Some properties of the spectrum of Rayleigh scattering of light in a weakly nonideal gas

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A microscopic approach, based on the kinetic equation, is developed to describe the spectrum of Rayleigh light scattering in a weakly nonlinear gas that consists of diatomic molecules. The calculated parameters of the spectrum are expressed in terms of the kinetic coefficients and the microscopic parameters of the gas. The contribution of the rotational degrees of freedom to the fine structure of the depolarized scattering spectrum is determined.

1. INTRODUCTION

The microscopic description of the spectrum of Rayleigh light scattering in a gas with rotational degrees of freedom, carried out in Refs. 1 and 2, predicted the presence of a fine structure in the depolarized part of the scattering spectrum in a dense gas when $l \ll \lambda$, where l is the free path length and λ is the light wavelength. The onset of the fine structure, which consists of three narrow dips in the spectrum of symmetric scattering, is connected with the interaction of the rotational and translational degrees of freedom of the molecules in the collisions. It has been shown that the contrast of the dips does not depend on the density of the gas and reflects the contribution of the rotational degrees of freedom to the kinetic coefficient. The entire analysis was carried out in the Boltzmann approximation, i.e., for an ideal gas.

There is interest in taking into account, within the framework of the developed method, the changes produced in the spectrum by the departure of the gas from ideal. In the present work, a kinetic equation for a gas with rotational degrees of freedom is obtained and used for the description of the Rayleigh-scattering spectrum in the next higher order in the gas-perfection parameter in comparison with the Boltzmann gas. Among the changes in the light-scattering spectrum, the greatest interest attaches to the narrow peak at the unshifted frequency in antisymmetric scattering, a peak lacking in the Boltzmann approximation.

2. KINETIC EQUATION FOR THE CORRELATION FUNCTION OF THE FLUCTUATIONS

For the calculation of the spectrum of scattered light in a weakly nonideal gas consisting of diatomic molecules, it is necessary to solve the linearized kinetic equation for the correlation function of the fluctuations[1–3]:

$$\Phi(t, \mathbf{r}, \mathbf{n}_1, \Gamma_1, \mathbf{n}_2, \Gamma_2) = \langle \delta f(t, \mathbf{r}, \mathbf{n}_1, \Gamma_1)\, \delta f(0, 0, \mathbf{n}_2, \Gamma_2) \rangle,$$

where t is the time, $\mathbf{r}$ is the coordinate, $\mathbf{n}$ is a unit vector directed along the axis of the molecule, the quantity $\Gamma = (\mathbf{p}, \mathbf{M})$ includes the momentum $\mathbf{p} = m\mathbf{v}$ (m is the mass of the molecule, $\mathbf{v}$ the velocity of the molecule) and the angular momentum $\mathbf{M}$ of the molecule—variables that are canonically conjugate to the variables $\mathbf{r}$ and $\mathbf{n}$, respectively: δf is the departure of the distribution function f of the gas molecules from the equilibrium Boltzmann function f_0; the angle brackets denote the usual averaging over the statistical ensemble of the molecules.

When there is a nonideal gas in the kinetic equation we must take into account corrections for the mutual correlation of the particles. In first approximation in the parameter Nd^3 (where d is the radius of action of the molecular forces, N is the concentration of particles in the gas [cm^{-3}]), these corrections, as is well known,[3–5] reduce to allowance for the local triple collisions and nonlocal pair collisions. Since the triple collisions in this case do not violate the local laws of conservation of the number of particles, of momentum and of energy, their contribution reduces to only a small change in the eigenvalues of the Boltzmann collision operator. More interesting results are obtained in the scattering spectrum upon consideration of nonlocal increments to the collision integral; therefore, principal attention will be devoted in this work to precisely these corrections.

As was shown earlier,[1,2] in the case of small departures from equilibrium it is convenient in the description of the scattering spectrum to transform to the function $\chi(\omega, \mathbf{q}, \mathbf{n}_1, \Gamma_1)$, which is connected with Φ in the following manner:

$$\begin{gathered} \chi(\omega, \mathbf{q}, \mathbf{n}_1, \Gamma_1) = \\ f_0^{-1}(\Gamma_1) \int \Phi(\omega, \mathbf{q}, \mathbf{n}_1, \Gamma_1, \mathbf{n}_2, \Gamma_2) B(\Gamma_2, \mathbf{n}_2)\, d\varphi_2\, d\Gamma_2, \\ B(\Gamma_2, \mathbf{n}_2) = e_{1s} \alpha_{st}(\Gamma_2, \mathbf{n}_2) e_{2t}, \end{gathered} \tag{1}$$

where $\mathbf{e}_1$ and $\mathbf{e}_2$ are the unit polarization vectors of the incident and scattered waves; $\alpha_{\mathrm{st}(\Gamma)}$ is the polarizability tensor of the molecule, which can be represented in the following form:

$$\alpha_{ik}(\Gamma, \mathbf{n}) = \alpha_0 \delta_{st} + \alpha_1 \varepsilon_{stj} M_j / M_0 + \alpha_2 (n_s n_t - {}^1/_3 \delta_{st}),$$
$$M_0 = (TI)^{1/2},$$

I is the moment of inertia. In this expression, the scalar α_0 and the symmetric α_2 parts of the polarizability of the molecule are determined by the geometric structure of the molecule itself, while the antisymmetric part α, arises only in a rotating molecule:

$$\Phi(\omega, \mathbf{q}) = \int \Phi(t, \mathbf{r}) \exp[i(\mathbf{q}\mathbf{r} - \omega t)]\, d\mathbf{r}\, dt$$

is the Fourier transform of the function $\Phi(t,\mathbf{r})$; integration

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over $\mathbf{n}_2$ at fixed $\mathbf{M}_2$ in (1) reduces to integration over the angle of rotation φ_2 of the vector $\mathbf{n}$ in the plane perpendicular to the $\mathbf{M}_2$ axis, since $\mathbf{M}$ and $\mathbf{n}$ are always mutually orthogonal in a diatomic molecule.

The linearized kinetic equation for the function in a weakly nonideal gas of diatomic molecules can be obtained from the set of equations for the single-particle and two-particle distribution functions, by following Klimontovich[6]:

$$i(\mathbf{q}\mathbf{v}_1-\omega)\chi+[\mathbf{\Omega}_1\times\mathbf{n}_1]\frac{\partial}{\partial\mathbf{n}_1}\chi+\hat{I}_0\chi+\hat{I}_2 i(\mathbf{q}\mathbf{v}_1-\omega)\chi+i\mathbf{q}\hat{\mathbf{I}}_1\chi+\Delta\hat{I}_0\chi$$
$$=B(\Gamma_1,\mathbf{n}_1)+N\int(e^{-U_{12}/T}-1)B(\Gamma_2,\mathbf{n}_2)e^{-i\mathbf{q}\mathbf{r}}\,d\mathbf{r}\,d\varphi_2\,do_{\mathbf{M}_2}, \tag{2}$$

where

$$\hat{I}_0\chi=-Nf_0^{-1}(\Gamma_1)\int\biggl(-\frac{\partial U_{12}}{\partial\mathbf{r}}\frac{\partial}{\partial\mathbf{p}_1}+\biggl[\mathbf{n}_1,\times\frac{\partial U_{12}}{\partial\mathbf{n}_1}\biggr]\frac{\partial}{\partial\mathbf{M}_1}\biggr)f_0(\Gamma_1)f_0(\Gamma_2)$$
$$\times e^{-U_{12}/T}[\chi(\mathbf{n}_{10},\Gamma_{10})+\chi(\mathbf{n}_{20},\Gamma_{20})]\,d\mathbf{r}\,d\varphi_2\,d\Gamma_2, \tag{2a}$$

$$\hat{I}_2\chi=-Nf_0^{-1}(\Gamma_1)\int\biggl(-\frac{\partial U_{12}}{\partial\mathbf{r}}\frac{\partial}{\partial\mathbf{p}_1}+\biggl[\mathbf{n}_1,\times\frac{\partial U_{12}}{\partial\mathbf{n}_1}\biggr]\frac{\partial}{\partial\mathbf{M}_1}\biggr)\int_{-\infty}^{(\tau_1\tau_2)}dt'$$
$$\times\{f_0(\Gamma_1')f_0(\Gamma_2')[\chi(\mathbf{n}_1,\Gamma_1')+\chi(\mathbf{n}_2,\Gamma_2')]$$
$$-f_0(\Gamma_{10})f_0(\Gamma_{20})[\chi(\mathbf{n}_1,\Gamma_{20})$$
$$+\chi(\mathbf{n}_2,\Gamma_{20})]\}\,d\mathbf{r}\,d\varphi_2\,d\Gamma_2, \tag{2b}$$

$$\hat{\mathbf{I}}_1\chi={}^1/{}_2Nf_0^{-1}(\Gamma_1)\int\biggl(-\frac{\partial U_{12}}{\partial\mathbf{r}}\frac{\partial}{\partial\mathbf{p}_1}+\biggl[\mathbf{n}_1\times\frac{\partial U_{12}}{\partial\mathbf{n}_1}\biggr]\frac{\partial}{\partial\mathbf{M}_1}\biggr)$$
$$\times f_0(\Gamma_1)f_0(\Gamma_2)e^{-U_{12}/T}$$
$$\times\{\mathbf{r}[\chi(\mathbf{n}_{10},\Gamma_{10})+\chi(\mathbf{n}_{20},\Gamma_{20})]$$
$$+\mathbf{r}_0[\chi(\mathbf{n}_{20},\Gamma_{20})-\chi(\mathbf{n}_{10},\Gamma_{10})]\}\,d\mathbf{r}\,d\varphi_2\,d\Gamma_2, \tag{2c}$$

$\Delta\hat{I}_0\chi$ is the local increment to the collision integral, due to triple collisions; $\Omega = M/I$ is the frequency of rotation of the molecule; $U_{12}(\mathbf{n}_1,\mathbf{n}_2,\mathbf{r})$ is the electrostatic potential of interaction of the colliding molecules; the integration over the time t' in Eq. (2b) is along the trajectory of the colliding particles, which is determined by the specification of the variables τ_1 and τ_2 (where $\tau_i = (\mathbf{r}_i,\mathbf{n}_i,\Gamma_i)$; the index "0" denotes the quantities $\Gamma_{i0},\mathbf{n}_{i0},\mathbf{r}_0$, which would have been obtained at the time t in place of $\Gamma_i,\mathbf{n}_i$ and $\mathbf{r}$, if the particles had moved freely (usually, the operator $\hat{s}_{12}$ is introduced for designation of this transformation[3,7]); ω and $\mathbf{q}$ are the differences of the frequency and of the wave vectors of the incident and scattered waves; T is the temperature of the gas in energy units.

The splitting of the collision integral in (2) into four components corresponds to the similar splitting used for a monatomic gas by Klimontovich.[4,6,8] The first operator $\hat{I}_0$ describes the local binary collisions (with account of the relaxation of the phase φ in the collision) and is equal in order of magnitude the gaskinetic collision frequency ν. The second and fourth components $\hat{I}_2 i(\mathbf{q}\mathbf{v}-\omega)$ and $\Delta\hat{I}_0$ have the order of magnitude ν^3_{Nd} and arise upon taking into account the finiteness of the collision time (the term $\hat{I}_2$) and the local triple collisions (the operator $\Delta\hat{I}_0$). The spatial nonlocality in binary collisions is described by the operator $i\mathbf{q}\hat{I}_1$, which is obtained by expansion of the nonlocal collision operator in the parameter $\mathbf{q}$ to first order. This operator is equal to $i(\mathbf{q}\cdot\mathbf{v})\mathrm{N}d^3$ in order of magnitude. We note that there are two characteristic length parameters in the scattering problem: the mean free path l and the light wavelength λ. Therefore, in the considered case of a dense gas ($l \ll \lambda$), we can assume that the nonlocal part of the collision integral $i\mathbf{q}\hat{I}_1$ is an increment of the order $\mathrm{N}d^3$ to the nonlocal collision operator of the free motion $i\mathbf{q}\cdot\mathbf{v}$, while the operators $\hat{I}_2$ and $\Delta\hat{I}_0$ are increments of the order of $\mathrm{N}d^3$ to the Boltzmann collision integral.

The right side of (2) arises as a result of account of the initial condition in the kinetic equation for the function χ. Here the first term refers to an ideal gas, while the second takes into account the finite correlation radius in the weakly nonideal gas.

3. SPECTRUM OF RAYLEIGH SCATTERING OF A NONIDEAL GAS

Equation (2) describes the complete light scattering spectrum (in classical language) in a gas, including the unshifted Rayleigh component and the rotational Raman components, shifted by the frequency $\pm 2\overline{\Omega} = \pm 2(T/I)^{1/2}$. In the case in which the central and shifted components are spectrally separated, the solution of Eq. (2) is conveniently sought in the form of an expansion in eigenfunctions of the operator $[\mathbf{\Omega}\times\mathbf{n}]\,\partial/\partial\mathbf{n}$, which have the form $\psi_k = \exp(ik\varphi)$. On this basis, the zeroth harmonic ($k = 0$) is separated spectrally from all the remaining harmonics, and describes the Rayleigh scattering. The rotational Raman scattering is described by the harmonics with $k = \pm 2$. In the present work, we have limited ourselves to the study of the spectrum of the unshifted Rayleigh component, when we can assume that the function χ in Eq. (2) does not depend on $\mathbf{n}$. In this case, the right and left sides of Eq. (2) can be integrated with respect to $d\varphi_1$ and the equation takes the form

$$i(\mathbf{q}\mathbf{v}_1-\omega)\chi+(\hat{I}_0+\Delta\hat{I}_0)\chi+\hat{I}_2 i(\mathbf{q}\mathbf{v}_1-\omega)\chi+i\mathbf{q}\hat{\mathbf{I}}_1\chi$$
$$=\tilde{B}(\mathbf{M}_1)+N\int(e^{-U_{12}/T}-1)B(\Gamma_2,\mathbf{n}_2)e^{-i\mathbf{q}\mathbf{r}}\,d\varphi_1\,d\varphi_2\,do_{\mathbf{M}_2}, \tag{3}$$

where

$$\tilde{B}(\mathbf{M})=B_0+B_1+B_2,\qquad B_0=\alpha_0(\mathbf{e}_1,\mathbf{e}_2)$$
$$B_1=\alpha_1([\mathbf{e}_1\times\mathbf{e}_2]\mathbf{M}/\mathbf{M}_0),$$
$$B_2=-\frac{1}{3}\alpha_2\biggl[\biggl(\mathbf{e}_1\frac{\mathbf{M}}{M}\biggr)\biggl(\mathbf{e}_2\frac{\mathbf{M}}{M}\biggr)-\frac{1}{3}(\mathbf{e}_1\mathbf{e}_2)\biggr]. \tag{3a}$$

The spectrum of the Rayleigh scattering $J(\omega,\mathbf{q})$ is expressed in terms of the solution of Eq. (3) in the following fashion:

$$J(\omega,\mathbf{q})=N\int\tilde{B}(\mathbf{M})f_0(\Gamma)\chi(\omega,\mathbf{q},\Gamma)\,d\Gamma. \tag{4}$$

As is seen from formulas (3) and (4), the integrated intensity of the Rayleigh light scattering is composed of two terms, one of which corresponds to an ideal gas and is proportional to $N\int\tilde{B}^2 f_0\,d\Gamma$, while the second is connected with the correlation of particles in the gas and is proportional to the quantity

$$N^2 \int B(\mathbf{n}_1) B(\mathbf{n}_2) (e^{-U_{12}/T}-1) e^{-i\mathbf{qr}} do_{\mathbf{n}_1} do_{\mathbf{n}_2} d\mathbf{r};$$

we can neglect here the antisymmetric scattering in B. The presence of a term nonlinear in the density in the integrated light scattering intensity leads to a quadratic dependence of the scattering indicatrix on the wave vector $\mathbf{q}$ for spherically nonsymmetric molecules (in the case of specified values of $\mathbf{e}_1$ and $\mathbf{e}_2$). The part of the scattering intensity that is anisotropic in $\mathbf{q}$ is of the order of $Nd^3(qd)^2$ of the total scattering intensity. In what follows, in the analysis of the scattering spectrum, these small increments will be discarded since they do not affect the shape of the scattering spectrum.

The microscopic expression for the collision integrals $\hat{I}_0$, $\hat{I}_2$, $i\mathbf{q}\hat{\mathbf{I}}_1$ are given by the formulas (2a,b,c) integrated over $d\varphi_1$, in which the function χ does not depend on $\mathbf{n}$. In this case, the integral $\hat{I}_0\chi$ is reduced by the usual procedure[3–5] to a linearized Boltzmann collision integral, in which the transition probability W is averaged over the vectors $\mathbf{n}_1$ and $\mathbf{n}_2$. The local increment $\Delta\hat{I}_0$ due to the triple collisions, just as in the Boltzmann integral $\hat{I}_0$, conserves locally the number of particles, the total momentum and the energy. The operator $\hat{I}_2$ conserves the number of particles and the momentum, but the nonlocal increment $i\mathbf{q}\cdot\hat{I}_1$, leads only to conservation of the number of particles in the collision.

In the considered case of a dense gas, the largest term in Eq. (3) is the Boltzmann operator $\hat{I}_0$, the characteristic frequency of which is $\nu \gg qv$, νNd^3, $qvNd^3$; therefore, the solution of Eq. (3) is conveniently sought in the form of an expansion in the eigenfunctions χ_α of the operator $\hat{I}_0$, while the remaining operators are considered as perturbations. In this basis, Eq. (3) breaks up into a coupled set of equations for the hydrodynamic and nonhydrodynamic modes of the operator $\hat{I}_0$.[1,9,10] As is known,[1] three hydrodynamic modes, the two acoustic modes

$$\chi_{1,2} = \left(\frac{c_v}{2c_p}\right)^{1/2}\left[1 \pm \left(\frac{c_p}{c_v}\right)^{1/2}\frac{v_x}{v_0} + c_v^{-1/2}\frac{E-\bar{E}}{\Delta E}\right.$$

where $v_0 = (T/m)^{1/2}$—is the thermal velocity $\bar{E} = c_v T$, $\Delta E = c_v^{1/2} T$, m is the mass of the molecule, c_p and c_v are the specific heats of a molecule of ideal gas at constant pressure and volume, respectively, and the third (thermal-conductivity) mode

$$\chi_5 = \left(\frac{c_v}{c_p}\right)^{1/2}\left(c_v^{-1/2} - \frac{E-\bar{E}}{\Delta E}\right)$$

all form a narrow triplet of scalar scattering. Here, for definiteness, the x axis is directed along the vector q. The two remaining hydrodynamic shear modes $\chi_3 = v_y/v_0$ and $\chi_4 = v_z/v_0$ appear only in the form of narrow dips in the depolarized spectrum of symmetric scattering. This effect arises due to the admixing, by the operator $i\mathbf{q}\cdot\mathbf{v}$, of the shear modes to the nonhydrodynamic modes that describe the symmetric scattering. In essence, if we restrict ourselves to the Boltzmann approximation (i.e., to the operators $\hat{I}_0$ and $i\mathbf{q}\cdot\mathbf{v}$), this covers all the possible interactions of the narrow hydrodynamic (with width $\gamma \sim (qv)^2/\nu$) and the broad nonhydrodynamic ($\gamma \sim \nu$) modes, which determine the fine structure in the scattering spectrum.

We now proceed to consideration of the effect exerted on the scattering spectrum by corrections connected with the departure of the gas from ideal. Solving Eq. (3) with account of small additions to the collision integral, we obtain the following expression for the intensity of the scattering spectrum[4]:

$$J(\omega, q) = J_0 + J_1 + J_2, \tag{5}$$

$$J_0 = B_0^2\left\{\frac{c_v}{2c_p}\left[\frac{\gamma_1}{(\omega+qu)^2+\gamma_1^2} + \frac{\gamma_2}{(\omega-qu)^2+\gamma_2^2}\right] + \frac{1}{c_p}\frac{\gamma_5}{\omega^2+\gamma_5^2}\right\}, \tag{5a}$$

$$J = \sum_{\alpha>5}\frac{B_{1\alpha}^2\nu_\alpha(1+\langle\Delta\hat{I}_0\rangle_\alpha)}{\omega^2(1+\langle\hat{I}_2\rangle_\alpha)^2+\nu_\alpha^2(1+\langle\Delta\hat{I}_0\rangle_\alpha)^2} + \frac{1}{2}\frac{[(\Delta B_3^{(0)})^2+(\Delta B_4^{(0)})^2]}{\omega^2+\gamma_3^2}, \tag{5b}$$

$$J_2 = \sum_{\alpha>5}\frac{B_{2\alpha}^2\nu_\alpha(1+\langle\Delta\hat{I}_0\rangle_\alpha)}{\omega^2(1+\langle\hat{I}_2\rangle_\alpha)^2+\nu_\alpha^2(1+\langle\Delta\hat{I}_0\rangle_\alpha)^2} - \frac{[(\Delta B_3)^2+(\Delta B_4)^2]}{\omega^2+\gamma_3^2} - \frac{\Delta B_1^2\gamma_1}{(\omega+qu)^2+\gamma_1^2} - \frac{\Delta B_2^2\gamma_2}{(\omega-qu)^2+\gamma_2^2}. \tag{5c}$$

Here

$$B_{i\alpha} = \int \chi_\alpha f_0 B_i \, d\Gamma \equiv \langle\chi_\alpha|B_i\rangle;$$

u is the velocity of sound in the nonideal gas, and is equal to

$$u = u_{\rm id} + \langle\chi_1|\hat{I}_{1x}+\hat{I}_2(v_x-u_{\rm id})|\chi_1\rangle, \qquad u_{\rm id} = \langle\chi_1|v_x|\chi_1\rangle = (c_p/c_v)^{1/2}v_0; \tag{6}$$

the line widths γ_j are determined by the following expressions:

$$\gamma_1 = \gamma_2 = \sum_{\alpha>5}\frac{q^2[v_x+\hat{I}_{1x}+\hat{I}_2(v_x-u_{\rm id})]_{1\alpha}^2}{\nu_\alpha+\langle\Delta\hat{I}_0\rangle_\alpha},$$

$$\langle\Delta\hat{I}_0\rangle_\alpha = \langle\chi_\alpha|\Delta\hat{I}_0|\chi_\alpha\rangle, \tag{7a}$$

$$\gamma_j = \sum_{\alpha>5}\frac{q^2(v_x+\hat{I}_{1x}+\hat{I}_2 v_x)_{j\alpha}}{\nu_\alpha+\langle\Delta\hat{I}_0\rangle_\alpha}, \quad j=3,4,5, \tag{7b}$$

while the mixing factors ΔB_j are equal to

$$\Delta B_j^{(0)} = \sum_{\alpha>5}(\mathbf{q}\hat{\mathbf{I}}_1)_{j\alpha}B_{1\alpha}\nu_\alpha^{-1}, \quad j=3,4, \tag{8a}$$

$$\Delta B_1 = \Delta B_2 = \sum_{\alpha>5}\frac{q[v_x+\hat{\tilde{I}}_{1x}+\hat{\tilde{I}}_2(v_x-u_{\rm id})]_{1\alpha}B_{2\alpha}}{\nu_\alpha+\langle\Delta\hat{I}_0\rangle_\alpha}, \tag{8b}$$

$$\Delta B_3 = \Delta B_4 = \sum_{\alpha>5}\frac{q(v_x+\hat{\tilde{I}}_{1x}+\hat{\tilde{I}}_2 v_x)_{3\alpha}B_{2\alpha}}{\nu_\alpha+\langle\Delta\hat{I}_0\rangle_\alpha}, \tag{8c}$$

$\tilde{I}_{1x}$ and $\tilde{I}_2$—are the Hermitian parts of the operators $\hat{I}_{1x}$ and $\hat{I}_2$; ν_a are the eigenvalues of the Boltzmann operator.

4. DISCUSSION

We now proceed to a more detailed analysis of the obtained spectrum. The changes in the spectrum of the scalar scattering [Eq. (5a)] are due to the appearance of a linear dependence on the density of the splitting of the Mandelstam-Brillouin doublet (or of the sound velocity) and to change in the character of the dependence of the width of the polarized triplet on the gas density. The velocity of sound, which is calculated from Eqs. (6) and (2), is identical with the well-known thermodynamic value, expressed in terms of the virial coefficient $B(T)$:

$$u=v_0\left(\frac{c_p}{c_v}\right)^{1/2}\left(1+NB(T)+\frac{NT}{c_p}\frac{dB(T)}{dT}\right.$$
$$\left.+\frac{N}{2c_pc_v}\frac{d}{dT}T^2\frac{dB(T)}{dT}\right),$$
$$B(T)=\int\left(1-e^{-U_{12}/T}\right)dr\,do_{\mathbf{n}_1}\,do_{\mathbf{n}_2}. \tag{9}$$

The last term in (9) arises because of the difference of the heat capacity at constant volume of an nonideal gas from the value c_v for an ideal gas, and vanishes in the case of a van der Waals gas. The sign of the increment linear in the density to the doublet splitting is determined by the temperature dependence of the virial coefficient and can in principle be positive as well as negative, depending on the parameter U_{12}/T. However, for ordinary neutral gases, the temperature at which the virial coefficient changes sign is close to the critical (condensation temperature); therefore, for a weakly nonideal gas $B(T)=b-a/T\gg 0$. In this gas, the sound velocity increases with increase of density. We note that the expression (6) for the sound velocity is identical with the thermodynamic value (9), since the possibility of sound dispersion has not been taken into account, i.e., the condition $\mathbf{q}\cdot\mathbf{v}\ll\Delta v\lesssim v,B$ has been assumed, while the region of dispersion $\mathbf{q}\cdot\mathbf{v}\sim\Delta v$. In the considered case of diatomic molecules, the relaxation of the angular momentum of the molecule $\mathbf{M}$ is a relatively slow process; the frequency of such collisions $\Delta v\sim\langle\chi_\alpha(\mathbf{M})|\hat{I}_0|\chi_\alpha(\mathbf{M})\rangle$.

The effect of the nonideal nature of the gas on the width of the polarized triplet reduces to the appearance of increments of the order of Nd^3 in the numerator and denominator of Eqs. (7a) and (7b). However, the corrections in the numerator are connected with the nonlocality of the pair collisions, while in the denominator they are connected only with the local triple collisions. Account of the triple collisions makes a positive contribution $\langle\Delta\hat{I}_0\rangle_\alpha>0$ to the collision frequency v_α, while the nonlocal increments have the same sign (most likely, positive) as the increment of the sound velocity [Eqs. (7) and (9)]. As a result, the widths of the triplet contain, along with the usual term $\propto 1/N$, a term that is independent of N, whose sign is determined by the combined action of the numerator and denominator of (7). Since the widths of the narrow hydrodynamic modes are directly connected with the kinetic coefficients,[9,10] the considered increments, in the language of kinetic coefficients, reduce to terms proportional to Nd^3.

We now consider the broad depolarized part of the light scattering spectrum ($\omega\sim\Delta v$), which is described by Eq. (3) for nonhydrodynamic modes χ_α ($\alpha>5$) (for symmetric scattering, $\chi_\alpha\propto Y_{2\varkappa}(\mathbf{M}/M)$, and for antisymmetric, $-\chi_\alpha\propto Y_{1\varkappa}(\mathbf{M}/M)$, where $Y_{j\varkappa}$ are the spherical harmonics). The damping frequencies of these modes, $\Delta\tilde{v}_\alpha$, with account of small corrections for the nonideality of the gas, have the following form:

(10)

As is seen from (10), allowance for the finite collision time (the operator $\hat{I}_2$) leads for the nonhydrodynamic modes to dispersion of the collision frequency.1) These corrections to the damping frequencies (10) change the width and the integrated intensity of the depolarized scattering by a value of order of Nd^3 [Eq. (5)]. We note that the frequency dispersion of the quantities $\Delta\tilde{v}_\alpha$ becomes significant at the high frequencies $\omega\sim 1/\tau_0\sim\overline{\Omega}$ (τ_0 is the collision time), where the rotational Raman spectrum is located. Therefore a more accurate description of this effect should be simultaneously accompanied by allowance for the rotational Raman scattering.

We now discuss the fine structure in the spectrum of depolarized scattering. This structure, as it turned out, is most sensitive to corrections associated with the nonideality of the gas. It is described by the second terms in Eqs. (5b) and (5c) for the antisymmetric and symmetric scattering, respectively.

As is seen from (5b), a narrow spike appears in the spectrum of antisymmetric scattering, in the center of the line ($\omega=0$), due entirely to the spatially nonlocal operator $i\mathbf{q}\cdot\hat{\mathbf{I}}_1$. The width of the spike is determined by the quantity γ_3 [see Eq. (7b)]. In the calculation of the intensity of the spike according to (8a) and (2c), the following relation is obtained for the direct and inverse matrix elements:

$$\left\langle\frac{v_y}{v_0}\middle|i\mathbf{q}\hat{\mathbf{I}}_1\middle|\frac{M_z}{M_0}\varphi_\alpha(M^2)\right\rangle$$
$$=-iq\left(\frac{I}{m}\right)^{1/2}\left\langle\frac{M_z}{M_0}\middle|\hat{I}_0\middle|\frac{M_z}{M_0}\varphi_\alpha(M^2)\right\rangle$$
$$=-2\left\langle\frac{M_z}{M_0}\varphi_\alpha(M^2)\middle|i\mathbf{q}\hat{\mathbf{I}}_1\middle|\frac{v_y}{v_0}\right\rangle$$
$$\left\langle\frac{v_z}{v_0}\middle|i\mathbf{q}\hat{\mathbf{I}}_1\middle|\frac{M_y}{M_0}\varphi_\alpha(M^2)\right\rangle$$
$$=iq\left(\frac{I}{m}\right)^{1/2}\left\langle\frac{M_y}{M_0}\middle|\hat{I}_0\middle|\frac{M_y}{M_0}\varphi_\alpha(M^2)\right\rangle$$
$$=-2\left\langle\frac{M_y}{M_0}\varphi_\alpha(M^2)\middle|i\mathbf{q}\hat{\mathbf{I}}_1\middle|\frac{v_z}{v_0}\right\rangle. \tag{11}$$

Here $\varphi_\alpha(M^2)$ is an arbitrary function of $|\mathbf{M}|$.

The relation (11) is a consequence of the law of conservation of the total angular momentum $\mathbf{M}+\mathbf{r}\times\mathbf{p}$, which is expressed in the language of matrix elements of the collision operator $\hat{I}_0+i\mathbf{q}\hat{\mathbf{I}}_1\mathbf{B}$ in the Fourier representation in the coordinates. The fact that the law of conservation of the total angular momentum, i.e., the sum of the rotational and orbital momenta of the molecules, is strictly satisfied only with account taken of the nonlocal collision integral, was first considered by Kaganov and Maksimov.[11] They took into account the new integral of motion, and supplemented the ordinary equations of hydrodynamics by an equation for the total angular momentum. It is interesting that in spectral language, a rigorous allowance for the law of conservation of angular momentum leads to the appearance of a narrow spike on the spectrum of the antisymmetric scattering. The intensity of the spike is connected with the relaxation of the vortices in the dense gas, i.e., with the transformation of the orbital angular momentum $\mathbf{r}\times\mathbf{p}$ of the vortices into the internal angular momentum **M**. We note that the orbital momentum is conserved in the Boltzmann approximation.[3]

Using (8a) and (11), we obtain the following expression for the intensity of the spike:

$$\Delta B_3^{(0)}=\sum_{\alpha>5}\nu_\alpha^{-1}(\mathbf{q}\mathbf{I}_1)_{3\alpha}B_{1\alpha}=-q\left(\frac{I}{m}\right)^{1/2}\left\langle\frac{M_z}{M_0}\middle|\,B_1\right\rangle$$

$$=-\frac{1}{3}q\left(\frac{I}{m}\right)^{1/2}\alpha_1[\mathbf{e}_1\mathbf{e}_2]\mathbf{e}_z,$$

$$\Delta B_4^{(0)}=\frac{1}{3}q\left(\frac{I}{m}\right)^{1/2}\alpha_1[\mathbf{e}_1\mathbf{e}_2]\mathbf{e}_y,$$

$$(\Delta B_3^{(0)})^2+(\Delta B_4^{(0)})^2\backsim\alpha_1^2\left(q^2\frac{I}{m}\right)\{[\mathbf{e}_1\mathbf{e}_2]^2-([\mathbf{e}_1\mathbf{e}_2]\mathbf{e}_x)^2\}. \tag{12}$$

The contrast of the spike, of order $(qd)^2 v\Delta v/(qv)^2\sim(\mathrm{Nd}^3)^2$, increases significantly only at very high gas densities ($\mathrm{ND}^3\to 1$), i.e., as the liquid state is approached.

In the spectrum of symmetric scattering (5c), a fine structure in the form of narrow dips at the unshifted frequency $\omega=0$ and at the Mandelstam-Brillouin frequencies $\omega=\pm\omega_{\mathrm{MB}}$ arises even in the Boltzmann approximation, and was treated in detail in Ref. 1. The effect of nonideality of the gas reduces in the given case only to a change in the contrast of the dips. From the formulas (7) and (8) we can obtain the following expression for the contrast R of the dips:

$$R(\omega=0)=\left[\sum_{\alpha>5}\frac{(v_x+\hat{I}_{1x}+\hat{I}_2v_x)_{3\alpha}B_{2\alpha}}{\Delta\nu_\alpha+\langle\Delta\hat{I}_0\rangle_\alpha}\right]^2$$

$$\times\left[\sum_{\alpha>5}\frac{B_{2\alpha}^2}{\Delta\nu_\alpha+\langle\Delta\hat{I}_0\rangle_\alpha}\right]^{-1}$$

$$\times\left[\sum_{\alpha>5}\frac{(v_x+\hat{I}_{1x}+\hat{I}_2v_x)_{3\alpha}^2}{\nu_\alpha+\langle\Delta\hat{I}_0\rangle_\alpha}\right]^{-1} \tag{13a}$$

$$R(\omega=\omega\quad)=\left\{\sum_{\alpha>5}\frac{[v_x+\hat{I}_{1x}+\hat{I}_2(v_x-u_{\mathrm{id}})]_{1\alpha}B_{2\alpha}}{\Delta\nu_\alpha+\langle\Delta\hat{I}_0\rangle_\alpha}\right\}^2$$

$$\times\left\{\sum_{\alpha>5}\frac{B_{2\alpha}^2}{\Delta\nu_\alpha+\langle\Delta\hat{I}_0\rangle_\alpha}\right\}^{-1}$$

$$\times\left\{\sum_{\alpha>5}\frac{[v_x+\hat{I}_{1x}+\hat{I}_2(v_x-u_{\mathrm{id}})]_{1\alpha}^2}{\nu_\alpha+\langle\Delta\hat{I}_0\rangle_\alpha}\right\}^{-1}. \tag{13b}$$

To estimate the contrast, we use the smallness of the parameter $\Delta\nu/\nu$, i.e., the ratio of the anisotropic part of the potential to the isotropic. In this case, Eqs. (13) for R take the simple form

$$R(\omega=0)\approx\Delta\eta/\eta_v\sim\Delta\nu/\nu,\quad R(\omega=\omega_{\mathrm{MB}})\approx\Delta\eta/\zeta\sim(\Delta\nu/\nu)^2 \tag{14}$$

where $\Delta\eta$, determined by the numerator of Eq. (13a), is the contribution of the rotational degrees of freedom to the shear viscosity coefficient, η_v is the part of the shear viscosity coefficient connected only with the translational degrees of freedom, ζ is the coefficient of bulk viscosity (for more details on the coefficients $\Delta\eta$, η_v, ζ, see Ref. 2). We note that in our research,[1] in the estimate of the contrast of the dips that has been discussed [Eq. (18)], an error was made that lowered the contrast by a factor $(\Delta\nu/\nu)^2$. We note that in the transition from a gas to a liquid, the representation of the contrast (14) in terms of the kinetic coefficients is more accurate, since the parameter $\Delta\nu/\nu$ is rigorously difined only for an ideal gas. For an estimate of the contrast of the dip at the unshifted frequency in an ideal gas, we represent (14) in the following form:

$$R(\omega=0)\sim\frac{\Delta\eta^{(0)}(1+C_1Nd_{\mathrm{anis}}^3)}{\eta_v^{(0)}(1+C_2Nd_{\mathrm{iso}}^3)}, \tag{15}$$

where the index "0" refers to the ideal gas and d_{anis} and d_{iso} are the characteristic dimensions of the anisotropic and isotropic parts of the interaction potential. For simple models (of the Chapman-Enskog type), numerical calculations give positive increments to the kinetic coefficients.[3] Therefore, assuming the coefficients C_1 and C_2 to be positive and of the same order of magnitude, we obtain the change in the value of the contrast R ($\omega=0$) in the case of a gas-density increase proportional to the parameter

$$N(d_{\mathrm{iso}}^3-d_{\mathrm{anis}}^3)\Delta\eta^{(0)}/\eta_v^{(0)}.$$

Thus, over a broad range of change in the gas pressure, the dip contrast is a measure of the relative contribution of the rotational degrees of freedom to the shear viscosity. We recall that the magnetic field acts on just this part $\Delta\eta$ of the shear viscosity.[2,12] The contrast of the dips at the Mandelstam-Brillouin frequency differs from the considered value at the unshifted frequency in the ratio $R(\omega=\omega_{\mathrm{MB}})\sim(\eta_v/\zeta)R(\omega=0)$.

It follows from analysis of the microscopic structure of the viscosity coefficients η_ν and ζ (see Eqs. (22), (25), (27) in Ref. 2), with increments that take into account the nonideality of the gas [Eq. (7)], that

$$\frac{\eta_v}{\zeta}\backsim\frac{\Delta\nu_\alpha+\langle\Delta\hat{I}_0\rangle_\alpha}{\nu_\alpha+\langle\Delta\hat{I}_0\rangle_\alpha}\sim\frac{\Delta\nu}{\nu}\frac{1+A_1Nd_{\mathrm{anis}}^3}{1+A_2Nd_{\mathrm{iso}}^3}. \tag{16}$$

Here the constants A_1 and A_2 are positive and determine the increments made by local triple collisions to the frequencies $\Delta\nu$ and ν. Since $d_{\mathrm{iso}}>d_{\mathrm{anis}}$, then the ratio η_ν/ζ increases with increase in the gas density. Consequently, the contrast of the dips in the depolarized scattering spectrum at the shifted frequencies, $R(\omega=\omega_{\mathrm{MB}})$, falls off with increase in the gas density more rapidly than the corresponding quantity R ($\omega=0$) at the unshifted frequency.

Thus, the interaction of the gas molecules manifests itself in a large number of characteristics of the spectrum of Rayleigh scattering. First, the dependence of the sound velocity on the gas density leads to a similar density dependence of the splitting of the Mandelstam-Brillouin doublet, with a relative change $\sim\mathrm{Nd}^3$ in the frequency of the doublet. Second, increments that do not depend on the density appear in the widths of the polarized triplet. Their relative value is also $\sim\mathrm{Nd}^3$. Third, in the spectrum of antisymmetric scattering, a narrow spike appears at the unshifted frequency whose contrast $\sim(\mathrm{Nd}^3)^2$, while the width γ_3 is determined by the shear viscosity coefficient η. Fourth, the contrast of the narrow dips in the center $\omega=0$ and at the frequencies $\omega=\pm\omega_{\mathrm{MB}}$ in the symmetric components of depolarized scattering become functions of the gas density. Here the change in the contrast (with increase in the density) at the shifted frequencies is greater than at the unshifted frequency.

As for the possibility of experimental observation of the

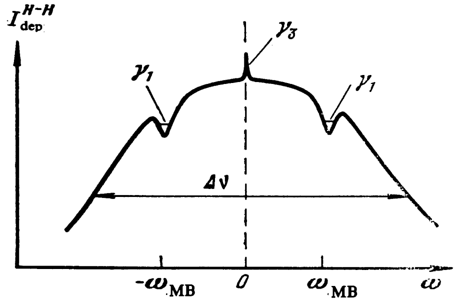

FIG. 1. Fine structure of the spectrum of the *H-H* component of depolarized scattering of light in a nonideal gas; $\Delta\nu$ is the width of the spectrum of depolarized scattering, $\pm\omega_{\text{MB}}$ are the frequencies of the Mandelstam-Brillouin components.

enumerated changes in the spectrum, in spite of their smallness ($\sim Nd^3$), this possibility is real at the contemporary level of development of laser technology and high resolution techniques. For example, frequency shifts $\Delta\omega/\omega \sim 10^{-3}$ (corresponding to a change in the gas pressure of about one atmosphere) are fully observable.[13]

The observation of the peak in the antisymmetric scattering is most difficult from the experimental viewpoint, because of the smallness of the cross section for the corresponding type of scattering $(\alpha_1/\alpha_0)^2 \sim 10^{-8}$. However, as shown in Ref. 14, this value can be increased to $(\alpha_1/\alpha_0)^2 \sim 10^{-2}$ upon approach to the electron absorption band of the molecules. A spike in the anisotropic scattering should be observed in the *H-H* component of the depolarized scattering, where there is no contribution at the unshifted frequency from the fine structure of symmetric scattering. The *H-H* polarization means that the polarization vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ lie in the plane of the scattering. This case is shown in the figure.

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[1] In Eq. (10) there is no increment proportional to *i***q** by virtue of the invariance of the complete collision integral to spatial inversion.

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