Broadening of nonlinear resonances by velocity-changing collisions

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(Submitted October 6, 1976)
Zh. Eksp. Teor. Fiz. **72**, 1358–1374 (April 1977)

We consider theoretically nonlinear-resonance broadening due to a collision-induced change of velocity, with allowance for phase memory, inelastic processes, degeneracy of the levels, and collisional disorientation. The structure of the nonlinear resonance and the effect exerted on it by the indicated factors are explained. An analysis is presented of the shape and width $\delta(p)$ of the resonance in a wide interval of pressures p. $\delta(p)$ is characterized by a rapid deviation from linearity at small p and by a much slower attainment of the asymptotic form at large p. Disorienting collisions influence strongly the structure of the resonance and change qualitatively the interpretation of its parameters. Numerical calculations are made of the shape of the resonance and of $\delta(p)$, and permit a quantitative comparison with experiment. This comparison was made for the data on the nonlinear resonance on the 001–100, P (20) transition in CO_2. It is shown as a result that in this case the nonlinear $\delta(p)$ dependence is due mainly to quantum (diffraction) effects in elastic scattering. It appears that this conclusion is general for all systems in which the change of the velocity influences the structure of the nonlinear resonance.

PACS numbers: 33.70.Jg

I. INTRODUCTION

Experiments[1–5] have revealed a nonlinear pressure dependence of the width and shift of the power resonance in lasers equipped with cells containing an absorbing gas. This nonlinearity cannot be explained as being due to hyperfine splitting, field effects, or violation of the impact approximation (the pressure in the experiments of[1–5] was hundredths or tenths of a Torr). Therefore, apart from its practical applications in the development of lasers with high emission frequency stability, this phenomenon is of great general importance in physics. The point is that phenomena of this kind, as shown in[6], can be due to small changes in the velocities of the emitting (absorbing) particles in scattering through small angles, particularly diffraction angles[1)]:

$$\Delta v \sim \hbar/m\rho_0, \quad \theta = \Delta v/v \sim \hbar/mv\rho_0 \tag{1.1}$$

(ρ_0 is the effective interaction radius). It has subsequently been found that related effects should take place also for other resonances in two- and three-level systems[8] as well as in photon echo.[9]

If the nonlinear dependence of the width and shift of the resonances on the pressure is indeed due under the conditions of[1–5] to diffraction scattering, then this uncovers an interesting possibility of studying quantum effects that are completely lost sight of in such phenomena as viscosity and diffusion.

The existing theories of nonlinear resonances do not make it possible, however, to connect the pressure dependence of their width with scattering through small angles: no attention is paid in a number of studies to the phase-memory effect,[9,10–12] while in other studies only limiting cases of low and high pressures are considered,[2,13] and nowhere is account taken of the degeneracy of the levels and of collision-induced disorientation. In view of the incomplete development of the theory, the interpretation of the experiments could not claim to be unambiguous, and only the order of magnitude of the parameters determined from the experiments had any meaning.

In the present article we develop the nonlinear-resonance theory in which account is taken of all the essential factors (Secs. 2–5) and which can be quantitatively compared with experiment (Sec. 6).

2. GENERAL RELATIONS

It is convenient to start the analysis with a simple model of nondegenerate states, within the framework of which it is easy to reveal effects due to changes of the velocity, and then introduce degeneracy of the combining levels (Sec. 5). Accordingly, we start in Secs. 2–4 from the following system of equations[6,8] for the elements of the density matrix $\hat{\rho}(\mathbf{r}, \mathbf{v}, t)$:

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\nabla + \Gamma_{jl}\right)\rho_{jl}(\mathbf{r}, \mathbf{v}, t) = S_{jl} + i[\hat{V}(\mathbf{r}, t), \hat{\rho}(\mathbf{r}, \mathbf{v}, t)]_{jl} + q_j(\mathbf{v})\delta_{jl}, \tag{2.1}$$

$$S_{jl} = -\nu_{jl}\rho_{jl}(\mathbf{r}, \mathbf{v}, t) + \int A_{jl}(\mathbf{v}, \mathbf{v}_1)\rho_{jl}(\mathbf{r}, \mathbf{v}_1, t)\,d\mathbf{v}_1. \tag{2.2}$$

Here $\mathbf{r}$ and $\mathbf{v}$ denote the coordinate and velocity of the molecule; $A_{jl}(\mathbf{v}, \mathbf{v}_1)$ are the kernels of the collision integrals S_{jl}, from which the spontaneous relaxation has been separated (the constants Γ_{jl}), and only the elastic parts of the arrival terms have been retained; $q_j(\mathbf{v})$ is the number of acts of excitation of the state $(j, \mathbf{v})$ per unit time; $\hat{V}(\mathbf{r}, t)$ describes the interaction of the molecule with the external field.

The relations between the scattering amplitudes $f_{jj}(\mathbf{u}, \mathbf{u}_1)$, the departure frequencies ν_{jl}, the arrival frequencies $\tilde{\nu}_{jl}$, and the kernels are best written, in contrast to[13,14], in the form

$$\nu_{jl} = \frac{2\pi\hbar}{i\mu} N_s \int [f_{jj}(\mathbf{u}, \mathbf{u}) - f_{ll}^*(\mathbf{u}, \mathbf{u})]\, W_{\text{per}}(\mathbf{v}-\mathbf{u})\,d\mathbf{u}, \tag{2.3}$$

$$A_{jl}(\mathbf{v}, \mathbf{v}_1) = 2N_{\text{per}} \int \sigma_{jl}(\mathbf{u}, \mathbf{u}_1)\,\delta(u^2 - u_1^2)\,\delta\left(\mathbf{v} - \mathbf{v}_1 - \frac{\mu}{m}(\mathbf{u} - \mathbf{u}_1)\right) \times W_{\text{per}}(\mathbf{v}_1 - \mathbf{u}_1)\,d\mathbf{u}\,d\mathbf{u}_1. \tag{2.4}$$

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$$\tilde{\nu}_{jl}=\int A_{jl}(\mathbf{v}',\mathbf{v})\,d\mathbf{v}'=2N_s\int\sigma_{jl}(\mathbf{u},\mathbf{u}_1)\,\delta(u^2-u_1^2)\,W_{per}(\mathbf{v}-\mathbf{u}_1)\,d\mathbf{u}d\mathbf{u}_1\,, \quad (2.5)$$

$$\sigma_{jl}(\mathbf{u},\mathbf{u}_1)=f_{jj}(\mathbf{u},\mathbf{u}_1)\,f_{ll}^{*}(\mathbf{u},\mathbf{u}_1), \quad (2.6)$$

where $W_{per}(\mathbf{v}-\mathbf{u})$ is the velocity distribution of the perturbing particles, which are assumed to be structureless; μ and $\mathbf{u}$ are the reduced mass and the relative velocity of the colliding particles, m is the mass of the perturbing particle, and N_{per} is the density of the perturbing particles.

For ν_{jj} and ν_{mn} pertaining to a single transition $m-n$, the following relations, which are easily derived from (2.3)–(2.6) of[15], are valid:

$$2\mathrm{Re}\,\nu_{mn}=\nu_{mm}+\nu_{nn}\geqslant\tilde{\nu}_{mm}+\tilde{\nu}_{nn}\geqslant 2\mathrm{Re}\,\tilde{\nu}_{mn}. \quad (2.7)$$

The quantity $\nu_{jj}-\tilde{\nu}_{jj}$ is, obviously, a measure of the inelasticity of the collisions. With respect to S_{mn}, the analogous characteristic is the quantity $\mathrm{Re}(\nu_{mn}-\tilde{\nu}_{mn})$, which is subject, besides the inelastic processes, also to the influence of the loss of phase stability in collisions: a measure of the violation of phase memory is the difference $\tilde{\nu}_{mm}+\tilde{\nu}_{nn}-2\mathrm{Re}\tilde{\nu}_{mn}$. The equality $\tilde{\nu}_{mm}+\tilde{\nu}_{nn}=2\mathrm{Re}\tilde{\nu}_{mn}$ is reached only at $f_{mm}(\mathbf{u},\mathbf{u}_1)=f_{nn}(\mathbf{u},\mathbf{u}_1)$, i.e., in the case of identical scattering in the states m and n.

According to (2.5) and (2.6) we have $\tilde{\nu}_{jj}>0$. In many cases, for example in the model of power-law potentials, we also have $\mathrm{Re}\tilde{\nu}_{mn}>0$. A "negative arrival," $\mathrm{Re}\tilde{\nu}_{mn}<0$, is also possible, however, if for example the interaction potentials in the states m and n are of opposite sign and the Born approximation is valid.

In problems of nonlinear spectroscopy, the electromagnetic field constitutes as a rule a set of plane waves and produces directly a disequilibrium in the distribution only with respect to the projection of the velocity on the wave vector. Generally speaking, collisions transfer the disequilibrium also to the distribution with respect to the orthogonal projections $\mathbf{v}_\perp$. However, as shown by analysis, this effect is negligible when selective scattering is considered and one can deal with "one-dimensional kernels"

$$A_{jl}(v,v_1)=\int A_{jl}(\mathbf{v},\mathbf{v}_1)\,W(\mathbf{v}_{1\perp})\,d\mathbf{v}_\perp\,d\mathbf{v}_{1\perp}, \quad (2.8)$$

by assuming $W(\mathbf{v}_{1\perp})$ to be a Maxwellian function.

In the selective-scattering case of interest to us, the eikonal method is applicable, and the scattering amplitudes are (see, e.g., [16,17]) sharp functions of $\mathbf{u}-\mathbf{u}_1$ or, taking into account the momentum conservation law, of $\mathbf{v}-\mathbf{v}_1$. The differential cross sections are therefore well approximated by the expressions

$$\sigma_{jl}(\mathbf{u},\mathbf{u}_1)=\bar{\sigma}_{jl}(u/\bar{u})^{s_1}H(\xi),\quad \xi=(\bar{u}/u)^{s_2}|\mathbf{v}-\mathbf{v}_1|/\eta, \quad (2.9)$$

where η is the characteristic width of the function $H(\xi)$ when measured in the scale of $\mathbf{v}$ (at $u=\bar{u}$).

A detailed analysis[18] has shown that the approximation (2.9) is valid for a large number of model potentials. It has turned out that in the case of (2.9) one-dimensional kernels depend on $|v-v_1|$, and their widths differ from η only by a numerical coefficient 0.7–1.5. A particularly graphic connection between the differential cross section and the kernel is observed in the case of light perturbing particles, when the following relation holds true[18]

$$A_{jl}(v-v_1)=\tilde{\nu}_{jl}[2\langle\xi\rangle\eta]^{-1}\int\limits_{|v-v_1|/\eta}^{\infty}H(\xi)\,d\xi, \quad (2.10)$$

where

$$\tilde{\nu}_{jl}=\frac{2}{\sqrt{\pi}}\bar{u}\bar{\sigma}_{jl}N_s\left(\frac{m\eta}{\mu\bar{u}}\right)^{2}\cdot 2\pi\Gamma\left(1+s_2+\frac{s_1}{2}\right)\langle\xi\rangle,$$

$$\langle\xi\rangle=\int\limits_0^\infty\xi H(\xi)\,d\xi.$$

We emphasize that the dependence of $A_{jl}(v-v_1)$ on $|v-v_1|$, of the type (2.10), leads to a break in the derivative of the kernel at the point $v=v_1$. This property, which is closely connected with the singularity of the kernels $A_{jl}(\mathbf{v},\mathbf{v}_1)$, [18,19] is common to one-dimensional kernels. An approximation that takes this circumstance into account and is confirmed by numerical calculations in[18], can be the expression[2)]

$$A_{jl}(v-v_1)=(\tilde{\nu}_{jl}/2\Delta v)\exp\{-|v-v_1|/\Delta v\}. \quad (2.11)$$

The calculations in[8] have made it possible to connect the width Δv of the kernel with the parameters of the potential; for a Lennard-Jones potential, for example, we have

$$\Delta v=1.38\hbar/m\rho_0, \quad (2.12)$$

if the masses of the colliding molecules are equal (ρ_0 is the Weisskopf radius). The coefficients for $\mu\ll m$ and $\mu=m$ are equal to 1.13 and 1.88, respectively.

3. ANALYSIS OF THE SOLUTIONS OF THE KINETIC EQUATIONS

When using the method of successive approximations in terms of the amplitude of the electromagnetic field, as is customarily done in nonlinear spectroscopy, it is most convenient to express the solution of (2.1) in terms of Green's functions that satisfy the following equations (the stationary problem, ω and k are the frequency and wave vector of the field)

$$\begin{aligned}&\Gamma_{jj}F_j(v-v')=S_{jj}+\delta(v-v'),\\ &[\Gamma_{mn}-i(\Omega-kv)]F_{mn}(v,v')=S_{mn}+\delta(v-v'),\end{aligned} \quad (3.1)$$

where $\Omega=\omega-\omega_{mn}$. In the case of a one-dimensional difference kernel we obtain

$$F_j(v-v')=\frac{1}{\Gamma_{jj}+\nu_{jj}}\left[\delta(v-v')+\frac{k}{2\pi}\int\limits_{-\infty}^{\infty}\frac{A_{jj}(\tau)\exp[-ik(v-v')\tau]}{\Gamma_{jj}+\nu_{jj}-A_{jj}(\tau)}\,d\tau\right], \quad (3.2)$$

$$F_{mn}(v,v')=\frac{k}{2\pi}\int\limits_{-\infty}^{\infty}d\tau\int\limits_{-\infty}^{\tau}d\tau_1\exp\{-i(kv-\Omega)\tau+i(kv'-\Omega)\tau_1\}\,\Phi(\tau)\,\Phi^{-1}(\tau_1), \quad (3.3)$$

$$\Phi(\tau)=\exp\left\{-(\Gamma_{mn}+\nu_{mn}-\tilde{\nu}_{mn})\tau-\int\limits_0^\tau[\tilde{\nu}_{mn}-A_{mn}(\tau)]\,d\tau\right\}, \quad (3.4)$$

$$A_{jl}(\tau)=\int_{-\infty}^{\infty}A_{jl}(v-v')\exp[ik(v-v')\tau]dv. \qquad (3.5)$$

The quantity with the simplest physical meaning is

$$\int F_{mn}(v,v')dv'=\int_0^{\infty}\Phi(\tau)\exp[i(\Omega-kv)\tau]d\tau, \qquad (3.6)$$

and determines the profile of the spectral line (in the absence of nonlinear effects) for molecules with different velocity v and having an equilibrium distribution with respect to v'. The term $(\Gamma_{mn}+\nu_{mn}-\bar{\nu}_{mn})\tau$ in the argument of the exponential of the correlation function $\Phi(\tau)$ of the molecular oscillators represents, as usual, the damping of the function as a result of inelastic processes and phase modulation. The integral term in (3.4) describes the influence of the frequency modulation as a result of the change in the velocity by collision. We write down this term in the form

$$\int_0^{\tau}[\bar{\nu}_{mn}-A_{mn}(\tau)]d\tau=\bar{\nu}_{mn}\int_0^{\tau}\langle 1-e^{ik\Delta v\tau}\rangle_{\Delta v}d\tau \qquad (3.7)$$

(the brackets denote averaging over Δv with weight $A_{mn}(\Delta v)/\bar{\nu}_{mn}$) and compare (3.7) with the analogous term due to the phase modulation,[20] which takes the following form in the case of a Poisson distribution of the moments of the collisions and when the discontinuities of the phases in the different collisions are independent:

$$(\nu_{mn}-\bar{\nu}_{mn})\tau=\bar{\nu}\int_0^{\tau}\langle 1-e^{i\psi}\rangle_{\psi}d\tau. \qquad (3.8)$$

The foregoing conditions are satisfied also in the case of a change in velocity, so long as $A_{mn}(v,v_1)$ depends on $v-v_1$. Therefore, setting the phase shift ψ in correspondence with the quantity $k\tau\Delta v$, which is due to the change of the velocity and to the Doppler effect, we obtain (3.7) from (3.8).

We proceed to the problem of power resonance in a gas laser operating at a single frequency. Using the standard method[6] and expressions (3.2) and (3.3) for the Green's functions, and taking into account the first corrections for the saturation and for the large Doppler broadening, we obtain

$$\rho_{jj}(v)=N_jW(v)\mp\frac{G^2}{2}NW(v)\frac{1}{\Gamma_{jj}+\nu_{jj}}\mathrm{Re}\int_0^{\infty}\left[1+\frac{A_{jj}(\tau)}{\Gamma_{jj}+\nu_{jj}-A_{jj}(\tau)}\right]$$
$$\times\Phi(\tau)\{\exp[i(\Omega-kv)\tau]+\exp[i(\Omega+kv)\tau]\}d\tau, \qquad (3.9)$$
$$N=N_m-N_n,\quad G=|d_{mn}E/2\hbar|; \qquad (3.10a)$$
$$P(\Omega)=G^2I_1(\Omega)[1-G^2I_2(\Omega)], \qquad (3.10b)$$
$$I_1(\Omega)=\frac{\sqrt{\pi}N}{k\bar{v}}\exp\left[-\frac{\Omega^2}{(k\bar{v})^2}\right]$$
$$I_2(\Omega)=\sum_{j=m,n}\mathrm{Re}\frac{1}{\Gamma_{jj}+\nu_{jj}}\int_0^{\infty}\left[1+\frac{A_{jj}(\tau)}{\Gamma_{jj}+\nu_{jj}-A_{jj}(\tau)}\right]$$
$$\times\{|\Phi(\tau)|^2+\Phi^2(\tau)e^{2i\Omega\tau}\}d\tau. \qquad (3.10c)$$

Here $P(\Omega)$ is the work performed by the field, E is the amplitude of the field in the antinode, and d_{mn} is the matrix element of the dipole moment.

Relations (3.10) differ only in notation from those obtained in[13]. In that paper, as well as in[2], it is shown that the frequency dependence of $I_2(\Omega)$ at low and high pressures takes the form of Lorentz curves with respective widths $\Gamma_{mn}+\nu_{mn}$ and $\Gamma_{mn}+\nu_{mn}-\bar{\nu}_{mn}$. It will be shown later on, however, that knowledge of these limiting cases is not sufficient for an unambiguous interpretation of the experimental data, and all the more for a determination of such parameters as the width of the elastic-scattering characteristic curve.

According to (3.9), the nonequilibrium part in the distribution in velocity consists of two components that are centered about $v=\pm\Omega/k$ and are due to interaction between molecules and waves traveling in opposite directions. Each of these components breaks up into two terms. The first, henceforth called the Bennet term, corresponds to unity in the square brackets of expression (3.9), and duplicates in form the line contour (3.6). This term is due to the interaction with the field during the time $(\Gamma_{jj}+\nu_{jj})^{-1}$ between the instant of excitation of the molecule to the level j and its elastic scattering. The second term in the square brackets of (3.9) is due to the change of the molecule velocity during the remaining time of its stay at the level j, and gives rise to an additional structure in the velocity distribution, called collision structure in[8]. The Bennet dip is always narrower than the collision dip, and the difference between the two decreases with the increasing pressure of the perturbing gas. In accordance with a general theorem,[8] the ratio of the areas of the indicated dips is equal to the number of elastic collisions n_j occurring during the molecule lifetime $(\Gamma_{jj}+\nu_{jj}-\bar{\nu}_{jj})^{-1}$ on the level j:

$$n_j=\bar{\nu}_{jj}/(\Gamma_{jj}+\nu_{jj}-\bar{\nu}_{jj}). \qquad (3.11)$$

The structure of the Ω-dependent part of the term $I_2(\Omega)$ in the expression for the work $P(\Omega)$ of the field is similar. Moreover, it can be easily verified that the plot of this part against the frequency Ω can be made to duplicate the contour of one of the terms in the nonequilibrium increment to $\rho_{jj}(v)$, if we are interested in the v-dependence of the latter, by replacing k with $k/2$.

According to (3.9) and (3.10), selective elastic scattering of molecules influences the shapes of the nonlinear resonances for two reasons: the frequency modulation of the oscillations induced by an external field (this is reflected also in $\Phi\tau$), and the change in the distribution of the molecules in velocity (the factors in the square brackets). The roles of the indicated causes, which find their expression in the off-diagonal and diagonal collision integrals and are represented by independent factors in (3.9) and (3.10), manifests itself clearly if $I_2(\Omega)$ is rewritten in a form equivalent to (3.10):

$$I_2(\Omega)=\sum_{j=m,n}\int_{-\infty}^{\infty}F_j(v)[B_1(\Omega-kv/2)+B_2(kv/2)]dv; \qquad (3.12)$$
$$B_1(\Omega)=\mathrm{Re}\int_0^{\infty}\Phi^2(\tau)e^{2i\Omega\tau}d\tau,$$
$$B_2(kv)=\mathrm{Re}\int_0^{\infty}|\Phi(\tau)|^2e^{2ikv\tau}d\tau, \qquad (3.13)$$

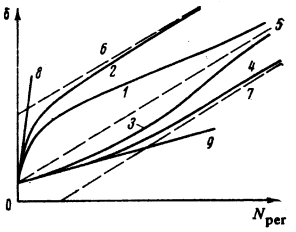

FIG. 1. Qualitative plot of the half-width δ of the Bennett dip against the density N_{per} of the perturbing particles. 1—$\bar{\nu}_{mn'} > 0$, $\alpha = 0$; 2—$\bar{\nu}'_{mn} > 0$, $\alpha \neq 0$; 3—$\bar{\nu}'_{mn} < 0$, $\alpha = 0$; 4—$\bar{\nu}'_{mn} < 0$, $\alpha \neq 0$; 5—$\delta = \Gamma_{mn} + \nu'_{mn} - \bar{\nu}'_{mn}$; 6—$\delta = \Gamma_{nm} + \nu'_{mn} - \bar{\nu}'_{mn} + \frac{3}{4}\alpha nk\Delta v$; 7—$\delta = \Gamma_{nm} + \nu'_{mn} - \bar{\nu}'_{mn} - \frac{3}{4}\alpha |n| k\Delta v$; 8, 9—$\delta = \Gamma_{nm} + \nu'_{mn}$.

i.e., in the form of a convolution of the Green's function F_j with the functions $B_1(\Omega)$ and $B_2(kv)$ of the type (3.6), which represents the influence of the frequency modulation.

A detailed analysis of the properties of the functions $F_j(v - v')$ is carried out in[8]. We consider now the singularities of $B_1(\Omega)$. If the time $(\Gamma_{mn} + \nu_{mn})^{-1}$ is larger than the width $1/k\Delta v$ of the function $A_{mn}(\tau)$ then, as can be easily shown, the integral of $A_{mn}(\tau)$ in (3.4) can be discarded and

$$B_1(\Omega) = {}^1/_2 \mathrm{Re}\,(\Gamma_{mn} + \nu_{mn} - i\Omega)^{-1}, \quad \Gamma_{mn} + \nu_{mn}' \ll k\Delta v. \tag{3.14}$$

In the opposite limiting case of high pressures, small values of τ are important, and we can use the expansion

$$\int_0^\tau A_{mn}(\tau)\,d\tau = \bar{\nu}_{mn}\tau[1 - {}^1/_2\alpha k\Delta v\tau - {}^1/_3\beta(k\Delta v\tau)^2], \tag{3.15}$$

where Δv is the width of the kernel and the numerical factors α and β depend on its form. If we retain in (3.15) only the principal term, then[2,13]

$$B_1(\Omega) = {}^1/_2 \mathrm{Re}\,(\Gamma_{mn} + \nu_{mn} - \bar{\nu}_{mn} - i\Omega)^{-1}. \tag{3.16}$$

To determine the region in which (3.16) is valid, we must take into account higher terms of the expansion in (3.15). If $A_{mn}(v - v_1)$ decreases as $|v - v_1| \to \infty$ not faster than $(v - v_1)^{-2}$, then $\alpha \neq 0$ and the criterion for the applicability of (3.16) takes the form

$$nk\Delta v/(\Gamma_{mn} + \nu_{mn}' - \bar{\nu}_{mn}') \ll 1, \quad n \equiv \bar{\nu}_{mn}'/(\Gamma_{mn} + \nu_{mn}' - \bar{\nu}_{mn}'). \tag{3.17}$$

On the other hand, if $A_{mn}(v - v_1)$ tends to zero as $|v - v_1| \to \infty$ more rapidly than $(v - v_1)^{-2}$, then $\alpha = 0$ and in place of (3.17) we obtain

$$n[k\Delta v/(\Gamma_{mn} + \nu_{mn}' - \bar{\nu}_{mn}')]^2 \ll 1. \tag{3.18}$$

Thus, the realization of the limiting cases (3.14) and (3.16) is regulated by different parameters that differ particularly strongly if $\bar{\nu}'_{mn}$ is positive and is close to ν'_{mn}. Therefore the region where the width of the dip becomes a nonlinear function of the pressure or of $\bar{\nu}'_{mn}$ cannot conform to the condition $\Gamma_{mn} + \nu'_{mn} \sim k\Delta v$, as is assumed in[2].

By analogy with n_j, the quantity n can be interpreted as the effective number of collisions that lead to deviation of the frequency of the molecular oscillator and occur within the dipole-moment relaxation time $(\Gamma_{mn} + \nu'_{mn} - \bar{\nu}'_{mn})^{-1}$. The role of n is clearly seen from the expressions for the first corrections to the width of the function $B_1(\Omega)$, which correspond to the expansion (3.15):

$$\delta = \Gamma_{mn} + \nu_{mn}' - \bar{\nu}_{mn}' + \frac{3}{4}\alpha nk\Delta v + \frac{3}{4}\beta n\frac{(k\Delta v)^2}{\Gamma_{mn} + \nu_{mn}' - \bar{\nu}_{mn}'}. \tag{3.19}$$

If $\alpha \neq 0$, then the term with β must be discarded, and the increment to δ is proportional to the total frequency deviation $nk\Delta v$ which is produced after n collisions. On the other hand, if $\alpha = 0$ and $\beta \neq 0$, then δ contains a frequency deviation $\sqrt{n}k\Delta v$ which is proportional to $\sqrt{n}$ (the diffusion law).

Relations (3.14) and (3.19) provide an approximate idea of the possible behavior of the half-width with changing pressure (Fig. 1). Depending on whether $\alpha = 0$ or $\alpha \neq 0$, i.e., on the character of the "wings" of the kernel, the asymptotic plot of δ at large pressures has an intercept on the ordinate axis at Γ_{mn} or $\Gamma_{mn} + \frac{3}{4}\alpha nk\Delta v$. We note that curves of this type are obtained also for the half-width of the total dip, if the phase-memory effects are neglected.[8] At $\bar{\nu}'_{mn} > 0$, the qualitative pressure dependence of the width of the total dip has also the form of the curves of Fig. 1. On the other hand, if $\bar{\nu}'_{mn} < 0$, the curves for the width $I_2(\Omega)$ are somewhat altered.[21]

If $\bar{\nu}'_{mn} > 0$, then the exponentials with higher exponents τ need not necessarily be expanded in a series, and $B_1(\Omega)$ can be represented in the form

$$B_1(\Omega) = \mathrm{Re}\int_0^\infty \exp\{-2(\Gamma_{mn} + \nu_{mn} - \bar{\nu}_{mn} - i\Omega)\tau - \alpha\bar{\nu}_{mn}k\Delta v\tau^2 - {}^2/_3\beta\bar{\nu}_{mn} \times (k\Delta v)^2\tau^3\}\,d\tau; \quad (k\Delta v/\bar{\nu}_{mn}')^{1/2} \ll 1, \ \alpha \neq 0; \quad (k\Delta v/\bar{\nu}_{mn}')^{3/2} \ll 1, \ \alpha = 0. \tag{3.20}$$

Relation (3.20) is meaningful at sufficiently large pressures, and the limit of the region of its applicability shifts towards pressures that are small in comparison with (3.17) and (3.18); the shift is larger the larger n. In the case $\alpha \neq 0$, the integral (3.20) is expressed in terms of the tabulated functions[22]:

$$B_1(\Omega) = \frac{\mathrm{Re}\,w(\zeta)}{(4\alpha\bar{\nu}_{mn}'k\Delta v/\pi)^{1/2}}, \quad w(\zeta) = e^{\zeta^2}\left[1 - \frac{2}{\sqrt{\pi}}\int_0^\zeta e^{-t^2}dt\right], \tag{3.21}$$

$$\zeta = \frac{\Gamma_{mn} + \nu_{mn} - \bar{\nu}_{mn} - i\Omega}{(\alpha\bar{\nu}_{mn}'k\Delta v)^{1/2}}.$$

A plot of the width of the function (3.21) is curve 7 of Fig. 2a (cf. Fig. 1). In the case $\alpha = 0$, the integral (3.20) was calculated numerically. The corresponding width is represented by curve 5 of Fig. 2a (cf. Fig. 1). If n is large enough, then the maximum of the curves turns out to be in the region of applicability of relation (3.20), so that this relation covers practically the entire pressure interval of interest from the point of view of the nonlinear dependence of δ on ν'_{mn}, with the exception of the region of very lowest pressures (3.14). We note that retention of only the cubic term in (3.20) is equivalent to writing down the collision integral in the Fokker–Planck form.[6]

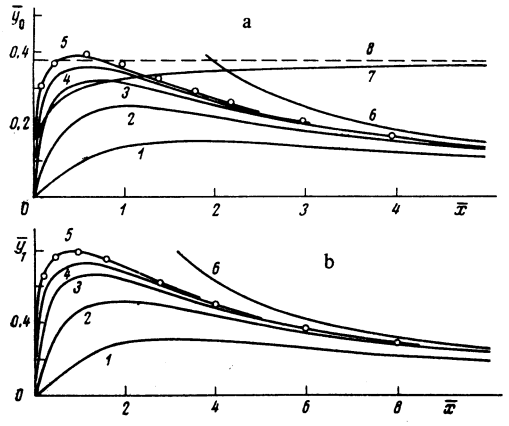

FIG. 2. Dependence of the quantities $\bar{\gamma}_{0,1}=(\delta_{0,1}-\Gamma_{mn}-\nu_{mn}+\tilde{\nu}_{mn})/\sqrt{n}k\Delta v$ on $\bar{x}=(\Gamma_{mn}+\nu_{mn}-\tilde{\nu}_{mn})/\sqrt{n}k\Delta v$ for the function $B(\Omega)$. a) 1—$n=0.25$, 2—$n=1$; 3—$n=3$; 4—$n=9$; 5—approximation (3.20), $\alpha=0$, $\beta=1$; 6—asymptotic form (3.19), $\alpha=0$, $\beta=1$; 7—approximation (3.20), $\alpha\sqrt{n}=0.5$, $\beta=0$; 8—$\delta_0-\Gamma_{mn}-\tilde{\nu}_{mn}=\frac{3}{4}\alpha nk\Delta v$. Points—approximation (4.1). The x scale for curve 7 is magnified 2.5 times. b) 1—$n=0.25$; 2—$n=1$; 3—$n=3$; 4—$n=9$; 5—approximation of type (3.20) for $dB_1(\Omega)/d\Omega$, $\alpha=0$, $\beta=1$; 6—asymptotic form of type (3.19), $\delta_1=\Gamma_{mn}+\nu_{mn}-\tilde{\nu}_{mn}+\frac{5}{2}n(k\Delta v)^2/(\Gamma_{mn}+\nu_{mn}-\tilde{\nu}_{mn})$, $\alpha=0$, $\beta=1$. Points—approximation (4.1).

At low pressures corresponding to (3.14), the width of the Green's function $F_j(v-v')$, amounting according to[8] to $(1+n_j)^{1/2}k\Delta_j v$, greatly exceeds $\Gamma_{mn}+\nu_{mn}$, so that the Bennet and the collision dips are readily distinguishable. On the other hand, if $(1+n_j)^{1/2}k\Delta_j v\sim\Gamma_{mn}+\nu'_{mn}-\tilde{\nu}'_{mn}$, then the two dips have approximately equal widths, and it is necessary to consider the entire expression (3.10) for $I_2(\Omega)$ as a unit, i.e., the separation of $B_1(\Omega)$ is not justified. The latter can be readily seen from the asymptotic expression, at high pressures, for the width of the function $I_2(\Omega)$

$$\delta=\Gamma_{mn}+\nu_{mn}'-\tilde{\nu}_{mn}'+\frac{3}{4}\beta\frac{n(k\Delta v)^2+n_j(k\Delta_j v)^2}{\Gamma_{mn}+\nu_{mn}'-\tilde{\nu}_{mn}'},\qquad(3.22)$$

where $\Delta_j v$ is the width of the kernel $A_{jj}(v-v_1)$, the form of which coincides with the form of $A_{mn}(v-v_1)(\alpha=0)$. Thus, frequency modulation and "population" effects make approximately identical contributions to $\delta(n_j\gtrsim n)$. In view of the complexity of the expression for $I_2(\Omega)$, we shall analyze it subsequently by numerical methods in Sec. 4.

We note that at $\tilde{\nu}''_{mn}\neq 0$ the function $I_2(\Omega)$ is not symmetrical, and the shift of its maximum is a nonlinear function of the pressure.[6] The question of the shift of the nonlinear resonances is considered in[21].

4. NUMERICAL CALCULATIONS WITH THE MODEL KERNEL (2.11)

The functions $B_1(\Omega)$ and $I_2(\Omega)$ and their half-widths δ_0 were calculated with a computer for the exponential kernel (2.11) under the assumptions $\Delta v=\Delta_j v$, $\nu''_{mn}=\tilde{\nu}''_{mn}=0$, and $n=n_j$ (total phase memory). Since the first derivative of the nonlinear resonance is frequently measured, we determined also the positions of the maxiam Ω_{max} for $dB_1/d\Omega$ and $dI_2/d\Omega$. If the resonance has a Lorentz shape, then $\Omega_{max}=\delta_0/\sqrt{3}$. For convenience in the comparison we therefore calculated the quantity $\delta_1\equiv\sqrt{3}\Omega_{max}$, which does not coincide with δ_0 because the resonance has a non-Lorentz shape.

Figures 2a and 2b show the values of $\delta_{0,1}-\Gamma_{mn}-\nu_{mn}+\tilde{\nu}_{mn}$ for $B_1(\Omega)$, the units along the axes being chosen in accordance with the diffusion approximation (3.15). Conforming to this approximation are the plots 5, which are well approximated by the expression

$$(\delta_{0,1}-\Gamma_{mn}-\nu_{mn}+\tilde{\nu}_{mn})/\sqrt{n}k\Delta v=a_{0,1}\bar{x}[(1+b_{0,1}/\bar{x}^2)^{1/2}-1],$$
$$\bar{x}=(\Gamma_{mn}+\nu_{mn}-\tilde{\nu}_{mn})/\sqrt{n}k\Delta v;\qquad(4.1)$$
$$a_0=0.45;\quad a_1=0.553;\quad b_0=9/4a_0;\quad b_1=15/2a_1$$

(the points near the curves 5). The remaining plots correspond to different values of n. At $n\gtrsim 3$ their difference from the plots 5 is not very large.

Figures 3a and 3b show the values of $\delta_{0,1}$ for the total resonance $I_2(\Omega)$ (solid curves). The units on the abscissa axis were chosen different from those of Fig. 2 in such a way that the positions of the maxima of the curves are practically independent of n:

$$x_{max}(a)\approx 0.6,\quad x_{max}(b)\approx 1.2.\qquad(4.2)$$

Thus, in qualitative agreement with the conclusions of Sec. 3, the nonlinear part of $\delta_{0,1}$ is governed by the parameter $x=(\Gamma_{mn}+\nu_{mn}-\tilde{\nu}_{mn})/(1+n)^{1/2}k\Delta v$ over the greater part of the pressure interval of interest to us. The dashed curves in Fig. 3 correspond to the width of the Bennet dip, and from a comparison of these curves with the solid curves we can assess the relative role of the collision term in $I_2(\Omega)$. The maximum value of $\delta_{0,1}-\Gamma_{mn}-\nu_{mn}+\tilde{\nu}_{mn}$ is 1.5–2 times larger for $I_2(\Omega)$ than for $B_1(\Omega)$, and its value at $n\gtrsim 3$ is

$$(\delta_0-\Gamma_{mn}-\nu_{mn}+\tilde{\nu}_{mn})_{max}/\sqrt{n}k\Delta v\approx 0.6,$$
$$(\delta_1-\Gamma_{mn}-\nu_{mn}+\tilde{\nu}_{mn})_{max}/\sqrt{n}k\Delta v\approx 1.0.\qquad(4.3)$$

A characteristic feature of the plots in Figs. 2 and 3 is that the maximum at $x<x_{max}$ is reached rapidly and that the plots fall off relatively slowly in the region $x>x_{max}$: the ratio of the value $x=x_{1/2}$, where $(\delta-\Gamma_{mn}-\nu_{mn}+\tilde{\nu}_{mn})=\frac{1}{2}(\delta-\Gamma_{mn}-\nu_{mn}+\tilde{\nu}_{mn})_{max}$, to x_{max} is $x_{1/2}/x_{max}=5-7$. In view of this slow decrease, failure to take into account the decrease of the velocity in the collisions may influence the results of the measurement of the broadening cross section, or $(\nu_{mn}-\tilde{\nu}_{mn})/N_{per}$: If, for example, the measurements are carried out in the interval $(x_{max}, x_{1/2})$, then the error in $(\nu_{mn}-\tilde{\nu}_{mn})/N_{per}$ is 6 to 8%. In addition, the value of Γ_{mn}, measured by linear extrapolation to zero pressure, will be incorrect: this method yields a quantity that differs from Γ_{mn} by approximately $\sqrt{n}k\Delta v$.

It follows from (2.7) that $n_j\gg n$. This inequality becomes stronger if account is taken of the disoriented collisions (see Sec. 5). With increasing n_j, the width of the Green's function (3.2) increases and the weight of the collision term in $I_2(\Omega)$ becomes larger. Therefore, at $n_j>n$ the values of δ are larger than for $n_j=n$.

The results of numerical calculations of $\delta_{0,1}$ in this case are given in[21].

5. DEGENERATE STATES AND DISORIENTING COLLISIONS

In the analysis of degenerate systems, the elements of the density matrix, which 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 $\rho_{jl}(J_jM_jJ_lM_l, \mathbf{v})$. Both the arrival terms and the departure terms of collision integrals become off-diagonal in M, if account is taken of the disorienting processes, It is known, however, that in the relaxation-constant model, under isotropic perturbation, the collision integral becomes diagonalized in the representation of the irreducible tensor operators (the $\varkappa q$ representation).[23] The connection between the M and $\varkappa q$ representations is given by the relations

$$F(JMJ'M')=\sum_{\varkappa q}(-1)^{J'-M'}C(JJ'\varkappa|M-M'q)F(JJ'\varkappa q),$$
$$F(JJ'\varkappa q)=\sum_{MM'}(-1)^{J'-M'}C(JJ'\varkappa|M-M'q)F(JMJ'M'). \tag{5.1}$$

where $C(\ldots|\ldots)$ are the vector-addition coefficients.

Proposing to advance as far as possible in this direction also in our case, when the changes of the velocities in the collisions are significant, we write down the equations for the matrix density in the $\varkappa q$ representation:

$$\mathscr{L}_m\rho_{mm}(\varkappa q)=q_m+S_{mm}(\varkappa q)+i\sum_{\varkappa'q'\alpha}(-1)^{J_m+J_n}[3(1+2\varkappa')]^{1/2}\begin{Bmatrix}1 & \varkappa' & \varkappa\\ J_m & J_m & J_n\end{Bmatrix}$$
$$\times[\rho_{mn}(\varkappa'q')V_{-\alpha}^{*}(-1)^{1+\varkappa'+\alpha}-(-1)^{\varkappa+q}V_{\alpha}\rho_{mn}^{*}(\varkappa'-q')]C(1\varkappa'\varkappa|\alpha q'q); \tag{5.2}$$

$$\mathscr{L}\rho_{mn}(\varkappa q)=S_{mn}(\varkappa q)+i\sum_{\varkappa'q'\alpha}(-1)^{1+\varkappa'+J_m+J_n}[3(1+2\varkappa')]^{1/2}V_{\alpha}$$
$$\times\left[\rho_{mm}(\varkappa'q')\begin{Bmatrix}1 & \varkappa' & \varkappa\\ J_m & J_n & J_m\end{Bmatrix}-(-1)^{1+\varkappa'+\varkappa}\rho_{nn}(\varkappa'q')\begin{Bmatrix}1 & \varkappa' & \varkappa\\ J_n & J_m & J_n\end{Bmatrix}\right]C(1\varkappa'\varkappa|\alpha q'q); \tag{5.3}$$

$$\mathscr{L}_m=\frac{\partial}{\partial t}+\mathbf{v}\nabla+\Gamma_{mm},\quad \mathscr{L}=\frac{\partial}{\partial t}+\mathbf{v}\nabla+\Gamma_{mn};$$

where V_α are the circular components of the interaction with the field. The equation for ρ_{nn} is obtained from (5.2) by making the substitution $m\rightleftarrows n$. The collision integrals take the form

$$S_{jl}(\varkappa q)=-\sum_{\varkappa,q_1}\nu_{jl}(\varkappa q|\varkappa_1q_1)\rho_{jl}(\varkappa q\mathbf{v})+\sum_{\varkappa_1q_1}\int d\mathbf{v}_1A_{jl}(\varkappa q\mathbf{v}|\varkappa_1q_1\mathbf{v}_1)\rho_{jl}(\varkappa_1q_1\mathbf{v}_1), \tag{5.4}$$
$$\int A_{jl}(\varkappa q\mathbf{v}|\varkappa_1q_1\mathbf{v}_1)d\mathbf{v}=\tilde{\nu}_{jl}(\varkappa q|\varkappa_1q_1). \tag{5.5}$$

The "departure" frequencies ν_{jl} and the kernels are connected with the scattering amplitudes:

$$\nu_{jl}(\varkappa q|\varkappa_1q_1)=\frac{2\pi\hbar}{i\mu}N_{\mathrm{per}}\sum_{\substack{M_jM_j'M_lM_l'\\ J_{\mathrm{per}}M_{\mathrm{per}}}}\int d\mathbf{u}\,W_{\mathrm{per}}(J_{\mathrm{per}},\mathbf{v}-\mathbf{u})C(J_jJ_l\varkappa|M_j-M_lq)(-1)^{2J_l-M_l-M_l'}C(J_jJ_l\varkappa_1|M_j'-M_l'q_1)$$
$$\times[f(J_jM_jJ_{\mathrm{per}}M_{\mathrm{per}}\mathbf{u}|J_jM_j'J_{\mathrm{per}}M_{\mathrm{per}}\mathbf{u})\delta_{M_lM_l'}-f^{*}(J_lM_lJ_{\mathrm{per}}M_{\mathrm{per}}\mathbf{u}|J_lM_lJ_{\mathrm{per}}M_{\mathrm{per}}\mathbf{u})\delta_{M_jM_j'}]; \tag{5.6}$$

$$A_{jl}(\varkappa q\mathbf{v}|\varkappa_1q_1\mathbf{v}_1)=2N_{\mathrm{per}}\sum_{\substack{M_jM_lM_jM_l'\\ J_{\mathrm{per}}M_{\mathrm{per}}J_{\mathrm{per}_1}M_{\mathrm{per}_1}}}\int d\mathbf{u}\,d\mathbf{u}_1\delta\left(\mathbf{v}-\mathbf{v}_1-\frac{\mu}{m}(\mathbf{u}-\mathbf{u}_1)\right)\delta(u^2-u_1^2)W_{\mathrm{per}}(J_{\mathrm{per}},\mathbf{v}_1-\mathbf{u}_1)$$
$$\times(-1)^{J_l-M_l}C(I_jJ_l\varkappa|M_j-M_lq)(-1)^{J_l-M_l'}C(J_jJ_l\varkappa_1|M_j'-M_l'q_1)f(J_jM_jJ_{\mathrm{per}}\mathbf{u}|J_jM_jJ_{\mathrm{per}_1}M_{\mathrm{per}_1}'\mathbf{u}_1)$$
$$\times f^{*}(J_lM_lJ_{\mathrm{per}}M_{\mathrm{per}}\mathbf{u}|J_lM_l'J_{\mathrm{per}_1}M_{\mathrm{per}_1}\mathbf{u}_1). \tag{5.7}$$

Here, just as in Secs. 2 and 3, we consider only the elastic part of the arrival. The subscript "per" marks the characteristics of the perturbing particles.

The isotropic-perturbation models correspond to neglect of the velocity v and of the function $W(\mathbf{v}-\mathbf{u})$. The diagonality of S_{jl} in the sense of[23] means that the difference $\nu_{jl}-\tilde{\nu}_{jl}$ is diagonal in $\varkappa$ and in q and is independent of q. On the basis of (5.6) and (5.7) it can be shown that under the indicated conditions ν_{jl} and $\tilde{\nu}_{jl}$ are separately diagonalized, while ν_{jl} depends neither on q nor on $\varkappa$. The kernels A_{jl} are not diagonal in $\varkappa$ and q even in the isotropic-perturbation model, but all of their moments are diagonal:

$$\{|\mathbf{v}-\mathbf{v}_1|^s\}\equiv\int|\mathbf{v}-\mathbf{v}_1|^sA_{jl}(\varkappa q\mathbf{v}|\varkappa_1q_1\mathbf{v}_1)d\mathbf{v}\propto\delta_{\varkappa\varkappa_1}\delta_{qq_1}.$$

Thus, on the basis of the isotropic-perturbation model, we can neglect some non-diagonality of the kernels and use the following form of the collision integrals for the description of small-angle scattering:

$$S_{jl}(\varkappa q)=-\nu_{jl}\rho_{jl}(\varkappa q,\mathbf{v})+\int A_{jl\varkappa}(\mathbf{v}-\mathbf{v}_1)\rho_{jl}(\varkappa q,\mathbf{v}_1)d\mathbf{v}_1. \tag{5.8}$$

The solution of Eqs. (5.2) and (5.3) with a collision integral (5.8) leads to the following expression for the function $I_2(\Omega)$ in (3.10)

$$I_2(\Omega)\propto\sum_{\substack{j=m,n\\ \varkappa=0,1,2}}\frac{a_{j\varkappa}}{\Gamma_{jj}+\nu_{jj}}\mathrm{Re}\int_0^{\infty}\left[1+\frac{A_{jj\varkappa}(\tau)}{\Gamma_{jj}+\nu_{jj}-A_{jj\varkappa}(\tau)}\right]$$
$$\times\{|\Phi(\tau)|^2+\Phi^2(\tau)\exp(2i\Omega\tau)\}d\tau, \tag{5.9}$$

where

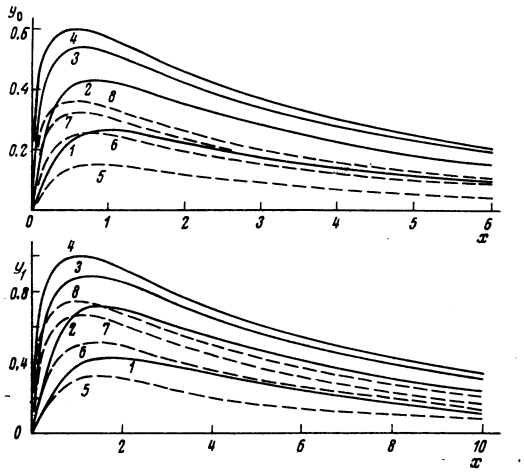

FIG. 3. Half widths $\delta_{0,1}$ of the resonance $I_2(\Omega)$; 1—$n=0.25$; 2—$n=1$; 3—$n=3$; 4—$n=9$; $n_j=n$. Half-widths $\delta_{0,1}$ of the Bennet dip $B_1(\Omega)$: 5—$n=0.25$; 6—$n=1$; 7—$n=3$; 8—$n=9$. The abscissas represent $x=(\Gamma_{mn}+\nu_{mn}-\bar{\nu}_{mn})/\sqrt{1+nk\Delta v}$, and the ordinates $y_{0,1}=(\delta_{0,1}-\Gamma_{mn}-\nu_{mn}+\bar{\nu}_{mn})/\sqrt{nk\Delta v}$.

$$a_{m\varkappa}=\sum_q |I(\varkappa q)|^2 \begin{Bmatrix} 1 & \varkappa & 1 \\ J_m & J_n & J_m \end{Bmatrix}^2,$$

$$a_{n\varkappa}=\sum_q |I(\varkappa q)|^2 \begin{Bmatrix} 1 & \varkappa & 1 \\ J_n & J_m & J_n \end{Bmatrix}^2,$$

$$I(\varkappa q)=\sum_{\alpha\alpha_1} (-1)^{1-\alpha_1} C(11\varkappa|\alpha-\alpha_1 q) E_\alpha E_{\alpha_1}^*.$$

The quantity $I(\varkappa q)$ is the radiation polarization tensor in the $\varkappa q$ representation,[24] $\Phi(\tau)$ is given as before by formula (3.4), where $A_{mn}(\tau)$ must be replaced by $A_{mn\,1}(\tau)$. We note that the relations between the $\nu_{jl\varkappa}$ are analogous to (2.7) and follow from (5.5)–(5.7). Just as in (2.7), the equality $2\,\mathrm{Re}\,\nu_{mn}=\nu_{mm}+\nu_{nn}$ is satisfied. In addition, the following inequalities hold

$$\bar{\nu}_{jl0}'\geqslant\bar{\nu}_{jl\varkappa}', \quad n_{jl0}\geqslant n_{jl\varkappa}, \quad n_{jl\varkappa}\equiv\bar{\nu}_{jl\varkappa}'/(\Gamma_{jl}+\nu_{jl}'-\bar{\nu}_{jl\varkappa}') \tag{5.10}$$

and reflect the role played by the disorientation of the states in the collisions.

Each term of the sum in $I_2(\Omega)$ yields a contour similar to that considered in Secs. 3 and 4 ((cf. (5.9) and (3.10)). The resultant contour $I_2(\Omega)$ obviously preserves all the qualitative features of the terms, and in particular, the characteristic pressure dependence of the width, with the relatively rapid increase and subsequent slow decrease of the difference $\delta-\Gamma_{mn}-\nu_{mn}'+\bar{\nu}_{mn1}'$. Allowance for the degeneracy and for the disorienting collisions has led to certain quantitative changes in $I_2(\Omega)$ and to a refinement of the interpretation of the parameters. Thus, in place of the three spectral components in (3.10), formula (5.9) yields in the general case seven terms. What is added is summation over $\varkappa=0$, 1, and 2 in accordance with the relaxation of the total population of the levels ($\varkappa=0$), of the orientation ($\varkappa=1$), and of the alignment ($\varkappa=2$). Next, if $f_{mm}=f_{nn}$, then in the model of nondegenerate states we have $n=n_j$, and (5.9) contains a term with a "diagonal number of collisions" n_{jj0} larger than n_{mn1}, and under certain conditions this term can be the principal one (see (5.12)). Finally, the disorienting collisions change the meaning of the width of the function $I_2(\Omega)$ at high pressures: the quantity $\Gamma_{mn}+\nu_{mn}'-\bar{\nu}_{mn}'$ is subject, besides loss of phase stability and inelasticity, also to the influence of collisional disorientation.

Let us examine in greater detail the case of a vibrational-rotational transition in a molecule, when the amplitudes of the scattering in states m and n can be assumed identical, as a result of which

$$A_{mm\varkappa}=A_{nn\varkappa}=A_{mn\varkappa}\equiv A_\varkappa, \quad \bar{\nu}_{mm\varkappa}=\bar{\nu}_{nn\varkappa}=\bar{\nu}_{mn\varkappa}\equiv\bar{\nu}_\varkappa \tag{5.11}$$

and summation over $\varkappa$ only is left in (5.9). Let the wave be linearly polarized, and then the only nonzero components are $I(\varkappa q)$ with $\varkappa=0$ and 2. The ratio of the coefficients $a_x=a_{mx}+a_{nx}$ in the sum (5.9) for the transition $J_m=J\to J_n=J+1$ is equal to

$$a_2/a_0={}^1/_2[1-{}^3/_2(J-1)/(J+1)^2]. \tag{5.12}$$

At large values of J, the term with $\varkappa=2$ is represented in (5.9) with a much smaller weight and it can be neglected. In molecular systems, besides, one can neglect the radiative relaxation relative to the collisional relaxation, so that the formula for $I_2(\Omega)$ takes the form

$$I_2(\Omega)\propto \mathrm{Re}\int_0^\infty \left[1+\frac{A_0(\tau)}{\nu-A_0(\tau)}\right]\{|\Phi(\tau)|^2+\Phi^2(\tau)\exp(2i\Omega\tau)\}d\tau,$$
$$n_0=\bar{\nu}_0/(\nu-\bar{\nu}_0)\geqslant n_1=\bar{\nu}_1/(\nu-\bar{\nu}_1). \tag{5.13}$$

If we assume in addition that $A_0(\tau)$ and $A_1(\tau)$ are identical in form, then (5.13) describes the nonlinear structure considered in detail in Secs. 3 and 4.

6. DISCUSSION. COMPARISON WITH EXPERIMENT

The foregoing analysis allows us to conclude that the shape and width of the nonlinear resonance is strongly influenced by many characteristics of the collision processes, namely, the form of the differential cross section of the elastic scattering, the form of the kernel of the collision integral, the departure and arrival frequency ratio, which reflects the presence of processes that are essentially inelastic; disorienting collisions increase the number of spectral components of the nonlinear resonance and alter the relations between such parameters as the numbers $n_{jl\varkappa}$ of the collisions.

Experimental investigations of the shapes of nonlinear resonances can, consequently, serve as the basis for the extraction of extensive information on the foregoing characteristics of the states of atoms and molecules, including excited ones. Thus, for example, from the asymptotic behavior of the width δ of the resonance as a function of the pressure we can estimate the "wings" of the kernels and of the differential cross section. In the simplest case, the pressure dependence of δ is determined by only two parameters (Δv and n), which can be easily obtained from the experimental curve.

The experimental material concerning the effect exerted on nonlinear resonances by collisions accompanied by change of velocity are still exceedingly scanty and constitute only the first steps in this field. Data on

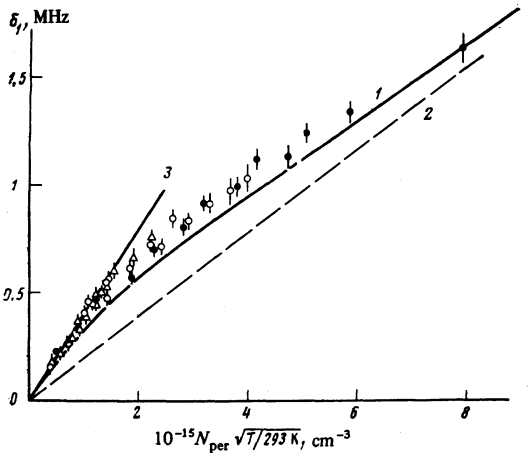

FIG. 4. Comparison of the experimental values of δ_1 with the theory. Points—experimental data[4]: $\Delta - T = 629$ K, $\circ - T = 587$ K, $\bullet - T = 465$ K. Curve 1—calculation for $I_2(\Omega)$, $n = n_j = 1$, $k\Delta v = 0.23$ MHz; 2—$\delta_1 = \nu - \tilde{\nu}_{dif} = \nu/(1+n) = 0.5\nu$; 3—$\delta_1 = \nu = 10.3\,p$ (p is in Torr and ν in MHz), $T = 465$ °K.

the width and shift, obtained in[1-5] do not make it possible, unfortunately, even to obtain the general functional connection between the width and the pressure, since they pertain to a relatively small pressure interval.

The existing theory has also a number of important gaps. Even though a general connection has been established between the collision integrals and the scattering amplitudes, the theory is phenomenological to a considerable degree, since there are practically no calculations of the differential cross section on the basis of microscopic representation. An exception is[16], where a calculation of this type was made for a Lennard-Jones potential, but no account was taken of inelastic and disorienting processes that may turn out to be substantial in the case of molecular systems. We emphasize also that in Secs. 2-4 of the present paper we have assumed that the kernels can be characterized by such a parameter as the width $\Delta\nu$. It is known, however, that besides scattering through diffraction angles, there exists scattering through "classical angles" which are small in comparison with unity but greatly exceed the diffraction angles, as follows from the obvious relations

$$\theta_{dif} \sim \lambda/\rho_0 \sim 10^{-2} \ll \theta_{cl} \sim U_0/k_B T \sim 10^{-1}, \tag{6.1}$$

where U_0 is a characteristic value of interaction potential.

Thus, the kernels describing the selective scattering should contain each two components, whose widths differ by one order of magnitude. The presence of small angle "classical scattering" leads, obviously, to a more complicated dependence of the width of the nonlinear resonance on the pressure: at the very lowest pressure, the nonlinear variation of the width is due only to diffraction scattering, and classical scattering assumes the role of strong collisions; on the other hand, the approach of the plots of Fig. 3 to their asymptotes will take place at much higher pressures, since this approach depends on the width of the kernel (see (3.18)) and is determined by the broadest component of the kernel.

Despite the foregoing circumstances, some quantitative comparison of the developed theory with experiment can be made by using the data of Vasilenko *et al.*,[4] which are at present the most reliable ones. They registered the first derivative of the power spectrum of a CO_2 laser with an absorbing sail on the $P(20)$ line of the transition 001-100 ($\lambda = 10.59$ μm) and obtained an experimental plot of δ_1 (Fig. 4). We assume that over the greater part of the pressure interval in Fig. 4 the arrival of the collision integral is determined by the most selective (diffraction) part of the scattering. It becomes reasonable to assume that no disorientation or inelastic processes take place in scattering through diffraction angles.[3)] Within the framework of this hypothesis we obviously have

$$\tilde{\nu}_0 = \tilde{\nu}_1 \equiv \tilde{\nu}_{dif}, \quad n_0 = n_1 \equiv n_{dif} = \tilde{\nu}_{dif}/(\nu - \tilde{\nu}_{dif}), \quad A_0(\tau) = A_1(\tau) \equiv A(\tau) \tag{6.2}$$

(the kernel $A(\tau)$ being due exclusively to diffraction).

A comparison of the experimental and experimental data will be carried out within the framework of the model of the Lennard-Jones potential.[18] From the slope of the experimental plot at low pressures we determined the Weisskopf radius ($d\delta_1/dp = 10.3$ MHz/Torr, $T = 465$ °K): From the relations obtained in[18] we get

$$\rho_0 = 0.365(\nu/N_{per}\,\bar{u})^{1/3} = 8.4\ \text{Å}. \tag{6.3}$$

On the other hand, if we calculate ρ_0 by using the Lennard-Jones potential parameters a and U_0, determined from viscosity data,[25] then it turns out that

$$\rho_0 = a\left(\frac{3\pi}{2}\frac{aU_0}{\hbar\bar{u}}\right)^{1/3} = 9.6\text{Å}. \tag{6.4}$$

Thus, the spectroscopic and gas-kinetic data give results that agree well, thus favoring the applicability of the models of the Lennard-Jones potential.

With the aid of (6.3) and (2.12) we calculate the theoretical width of the kernel of the collision integral:

$$\Delta\nu = 2.4\ \text{m/sec}, \quad T = 465\ \text{K}. \tag{6.5}$$

The number n of the collisions can be obtained from the results of the calculation of the kernel in[18], according to which $n = 1-1.5$. A plot of δ_1 at $n = 1$ and $\Delta\nu = 2.4$ m/sec is shown in Fig. 4 (curve 1). Taking into consideration the simplifying assumptions made, the agreement between the theoretical and experimental results should be regarded as perfectly satisfactory. We note that allowance for the disorientation in diffraction scattering leads to a decrease of n_1 at a fixed value n_{j0}, and the theoretical curve will lie higher, i.e., closer to the experimental points. We emphasize also that the values of the parameters n and v were calculated theoretically, i.e., no "fitting" parameters were used in this comparison, so that Fig. 4 illustrates the "absolute" relation between theory and experiment.

We believe that the foregoing analysis inspires confidence in the quantum (diffraction) character of the change of the velocity in the collisions that lead, under the conditions of[1-5], to a nonlinear dependence of the width and shift of the power resonance on the pressure. By the same token, the hopes expressed in Secs. 1 and 6 to be able to investigate the collision processes mentioned there by nonlinear-spectroscopy methods become realistic.

In conclusion, let us dwell briefly on the results of Meyer *et al.*[5] and Berman *et al.*[9] Berman *et al.* determined from the data on the photon-echo signal a value $\Delta v = 0.85$ m/sec (CH_3F molecule). Recognizing that CH_3F has a dipole moment ($d = 1.79$ D[28]), and estimating the Weisskopf radius from the formula $\rho_0 \sim d/\sqrt{\hbar \bar{u}}$ ≈ 13 Å, we obtain from (1.1) $\Delta v \approx 0.7$ m/sec. Thus, in this case, too, we are apparently dealing with diffraction scattering.

Meyer *et al.*[5] have also observed a nonlinear dependence of the width on the pressure for the fluorescence resonance, which has the same shape as the power resonance. They interpret this phenomenon, however, as the consequency of the joint influence of the saturation effect and of the so-called transit effects. We believe that this conclusion does not correspond to reality, since the allowance for the transit effects in[5] is incorrect, as can be concluded on the basis of our earlier results.[27]

[1)] The possible influence of diffraction effects on the width of the Lamb dip is mentioned in[7].

[2)] The approximation of the kernels by Gaussian[11,12] or Lorentzian[10] curves seems less appropriate in light of the foregoing.

[3)] Some justification for this hypothesis may be the fact that the cross section of the disorienting and inelastic collisions is much smaller than the total scattering cross section. This is indicated by the noticeable difference between the slopes of the experimental $\delta_1(N_{per})$ plot at large and small N_{per}.

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Translated by J. G. Adashko