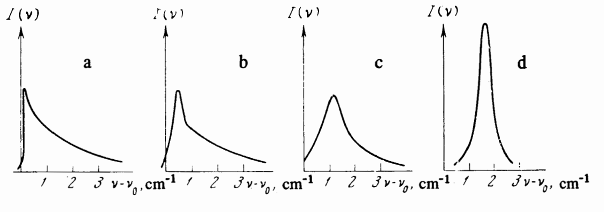

FIG. 2. Structure of A branch of N_2 molecule, kT = 200cm^{-1}; a) N – 0.7 × 10^{20}, b) N = 2.8 × 10^{10}, c) N = 4.5 × 10^{21}, d) N = 7 × 10^{22}.

[1)] We note that in the far wing $\omega \gg \gamma_1, \gamma_2, \delta$ we have $I(\omega) \infty \omega^{-4}$, in accord with (22).

components, in agreement with the experimental results[2]. It is seen from the figure that the total width of the Q branch remains constant in the pressure interval 15—125 atm, in full agreement with the experimental data[2].

As to the possible observation of the effect of the narrowing of the Q branch at large values of the density N, it must be emphasized that this effect is connected with neglect of the dependence of the S matrix on the vibrational quantum number v. In a real case, such a dependence does exist, and we can expect the total width of the Q branch to remain constant in a certain interval of density values N, and then increase with further increase of the density, but much more slowly than expected without allowance for the described interference effect. In addition, as seen from Fig. 2, in the case of N_2 the Q branch begins to narrow down only at very large values of the density N. At such values of N, the employed calculation is not applicable.

We note in conclusion that to determine the complete structure of the Q branch it would be necessary in principle to take into account the degeneracy in the magnetic quantum number M. In this general form, however, the problem is very complicated, owing to the large number of equations in the system (12). The degeneracy in M was therefore disregarded in our calculations. This simplification is equivalent to assuming that, after averaging over all possible orientations of the impact parameter b and the relative velocity v, the products of the elements of the S matrix, which enter in Eq. (12), do not depend on the magnetic quantum numbers.

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