Kinetic description of Rayleigh scattering of light in dense gases

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A microscopic calculation is presented of the Rayleigh light scattering spectrum in a dense gas (in which the mean free path $l \ll \lambda$, where λ is the light wavelength) consisting of diatomic molecules. The fine structure in the depolarized components of the scattering spectrum is attributed to interaction between the rotational and translational degrees of freedom of the molecules. All the spectrum parameters are expressed in terms of the eigenfunctions and eigenvalues of the Boltzmann collision integral.

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1. INTRODUCTION

In connection with recent advances in laser technology and high-resolution spectral apparatus, it became possible to observe in experiment subtle effects in the structure of the spectrum of molecular scattering of light. Thus, it became possible to measure the unshifted scattering line width connected with entropy fluctuations, whose value in pure liquids does not exceed 10^{-3} cm^{-1} (Ref. 1). In depolarized light scattering, a fine structure of the wing (*FWS*) of the Rayleigh line was observed in the form of nonmonotonicities at frequencies close to the Mandel'shtam-Brillouin frequencies, by Starunov, Tiganov, and Fabelinskiĭ in one polarization,[2] and by Stegeman[3] in another polarization.

These singularities in the depolarized components of scattered light agree quanitatively with the predictions of the phenomenological theory of Reyleigh scattering of light in liquids, first constructed by Leontovich[4] and then developed and generalized by Rytov[5] and by Romanov and Solov'ev.[6] Other numerous phenomenological theories of light scattering[7–10] are essentially close to Rytov's theory, or stem from it,[11] therefore Rytov's theory is most frequently used in the analysis of experimental data (see, e.g., Ref. 12). The Leontovich theory and its generalization are based on Maxwell's idea of the viscous-elastic behavior of liquids, which behave at high frequencies like an amorphous solid, and on the presence in the liquid of one or several slowly relaxing parameters. It should be noted that a quantitative agreement between the experimental data and the theory can be achieved with the aid of Rytov's theory with two anisotropy relaxation times, and not with one as in the initial Leontovich theory.[11,12] Since Rytov's theory is phenomenological, the microscopic meaning of the internal relaxation parameters, as well as of the corresponding relaxation times and kinetic coefficients, remains unexplained. The existing statistical theories of molecular scattering of light (see the references in the review[11]) do not answer these questions unequivocally. In particular, the concrete choice of the two "optically active" parameters responsible for the structure of the spectrum of depolarized scattering of light in liquids remains open.

In this paper we consider the spectrum of Rayleigh scattering of light in a dense gas (we have in mind the condition $l \ll \lambda$, where l is the mean free path in the gas and λ is the wavelength of the light) consisting of diatomic molecules and for which the role of the equations of motion is played by the Boltzmann kinetic equation. In this case it becomes possible, in contrast to the case of liquids, to provide a detailed microscopic description of the structure of the spectrum. The scalar scattering in a dense gas is determined here by the same hydrodynamic modes as in a liquid. The analysis has shown that a fine structure appears in the depolarized components of the scattering spectrum of a dense gas, and agrees with the experimentally observed picture in low-viscosity liquids. It is demonstrated by the same token that at the onset of the fine structure is not connected with the assumptions of the phenomenological theories concerning the elastic behavior of the system at high frequencies, inasmuch as in a gas there is no slow relaxation of the transverse (shear) strains at practically all frequencies. It is shown that a fine structure occurs also in the depolarized scattering spectrum of a gas in the absence of a slowly relaxing parameter, and the necessary condition for its onset is a coupling of the rotational and translational motion of the molecules. In the case of a weakly anisotropic potential of the interaction of the gas molecules there appears in the microscopic description a slowly relaxing parameter, namely the angular momentum of the molecule. It was found that the slowly relaxing parameter leads to a very abrupt decrease of the contrasts of the fine structure under discussion. All the parameters of the spectrum, including Maxwell's constant M that determines the intensity of the fine structure and the widths of both the scalar and depolarized light scattering, are expressed in terms of the eigenvalues of the Boltzmann collision integral.

2. EQUATION FOR THE CORRELATION FUNCTION OF THE FLUCTUATIONS

In the microscopic description of the spectrum of Rayleigh scattering in a gas, the problem reduces to the calculation of the fluctuation correlation function

$$\Phi(t_1, \mathbf{r}_1, \Gamma_1; t_2, \mathbf{r}_2, \Gamma_2) = \langle \delta f(t_1, \mathbf{r}_1, \Gamma_1) \delta f(t_2, \mathbf{r}_2, \Gamma_2) \rangle,$$

where t is the time, $\mathbf{r}$ is the coordinate, Γ is the aggregate of all the remaining variables on which the distribution func-

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tion f depends, and δf is the deviation of the distribution function f of the gas molecules from the equilibrium Boltzmann function f_0; the angle brackets *denotes* the usual averaging over one of the instants t_1 or t_2 at a given value of their difference. In the present paper we confine ourselves to a diatomic molecule with account taken of only translational and rotational degrees of freedom. In this case the quantities Γ are the three components of the molecule velocity $\mathbf{v}$ and the three components of the angular momentum $\mathbf{M}$ (Ref. 13). It is known that for most molecules (with the possible exception of hydrogen) the condition for classical rotation $B \ll T$ is satisfied, where B is the rotational constant and T is the gas temperature.

The form $I(\omega,\mathbf{q})$ of the Rayleigh-scattering spectrum in an equilibrium and homogeneous gas is expressed in terms of Φ in the following manner:

$$I(\omega,\mathbf{q})=\int d\Gamma_1\, d\Gamma_2 e_{1i}^* \alpha_{ik}^*(\Gamma_1) e_{2k}^* 2\,\mathrm{Re}\,\Phi(\omega,\mathbf{q},\Gamma_1,\Gamma_2) \times e_{1s}\alpha_{st}(\Gamma_2) e_{2t}, \tag{1}$$

where

$$\Phi(\omega,\mathbf{q},\Gamma_1,\Gamma_2)=\int_0^\infty dt\, d\mathbf{r}\, \Phi(t,\mathbf{r},\Gamma_1;0,0,\Gamma_2)\, e^{i(\mathbf{qr}-\omega t)},$$

e_{1i} and e_{2k} are the unit vectors of the polarizations for the incident and scattered waves, $\omega=\omega_2-\omega_1$ and $\mathbf{q}=\mathbf{k}_2-\mathbf{k}_1$ are the differences of the frequencies and of the wave vectors of the scattered (2) and incident (1) waves, and $\alpha_{ik}(\Gamma)$ is the gas-molecule polarizability tensor. An asterisk denotes here the complex conjugate and, as usual, summation over repeated indices is implied.

In an ideal gas, the function Φ satisfies the equation (see Ref. 13, p. 108)

$$[i(\mathbf{qv}_1-\omega)-\hat{I}_1]\,\Phi(\omega,\mathbf{q},\Gamma_1,\Gamma_2)=f_0(\Gamma_1)\,\delta(\Gamma_1-\Gamma_2), \tag{2}$$

where I_1 is a linear integral operator acting on the variables Γ_1 in the following manner:

$$\hat{I}_1\Phi(\Gamma_1)= \quad w(\Gamma,\Gamma_1;\Gamma',\Gamma_1')\{f_0(\Gamma_1')\Phi(\Gamma')+f_0(\Gamma')\Phi(\Gamma_1') -f_0(\Gamma)\Phi(\Gamma_1)-f_0(\Gamma_1)\Phi(\Gamma)\}\,d\Gamma\, d\Gamma'\, d\Gamma_1'.$$

The function $w(\Gamma,\Gamma_1;\Gamma',\Gamma_1')$ determines the probability of the collisions with the transition $\Gamma',\Gamma_1' \to \Gamma,\Gamma_1$. We shall assume that the function w has the symmetry property $w(\Gamma,\Gamma_1;\Gamma',\Gamma_1')=w(\Gamma',\Gamma_1';\Gamma,\Gamma_1)$. This property is known to be satisfied for purely electrostatic interactions, for in this case the operator I_1 commutes with time-reversal operator, i.e.,

$$w(\Gamma,\Gamma_1;\Gamma',\Gamma_1')=w(\Gamma^T,\Gamma_1^T;\Gamma'^T,\Gamma_1'^T),$$

where Γ^T is the state obtained from Γ by time reversal (see Ref. 13, pp. 13 and 46).

In what follows it is convenient to integrate in the expression for Φ with respect to $d\Gamma_2$ with a weight factor

$$B(\Gamma_2)=e_{1s}\alpha_{st}(\Gamma_2)e_{2t}$$

and separate from Φ the equilibrium function $f_0(\Gamma_1)$, to transform in fact to a new unknown function

$$\chi(\omega,\mathbf{q},\Gamma_1)=f_0^{-1}(\Gamma_1)\int\Phi(\omega,\mathbf{q},\Gamma_1,\Gamma_2)B(\Gamma_2)\,d\Gamma_2,$$

that satisfies the equation

$$[i(\mathbf{qv}-\omega)-\hat{K}]\,\chi(\omega,\mathbf{q},\Gamma)=B(\Gamma), \tag{3}$$

where the linear operator $\hat{K}$ is defined as follows:

$$\hat{K}\chi(\Gamma)=\int d\Gamma_1\, d\Gamma'\, d\Gamma_1'\, w f_0(\Gamma_1)\{\chi(\Gamma')+\chi(\Gamma_1')-\chi(\Gamma)-\chi(\Gamma_1)\}.$$

The Reyleigh-scattering spectrum $I(\omega,\mathbf{q})$ takes then the form

$$I(\omega,\mathbf{q})=\mathrm{Re}\int d\Gamma B^*(\Gamma)f_0(\Gamma)\chi(\omega,\mathbf{q},\Gamma). \tag{4}$$

In the considered case of a dense gas, when the collision frequency $\nu \gg \mathbf{q}\cdot\mathbf{v}$, the collisional term $\hat{K}\chi$ in Eq. (8) is much larger than the term $\mathbf{q}\cdot\mathbf{v}\chi$ connected with the free motion of the molecule. It is therefore convenient, when solving Eq. (3), to use perturbation theory in the parameter $\mathbf{q}\cdot\mathbf{v}/\nu \ll 1$, and choose the eigenfunctions of the operator $\hat{K}$ as the basis. It follows from the symmetry property of the function w that the operator $\hat{K}$ is self-adjoint, i.e.,

$$\int\varphi^*(\Gamma)f_0(\Gamma)\hat{K}\psi(\Gamma)\,d\Gamma=\int\psi^* f_0\hat{K}\varphi\, d\Gamma,$$

or

$$\langle\varphi|\hat{K}|\psi\rangle=\langle\psi|\hat{K}|\varphi\rangle$$

and an orthonormal base can be constructed out of its eigenfunctions.

It is known[13-15] that five of these eigenfunctions have zero eigenvalues, correspond to five conservation laws for the particle number, for the three momentum components mv_x, mv_y, and mv_z, and for the energy E. These functions can be easily written out explicitly:

$$\varphi_1=1,\quad \varphi_2=v_x/v_0,\quad \varphi_3=v_y/v_0,\quad \varphi_4=v_z/v_0,\quad \varphi_5=(E-\bar{E})/\Delta E,$$

where $v_0=(T/m)^{1/2}$ is the thermal energy, $\bar{E}=c_v T$ is the average energy of the molecule, $\Delta E=\sqrt{c_v}\,T$ is the energy dispersion, T is the gas temperature (in energy units), and c_v is the specific heat of the molecules at constant volume with allowance for the translational and rotational degrees of freedom.

We construct orthonormalized linear combinations of the functions $\varphi_1,\ldots,\varphi_5$ in which the operator $\mathbf{q}\cdot\mathbf{v}$ is diagonal. To be definite, we direct the x axis along the vector $\mathbf{q}$

$$\chi_1=(c_v/2c_p)^{1/2}[\varphi_1-(c_p/c_v)^{1/2}\varphi_2+c_v^{-1/2}\varphi_5],$$

$$\chi_2=(c_v/2c_p)^{1/2}[\varphi_1+(c_p/c_v)^{1/2}\varphi_2+c_v^{-1/2}\varphi_5],$$

$$\chi_3=\varphi_3,\quad \chi_4=\varphi_4,\quad \chi_5=(c_v/c_p)^{1/2}(c_v^{-1/2}\varphi_1-\varphi_5).$$

The functions χ_1 and χ_2 correspond to acoustic modes, χ_3 and χ_4 to shear modes, χ_5 to the heat-conduction mode, and c_p is the specific heat of the molecule at constant pressure.

We seek the solution of Eq. (3) in the form of an expansion in the eigenfunctions of the operator $\hat{K}$:

$$\chi(\omega,\mathbf{q},\Gamma)=\sum_{\alpha=1}^{\infty}a_\alpha(\omega,\mathbf{q})\chi_\alpha(\Gamma),$$

where $\chi_\alpha(\Gamma)$ at $\alpha>5$ are the eigenfunctions corresponding to the nonzero eigenvalues $-\nu_\alpha$. Since the operator $\hat{K}$ is negative-definite, all the eigenvalues are $-\nu_\alpha < 0$.

From Eq. (3) we can change over to the equations for the coefficients a_α:

$$\begin{aligned} & i(-\omega-qu)a_1+i\sum_{\alpha>5}(\mathbf{qv})_{1\alpha}a_\alpha=B_1, \\ & i(-\omega+qu)a_2+i\sum_{\alpha>5}(\mathbf{qv})_{2\alpha}a_\alpha=B_2, \\ & -i\omega a_\beta+i\sum_{\alpha>5}(\mathbf{qv})_{\beta\alpha}a_\alpha=B_\beta \quad (\beta=3,4,5), \\ & (-i\omega+\nu_\alpha)a_\alpha+i\sum_{\alpha'\geq 1}(\mathbf{qv})_{\alpha\alpha'}a_{\alpha'}=B_\alpha \quad (\alpha>5). \end{aligned} \tag{5}$$

In this case we obtain in place of (4)

$$I(\omega,\mathbf{q})=\operatorname{Re}\sum_{\beta\leq 5}B_\beta^* a_\beta+\operatorname{Re}\sum_{\alpha>5}B_\alpha^* a_\alpha. \tag{6}$$

The system (5) contains the speed of sound $u=v_0\,(c_p/c_v)^{1/2}$ and the matrix element of the operator $\mathbf{q}\cdot\mathbf{v}$ between the states χ_α and $\chi_{\alpha'}$

$$(\mathbf{qv})_{\alpha\alpha'}=\int\chi_\alpha f_0\mathbf{qv}\chi_{\alpha'}\,d\Gamma.$$

Let us dwell in somewhat greater detail on the properties of $B(\Gamma)$. It can be seen from the definition of $B(\Gamma)$ that its properties are closely related with the properties of the molecule polarizability tensor $\alpha_{st}(\Gamma)$. In particular, the independence of the molecule polarizability tensor of the velocity $\mathbf{v}$ makes B dependent only on the angular momentum $\mathbf{M}$. It is convenient to express $B(\Gamma)$ as a sum of three terms corresponding to the breakup of α_{st} into scalar $(\alpha_0\delta_{st})$, antisymmetrical (α_{st}^a), and symmetrical (α_{st}^s) parts[16]:

$$B(\Gamma)=B_0+B^s(\Gamma)+B^a(\Gamma), \tag{7}$$

where

$$B_0=(\mathbf{e}_1\mathbf{e}_2)\alpha_0, \quad B^s(\Gamma)=e_{1i}\alpha_{ik}^s(\mathbf{M})e_{2k}, \quad B^a(\Gamma)=e_{1s}\alpha_{st}^a(\mathbf{M})e_{2t}.$$

As a rule, the antisymmetrical part of the polarizability tensor of the molecule is small and is therefore disregarded in the present paper, i.e., $B^a(\Gamma)=0$. The hydrodynamic modes $\chi_1,\ldots,\chi_5$ are pure scalars and do not depend on the direction of the vector $\mathbf{M}$. As a result the symmetrical part of the function $B(\Gamma)$ makes no contribution to $B_1,\ldots,B_5$, so that

$$\int\alpha_{ik}^s(\mathbf{M})\,do_{\mathbf{M}}=0.$$

It is easy to calculate the values of $B_1,\ldots,B_5$:

$$\begin{aligned} & B_1=B_2=(c_v/2c_p)^{1/2}\alpha_0(\mathbf{e}_1\mathbf{e}_2)\equiv B, \\ & B_3=B_4=0, \quad B_5=c_p^{-1/2}\alpha_0(\mathbf{e}_1\mathbf{e}_2)=(2/c_v)^{1/2}B. \end{aligned} \tag{8}$$

We see therefore that the scalar-scattering intensities integrated over the frequencies satisfy the Landau-Placzek relation

$$\frac{h_{\text{doubl}}}{h_{\text{tot}}}=\frac{2|B_1|^2}{2|B_1|^2+|B_5|^2}=\frac{c_v}{c_p}.$$

From the orthogonality of the functions 1 and χ_α, where $\alpha>5$, it follows that the scalar part of the polarizability tensor makes no contribution to the values of B_α, where $\alpha>5$. Thus, the terms in the expression for the intensity (6) correspond to the scalar and symmetrical types of scattering without allowance for the spatial dispersion of the medium. We note that this breakdown in the basis of the eigenfunctions of the operator $\hat{K}$ takes place if the polarizability of the molecules does not depend on the modulus of $\mathbf{M}$.

As seen from the system (5), when account is taken of the spatial dispersion of the medium the spectra of the scalar and symmetrical scattering are not independnet, since the equations for the coefficients $a_1,\ldots,a_5$ are coupled with the equations for a_α, where $\alpha>5$, with the aid of the matrix elements $(\mathbf{q}\cdot\mathbf{v})_{\beta\alpha}$. We proceed now to solve the system (5), using perturbation theory in the parameter $\mathbf{q}\cdot\mathbf{v}/\nu$. In this case we can neglect the sums with $\alpha'>5$ in the last equation of the system (4) compared with the terms $\nu_\alpha a_\alpha$, and solve them for the coefficients a_α, obtaining

$$a_\alpha=\frac{B_\alpha}{-i\omega+\nu_\alpha}-i\sum_{\beta\leq 5}\frac{(\mathbf{qv})_{\alpha\beta}a_\beta}{\nu_\alpha}, \quad \alpha>5.$$

Substituting the expression for a_α in the first five equations of the system (5), we obtain

$$-i(\omega+\Omega_j)a_j+\gamma_j a_j=B_j-i\Delta B_j, \quad j=1,\ldots,5, \tag{9}$$

where

$$\Omega_1=qu, \quad \Omega_2=-qu, \quad \Omega_{3,4,5}=0;$$

$$\gamma_j=\sum_{\alpha>5}\nu_\alpha^{-1}(\mathbf{qv})_{j\alpha}(\mathbf{qv})_{\alpha j}, \quad \gamma_1=\gamma_2, \quad \gamma_3=\gamma_4;$$

$$\Delta B_j=\sum_{\alpha>5}\nu_\alpha^{-1}(\mathbf{qv})_{j\alpha}B_\alpha, \quad \Delta B_1=\Delta B_2, \quad \Delta B_3=\Delta B_4, \quad \Delta B_5=0.$$

In the equations for a_1 and a_2 we discarded all the terms that connect a_1 and a_2 with one another and with the terms a_β, where $\beta=3$, 4, and 5 since the quantities a_1 and a_2 are spectrally separated from all the a_β. The functions a_1 and a_2 are narrow resonances at frequencies $\pm qu$. The width of these resonances $(\mathbf{q}\cdot\mathbf{v})^2/\nu_\alpha$ is much less than qu. It is easy to verify that the widths of the resonances coincide because the functions χ_1 and χ_2 are connected by the relation $\chi_1=\hat{T}\chi_2$, where $\hat{T}$ is the time-reversal operator. The quantities a_3, a_4, and a_5 have a resonance at zero frequency $\omega=0$, but also turn out to be unrelated. The quantity a_5 is not connected with a_3 and a_4 on account of the T-parity selection rule. In fact, since the operator $\hat{K}$ is self-adjoint, it commutes with the time-reversal operator $\hat{T}$, i.e., all the eigenfunctions χ_α have definite T-parity. It follows from this property that the "inverse" operator

$$\hat{K}^{-1}=\sum_{\alpha>5}\frac{|\alpha\rangle\langle\alpha|}{\nu_\alpha},$$

which has the same eigenfunctions as $\hat{K}$ (in particular, $\hat{K}^{-1}\chi_\beta=0, \beta=1,\ldots,5$) also commutes the operator $\hat{T}$ and therefore relates with one another only states of like T-parity. And since the function χ_5 is T-even while χ_3 and χ_4 are T-odd, the matrix elements

$$\sum_{\alpha>5} \nu_\alpha^{-1} (\mathbf{qv})_{5\alpha} (\mathbf{qv})_{\alpha\beta},$$

where $\beta = 3$ or 4, are equal to zero, i.e., the equation for a_5 is decoupled from the equations for a_3 and a_4. In the right-hand side of the equation for a_5 in the system (9), there is no term $-i\Delta B_5$, likewise by virtue of the T-parity selection rules (use is made of the fact that β_α is T-even in the absence of antisymmetric scattering). The spherical symmetry of the operator $\hat{K}^{-1}$ decouples the equations for a_3 and a_4 and makes the resonance widths of a_3 and a_4 equal. The right-hand sides of these equations also coincide, therefore $a_3 = a_4$.

In the equations for narrow resonances a_β ($\beta = 1,...,5$) we can neglect the quantity $i\omega$ compared with ν_α in the factors $(-i\omega + \nu_\alpha)^{-1}$, since the considered narrow structure plays an essential role only in the frequency region $\omega \ll \nu_\alpha$.

3. FORM OF THE SPECTRUM

We consider first the "scalar"[1)] part of the scattering spectrum; this corresponds to the first term in Eq. (6):

$$I_{sc}(\omega, \mathbf{q}) = \frac{|B|^2\gamma_1}{(\omega+qu)^2+\gamma_1^2} + \frac{|B|^2\gamma_2}{(\omega-qu)^2+\gamma_2^2} + \frac{2}{c_v}\frac{|B|^2\gamma_5}{\omega^2+\gamma_5^2} + B\Delta B_1\left\{\frac{\omega+qu}{(\omega+qu)^2+\gamma_1^2} - \frac{\omega-qu}{(\omega-qu)^2+\gamma_2^2}\right\}. \tag{10}$$

We note that a contribution to ΔB_1 is made only by the symmetrical part of the polarizability of the molecule, i.e., by the component $B^s(\Gamma)$ of the total quantity $B(\Gamma)$ in Eq. (7). The reason is that at $\alpha > 5$ all the functions χ_α are orthogonal to unity (or to the scalar quantity b_0).

The scalar spectrum, as expected, consists of two acoustic components having maxima at the frequencies $\omega = \pm qu$, and the central component determined by the heat-conduction mode χ_5. The central component has the shape of an ordinary Lorentz contour whose width is a generalization of a previously obtained expression[14,15] with allowance for the rotational degrees of freedom of the molecule.

The shape of the acoustic doublet is more complicated. As can be seen from (10), it is the superposition of symmetrical Lorentz contours with asymmetric additions whose signs are opposite for the Stokes and anti-Stokes components. The degree of asymmetry of the resultant contours is determined by the parameter $\Delta B_1/B$ and decreases with increasing gas density in proportion to $\mathbf{q}\cdot\mathbf{v}/\nu_\alpha$.

In the same approximation in the parameter $\mathbf{q}\cdot\mathbf{v}/\nu_\alpha$, the spectrum of the depolarized scattering (for which $\mathbf{e}_1\cdot\mathbf{e}_2 = 0$ and therefore $B_0 = 0$) is described by the following equation

$$I_{\text{dep}}(\omega, \mathbf{q}) = \sum_{\alpha>5} \frac{|B_\alpha|^2\nu_\alpha}{\omega^2+\nu_\alpha^2} - \left\{\frac{|\Delta B_1|^2\gamma_1}{(\omega+qu)^2+\gamma_1^2} + \frac{|\Delta B_2|^2\gamma_2}{(\omega-qu)^2+\gamma_2^2} + \frac{(|\Delta B_3|^2+|\Delta B_4|^2)\gamma_3}{\omega^2+\gamma_3^2}\right\}. \tag{11}$$

It can be seen from (11) that the spectrum of the depolarized scattering acquires narrow dips, against the background of a broad contour of width $\sim\nu_\alpha$, at the frequencies of the acoustic components $\omega = \pm qu$ as a result of the admixture of acoustic modes χ_1 and χ_2, and at the center line as a result of admixture of shear modes $\chi_3 = \chi_4$. The integrated intensity of the dips, which is proportional to the quantities $|\Delta B_1|^2$ and $|\Delta B_3|^2$, decreases with increasing density in proportion to ν_α^{-2}. It must be noted, however, that the contrast of the resonances, i.e., the ratio of the depth of the dips to the height of the broad contour of the depolarized scattering $R = h_{\text{dip}}/h_{\text{dep}}$, is independent of the gas density. Let us examine the factors that influence $\Delta B_{1,3}$ and lead to the mixing of the scalar and symmetrical contours. To this end, using the invariance of the operator $\hat{K}^{-1}$ in ΔB to rotations in space, we can separate the dependences of $B_{1,3}$ on the polarization of the incident and scattered waves,

$$\begin{aligned} \Delta B_1 &= \langle\chi_1|\mathbf{qv}\hat{K}^{-1}|B\rangle \propto \int \frac{M_x^2}{|\mathbf{M}|^2} B(\mathbf{M})\, do_{\mathbf{M}}, \\ \Delta B_3 &= \langle\chi_3|\mathbf{qv}\hat{K}^{-1}|B\rangle \propto \int \frac{M_x M_y}{|M|^2} B(\mathbf{M})\, do_{\mathbf{M}}, \end{aligned} \tag{12}$$

where

$$B(\mathbf{M}) = e_{1s}\alpha_{st}(\mathbf{M})e_{2t},$$

and the matrix elements of the operator $\hat{K}^{-1}$ are defined in the same manner as for the operator $\mathbf{q}\cdot\mathbf{v}$ (see above).

Since the polarizability tensor α_{iq} depends only on the vector $\mathbf{M}$ it can be expressed in terms of the components of this vector:

$$\alpha_{ik} = a\delta_{ik} + b(M_i M_k/|\mathbf{M}|^2 - {}^1/_3\delta_{ik}), \tag{13}$$

where a and b are constants. The subdivision in (13) corresponds to resolution of the tensor into a scalar part and a symmetrical zero-trace part. Substituting (13) in (12) we obtain

$$|\Delta B_1|^2 = |\Delta B_2|^2 \propto e_{1x}^2 e_{2x}^2,$$
$$|\Delta B_3|^2 + |\Delta B_4|^2 \propto {}^1/_2 e_{1x}^2 + {}^1/_2 e_{2x}^2 - e_{1x}^2 e_{2x}^2.$$

We recall that the x axis is directed along the scattering vector $\mathbf{q} = \mathbf{k}_2 - \mathbf{k}_1$, and the xy plane coincides with the scattering plane and is determined by the vectors $\mathbf{k}_1$ and $\mathbf{k}_2$. The yx polarization (or $H\cdot H$, where H is horizontal and V is vertical) denotes that the polarization of the incident light is directed along the y axis (horizontal component H), and the depolarized spectra of the scattering is investigated for the polarization along the x axis (also horizontal component H). Thus, the fine structure, obtained in the present paper for dense gases, manifests itself in the form of the two narrow dips in I_{yx} (I_{HH}) polarization and one dip at the center in the case of the polarization $I_{zx} = I_{yz}$ ($I_{VH} = I_{HV}$), in accord with the experimentally observed fine structure in the depolarized components of the scattering spectrum in low-viscosity liquids.[2,3] The connection between the obtained fine structure in gases and the predictions of the phenomenological theories of light scattering[4-10] will be discussed below.

4. COLLISIONS WITH ALMOST ISOTROPIC POTENTIAL

For a number of simple molecules, collisions with change of velocity usually take place more frequently than collisions with change of the angular momentum, i.e., the anisotropic part of the potential is relatively small compared with the isotropic.[17,18] In this approximation it can be assumed that the probability of the change of velocity depends little on the change of the angular momentum of the molecule, i.e., the collision operator $\hat{K}$ can be expanded in the following fashion:

$$\hat{K}=\hat{K}_0+\Delta\hat{K},$$

where the function w before the operator $\hat{K}_0$ is of the form

$$w(\Gamma,\ \Gamma_1;\ \Gamma'\Gamma_1')=w(\mathbf{v},\ \mathbf{v}_1;\ \mathbf{v}',\ \mathbf{v}_1')\,\delta(\mathbf{M}-\mathbf{M}')\,\delta(\mathbf{M}_1-\mathbf{M}_1'). \tag{14}$$

Since the resolution of the collision probability into two terms, one of which describes processes with change of the angular momentum **M** and the other independent of the change of **M**, is ambiguous, this ambiguity must be eliminated by imposing conditions on the choice of $w(\mathbf{v}, \mathbf{v}_1; \mathbf{v}', \mathbf{v}_1')$ in (14). There are physical grounds for choosing in (14) the $w(\mathbf{v}, \mathbf{v}_1; \mathbf{v}', \mathbf{v}_1')$ obtained from $w(\Gamma,\Gamma_1;\Gamma'\Gamma_1')$ in the following manner

$$w(\mathbf{v},\mathbf{v}_1;\mathbf{v}',\mathbf{v}_1')=\int f_0(M)\,f_0(M_1)\,w(\Gamma,\Gamma_1;\Gamma',\Gamma_1')\times d\mathbf{M}\,d\mathbf{M}_1\,d\mathbf{M}'\,d\mathbf{M}_1'.$$

It can be seen from this definition that the transition probability $w(\Gamma,\Gamma_1,\Gamma'\Gamma_1')$ is integrated over the final states of the angular momenta of the molecules after the collisions and is averaged over the initial states **M** and $\mathbf{M}_1$ with equilibrium distribution functions $f_0(M)$ and $f_0(M_1)$. It follows from the conditions imposed that all the matrix elements of the operator $\Delta\hat{K}$ in the space of the functions that depend on **v** are equal to 0. The operator $\Delta\hat{K}$ is determined by a general expression and describes collisions with change of the angular momentum **M**, as well as the correlation in the collisions of **v** with **M**.

It can thus be assumed that $\Delta\hat{K}\ll\hat{K}_0$, and its contribution can be taken into account by perturbation theory.

It is convenient to choose the orthonormalized eigenfunctions of the operator $\hat{K}_0$ in the form of irreducible spherical tensors

$$\chi^{(0)}(\mathbf{v},\ \mathbf{M})=a_{\alpha l}(v)\,b_{\alpha' l'}(M)\,\{Y_l(\mathbf{v}/v)\otimes Y_{l'}(\mathbf{M}/M)\}_{LN}, \tag{15}$$

where the curly brackets denote bipolar harmonics.[19] In this $\chi_{(0)}$ basis the matrix elements of the operator $\Delta\hat{K}$ are diagonalized with respect to the numbers L and N and are independent of N.

For the calculations that follow it is convenient to divide the set of eigenfunctions of the operator $\hat{K}_0$ into three classes: a) functions that depend only on **v**; b) functions that depend only on **M**; c) functions that depend on both **v** and **M**. We shall designate them by χ_α^v, χ_α^M, and χ_α^{Mv}. The corresponding eigenvalues are designated ν_α^v, ν_α^M, and ν_α^{Mv}. In the introduced symbols, the subscript α stands for the group α, α', l, l', L, and N. If any of the latter subscripts must be specified, we shall write it in parentheses after the indicated function or eigenvalue. We note now the properties of the eigenvalues of the operator $\hat{K}_0$. By direct substitution of (14) in the operator $\hat{K}_0$ we can verfify that the eigenfunctions χ_α^M and χ_α^{Mv} are degenerate with respect to the numbers α' and l' that describe the dependence on M, while all the eigenvalues ν_α^M are equal to zero. It follows therefore that in the zeroth approximation in $\Delta\hat{K}$ the spectrum of the depolarized scattering is described by one eigenfunction $\chi = Y_{2m}(\mathbf{M}/M)$ and has a zero width, i.e., it is a delta function. A finite width of the depolarized spectrum is obtained in the next order of perturbation theory in $\Delta\hat{K}$ upon diagonalization of the operator $\Delta\hat{K}$ in degenerate M space.

Let

$$\chi_\alpha{}^M=C_\alpha(M)\,Y_{2m}(\mathbf{M}/M)$$

be the eigenfunction of the operator $\Delta\hat{K}$ in **M** space with eigenvalue

$$\Delta\nu_\alpha(L=2)=\langle\chi_\alpha{}^M|\Delta\hat{K}|\chi_\alpha{}^M\rangle,$$

obtained as a result of diagonalization of the operator $\Delta\hat{K}$ in **M** space. The contour of the depolarized scattering is a superposition of Lorentz contours with widths $\Delta\nu_\alpha$ $(L = 2)$ and with intensities proportional to $|\int C_\alpha(M)dM|^2$.

In the next order of perturbation theory in $\Delta\hat{K}$, there appears in the spectrum of the depolarized scattering an additional structure with a characteristic width of the order of the collision frequency in **v**-subspace. The shape of the broad part of the depolarized spectrum is given by

$$I_{\text{dep}}(\omega)=\sum_{\alpha>5}\frac{|B_\alpha|^2\Delta\nu_\alpha(L=2)}{\omega^2+[\Delta\nu_\alpha(L=2)]^2}+\sum_{\alpha>5}\frac{|A_\alpha{}^v|^2\nu_\alpha{}^v(L=2)}{\omega^2+[\nu_\alpha{}^v(L=2)]^2}+\sum_{\alpha>5}\frac{|A_\alpha{}^{Mv}|^2\nu_\alpha{}^{Mv}(L=2)}{\omega^2+[\nu_\alpha{}^{Mv}(L=2)]^2}, \tag{16}$$

where

$$A_\alpha{}^v=\sum_{\alpha'>5}\frac{B_{\alpha'}\langle\chi_{\alpha'}{}^M|\Delta\hat{K}|\chi_\alpha{}^v\rangle}{\nu_\alpha{}^v(L=2)},$$

$$A_\alpha{}^{Mv}=\sum_{\alpha'>5}\frac{B_{\alpha'}\langle\chi_{\alpha'}{}^M|\Delta\hat{K}|\chi_\alpha{}^{Mv}\rangle}{\nu_\alpha{}^{Mv}(L=2)},\qquad B_\alpha=\langle\chi_\alpha{}^M|B\rangle.$$

The ratio of A_α to B_α is of the order of the ratio $\Delta\nu/\nu$ of the collision frequencies in **M** and **v** spaces. The first term in (16) describes the ordinary depolarized-scattering contour whose width is determined by the frequency $\Delta\nu_\alpha$ $(L = 2)$ of the collisions that reorient the proper angular momentum of the molecule **M**. The two remaining terms are due only to the interaction of the translational and rotational degrees of freedom of the molecule in the collisions. The first term corresponds to an admixture, to the depolarized scattering, of functions that depend only on the molecule velocity **v**, and the second to the admixture of functions that depend on **v** and **M**. In order of magnitude, the ratio of the integrated intensities of the broad contours admixtured to the narrow ones is of the order of $|A_\alpha/B_\alpha|^2\sim(\Delta\nu/\nu)^2$. In view of this smallness, the contribution to the intensity from the wing of the narrow contour exceeds the intensity of the admixed broad contour by a factor $\nu/\Delta\nu$ even on the wings of a broad structure $\omega\gtrsim\nu$. Actually, therefore, the admixing of the broad contour with width of the order ν to the narrow contour of width $\Delta\nu$ hardly manifests itself in scattering in gases.

Another result, more favorable from the viewpoint of experimental observation, is obtained when a narrow structure ($\omega \leqslant qv$) is added to the depolarized-scattering contour, in accordance with formula (11). In this case the intensity of the mixed acoustic and shear modes, calculated by perturbation theory, takes the form

$$\Delta B_1 = \sum_{\alpha>5} \frac{\langle \chi_1 | \mathbf{qv} | \chi_\alpha{}^v \rangle}{\nu_\alpha{}^v (L=2)} A_\alpha{}^v, \qquad \Delta B_{3,4} = \sum_{\alpha>5} \frac{\langle \chi_3 | \mathbf{qv} | \chi_\alpha{}^v \rangle}{\nu_\alpha{}^v (L=2)} A_\alpha{}^v. \tag{17}$$

As seen from (17), the factor A_α^v, which determines the admixture of hydrodynamic modes, is the same factor that determines the complicated structure in the broad part of the depolarized spectrum. The quantity A_α^v describes also collisions that connect the orientation along the angular momentum M with the orientation along the velocity v. The ratio R of the depth of the narrow dips to the height of the depolarized contour does not depend on the gas density and its value at the line center is of the order of

$$R(\omega=0) \propto \left| \frac{\Delta B_3}{B} \right|^2 \frac{\Delta\nu}{\gamma_3} \propto \frac{\Delta\nu}{\nu} \left| \frac{A_\alpha{}^v}{B_\alpha} \right|^2 \propto \left(\frac{\Delta\nu}{\nu} \right)^3, \tag{18}$$

and at the shifted frequencies

$$R(\omega=\pm\omega_{\mathrm{MB}}) \sim \left| \frac{\Delta B_1}{B} \right|^2 \frac{\Delta\nu}{\gamma_1} \sim \left(\frac{\Delta\nu}{\nu} \right)^2 \left| \frac{A_\alpha{}^v}{B_\alpha} \right|^2 \sim \left(\frac{\Delta\nu}{\nu} \right)^4.$$

Thus, the depth of the narrow structure of the depolarized scattering decreases very rapidly with decreasing parameter $\Delta\nu/\nu$. We note that the integrated intensity of the dips at the center of the line and at the shifted frequencies is of the same order. However, the widths of these dips differ by a factor $\Delta\nu/\nu$. Therefore the depth of the dip at the center of the line decreases at a lower rate than the depth of the dips at the acoustic frequencies with decreasing parameter $\Delta\nu/\nu$. In the estimate of the depth of the dips we used the fact that the width of the acoustic components is determined by the quantity $\gamma_1 \sim (qv_0)^2/\Delta\nu$, whereas for the shear mode $\gamma_3 \sim (qv_0)^2/\nu$. We shall show this result by using perturbation theory in $\Delta\hat{K}/\hat{K}_0$. For the widths of the narrow components we obtain the following equations:

$$\gamma_1 = \sum_{\alpha>5} \frac{|\langle \chi_1 | \mathbf{qv} | \chi_\alpha{}^v \rangle|^2}{\nu_\alpha{}^v (L=1,2)} + \frac{|\langle \chi_1 | \mathbf{qv} | \chi_6 \rangle|^2}{\Delta\nu_6 (L=0)} + \sum_{\alpha>5} \frac{|\langle \chi_1 | \mathbf{qv} | \Delta\chi{}^M \rangle|^2}{\Delta\nu_\alpha{}^M (L=0,2)}; \tag{19a}$$

$$\gamma_3 = \sum_{\alpha>5} \frac{|\langle \chi_3 | \mathbf{qv} | \chi_\alpha{}^v \rangle|^2}{\nu_\alpha{}^v (L=2)} + \sum_{\alpha>5} \frac{|\langle \chi_3 | \mathbf{qv} | \Delta\chi_\alpha{}^M \rangle|^2}{\Delta\nu_\alpha{}^M (L=2)}; \tag{19b}$$

$$\gamma_5 = \sum_{\alpha>5} \frac{|\langle \chi_5 | \mathbf{qv} | \chi_\alpha{}^v \rangle|^2}{\nu_\alpha{}^v (L=1)}. \tag{19c}$$

Here $\Delta\chi_\alpha^M$ is the correction of first order in the operator $\Delta\hat{K}$ to the function χ_α^M. The summation over α in Eqs. (19) is over all the indicated functions, with exception of the hydrodynamic $\chi_1, \dots, \chi_5$, and χ_6. The function χ_6 is equal to

$$\chi_6 = \frac{\Delta E_{\mathrm{kin}}}{\Delta E} \frac{E_{\mathrm{rot}} - \bar{E}_{\mathrm{rot}}}{\Delta E_{\mathrm{rot}}} - \frac{\Delta E_{\mathrm{rot}}}{\Delta E} \frac{E_{\mathrm{kin}} - \bar{E}_{\mathrm{kin}}}{\Delta E_{\mathrm{kin}}} \tag{20}$$

and is the result of a linear combination of two eigenfunctions of the operator $\hat{K}_0$ (translational energy E_{kin} and rotational energy E_{rot}), a combination orthogonal to the five hydrodynamic functions. The corrections $\Delta\nu_\alpha^v$ and $\Delta\chi_\alpha^v$ are equal to zero in first order in $\Delta\hat{K}$, inasmuch as in accordance with the subdivision in (14) all the matrix elements of $\Delta\hat{K}$ are zero in v-space. The function χ_6 appears when the operator $\Delta\hat{K}$ is diagonalized in the space of the zero eigenfunctions of the operator $\hat{K}_0$. It must be treated separately in equation (19a), because the function χ_6, just as $\chi_1, \dots, \chi_5$ cannot be factorized in terms of the variables v and M, and it does not belong to any of the three classes χ_α^v, χ_α^M, and χ_α^{Mv}. The second term in (19a) which is connected with χ_6, makes the principal contribution to the width of the acoustic components, since $1/\Delta\nu_6 \gg 1/\nu_\alpha^v$. This part of the width is connected with the second (or bulk) viscosity in the medium. The first term in the expression (19) takes into account only translational degrees of freedom (the corresponding collision frequency ν_α^v is simply the gaskinetic collision frequency) while the second and third in (19a) and the second in (19b) take into account the influence of the rotational degrees of freedom. In the indicated approximation, the ratio of these terms to the first term is of the order of $\Delta\nu/\nu$. Using the explicit expressions for χ_i in terms of $_i$, we can show that, accurate to small terms of order $\Delta\nu/\nu$, the following relation is satisfied for the widths of the narrow components,

$$\gamma_1 = \frac{|\langle \chi_1 | \mathbf{qv} | \chi_6 \rangle|^2}{\Delta\nu_6 (L=0)} + \frac{2}{3}\gamma_3 + \frac{1}{2c_v}\gamma_5, \tag{21}$$

which corresponds to the usual expression for the sound absorption coefficient γ in terms of the values of the first and second viscosities η and ζ, and of the proportionality coefficient $\varkappa$ (Ref. 20)

$$\gamma = \frac{q^2}{2\rho} \left[\frac{4}{3}\eta + \zeta + \varkappa \left(\frac{1}{c_v} - \frac{1}{c_p} \right) \right],$$

$$\eta = \frac{\rho}{q^2}\gamma_3, \qquad \zeta = \frac{\rho}{q^2} \frac{|\langle \chi_1 | \mathbf{qv} | \chi_6 \rangle|^2}{[\Delta\nu_6 (L=0)]}, \qquad \varkappa = \frac{\rho}{q^2} c_p \gamma_5, \tag{21a}$$

ρ is the density of the gas or the liquid.

Thus, formulas (19)–(21) generalize the one-to-one correspondences between the kinetic and hydrodynamic modes, first obtained in Refs. 14 and 15 for monatomic gases, to include the case of diatomic molecules with allowance for the rotational degrees of freedom.

5. DISCUSSION

We determine first the gas-density limit of applicability of the employed approach. The main restriction on the gas density is connected with the assumption of binary collisions or of the impact approximattion in the description of the collisions, according to which $\tau_c \ll \tau = 1/\nu$, where τ_c is the collision time, τ is the time between the collisions, and ν is the frequency of the gaskinetic collisions. The same condition can be written in the form $r_c^3 N \ll 1$, where r_c is the effective gas-molecule interaction radius and N is the gas density. In ordinary gases r_c is of the order of $\sim 10^{-7}$ cm, leading to the following known restriction imposed by the impact approximation on the gas density, namely $N \ll 10^{21}\ \mathrm{cm}^{-3}$ (this corresponds to a gas pressure < 30 atm).[21]

The second necessary condition is that the gas-molecule rotation be free, $\Omega = M/I \gg \nu$, where Ω is the angular velocity of the molecule rotation, and I is the moment of inertia of the molecule. In the classical description of rotation this condition reduces essentially to the preceding one, since $\Omega \sim \bar{v}/d \gtrsim 1/\tau_c$, where d is the molecule diameter and $\bar{v}$ is the average linear velocity.

The lower bound on the gas density is determined by the condition $\nu \gg qv_0$, which leads, for visible light ($q \approx 10^5\ \mathrm{cm}^{-1}$) and for typical values of the mean thermal velocities $v_0 \approx 5\times 10^4$ cm/sec, to the following restriction on the gas density: $\nu \gg 5\times 10^9\ \mathrm{sec}^{-1}$, corresponding to the frequency of the gas kinetic collisions at a gas pressure ~ 1 atm.

Thus, the gas-pressure range for which the foregoing analysis is valid is $1\ \mathrm{atm} < P < 30$ atm.

So far we have considered only the unshifted component of the Rayleigh scattering of light. It is known that acjacent to the Rayleigh spectrum is a rotational Raman spectrum. Two different cases are then possible. For sufficiently light diatomic molecules these two spectra do not overlap in practice. Actually, the distance from the unshifted frequency $\omega = 0$ to the component, closest to the center, of the rotational Raman scattering of a diatomic molecule is known[22] to be $6\,B$. The value of B for light molecules is $B(\mathrm{N}_2) = 2\mathrm{cm}^{-1}, B(\mathrm{O}_2) = 1.5\mathrm{cm}^{-1}$, and $B(\mathrm{HI}) = 6.5\mathrm{cm} - {}^{1}$ (Ref. 22), from which it is seen that $6\,B \gtrsim 10\ \mathrm{cm}^{-1}$. The width of the depolarized Rayleigh-scattering line wing is determined by the quantity $\Delta\nu$ and constitutes the frequency of the collisions in which reorientation of the molecule angular momentum $\mathbf{M}$ takes place. For light diatomic molecules $\Delta\nu$ fluctuates in the range $\Delta\nu \sim (1\text{–}0.1)\nu$ (Refs. 17 and 18). Therefore $\Delta\nu$ remains less than $6\,B \gtrsim 10\ \mathrm{cm}^{-1}$ even for the maximum permissible gas pressure $P = 30$ atm, since $\Delta\nu_{\max} \sim \nu(P = 30\ \mathrm{atm}) \sim 3\ \mathrm{cm}^{-1}$, i.e., $\Delta\nu_{\max} < 6\,B$.

For heavy molecules (Cl_2, Br_2, I_2, and others) the constant $B \sim 0.01\text{–}0.1$ cm and $\Delta\nu \gg B$, the rotational Raman spectrum comprises two broad bands that have maxima at frequencies $\omega = \pm 2\bar{\Omega}$, where $\bar{\Omega} = (2P/I)^{1/2} = 2(BT)^{1/2}$, and the width is determined by the equilibrium distribution of the molecules over the rotational levels, i.e., by the value of $\bar{\Omega}$.

Thus, in this case the entire depolarized spectrum consists of a relatively narrow pure Rayleigh component of width $\Delta\nu$ and with wide wings having a width of the order of $\bar{\Omega} \gg \Delta\nu$. It is interesting that the width $\Delta\nu$ of the Rayleigh component increases linearly with increasing gas pressure, while the width $\bar{\Omega}$ of the wing does not depend at all on the gas pressure so long as $\bar{\Omega}$ remains larger than $\Delta\nu$, i.e., $\bar{\Omega} > \Delta\nu$. In the pressure region in which the condition $\bar{\Omega} < \Delta\nu$ is satisfied, the width of the spectrum of the rotational Raman scattering begins to narrow down with increasing pressure and is determined by the quantity $\bar{\Omega}\,(\bar{\Omega} < \Delta\nu)$ [in complete analogy with the narrowing of the Doppler contour $qv_0\,(qv_0/\nu)$ under conditions when $\nu > qv_0$, where $v_0 = (T/m)^{1/2}$]. In this pressure region the molecule rotation ceases to be free and, as shown above, the Boltzmann kinetic equation is no longer valid. The described situation for heavy molecules, when two characteristic widths are present in the wing of the linearized scattering spectrum ($\Delta\nu$ and $\bar{\Omega}$, with $\bar{\Omega} > \Delta\nu$), one of which, $\Delta\nu$, in inversely proportional to the gas viscosity, $\Delta\nu \sim T/\eta$ (and is therefore strongly dependent on the gas temperature), while the other, $\bar{\Omega}$, does not depend on the viscosity at all and is quite similar to the experimentally observed picture of the wing of the depolarized light scattering in liquids (see, e.g., the monograph[23]). It is possible that the structure of the depolarized scattering of liquids in liquids is qualitatively similar to that described above for a dense gas made up of heavy molecules, for which the parameter $\bar{\Omega}$ has the meaning of slowed-down rotation frequency, i.e., $\sim\bar{\Omega}\,(\bar{\Omega}/\Delta\nu)$.

Before we proceed to discuss the results, we wish to point out the convenience of the method used in the present paper to solve the kinetic equation in the basis of the eigenfunctions of the collision operator $\hat{K}$. It was found that in this basis the Rayleigh-scattering spectrum, without allowance for the dependence on $\mathbf{q}$, consists of two terms, scalar and depolarized scattering, each of which is described by its own set of eigenfunctions of the operator $\hat{K}$, and the two sets are connected with each other with the aid of the operator $\mathbf{q}\cdot\mathbf{v}$. As a result of this connection, a fine structure is produced in the depolarized scattering. This connection is of the same character as the one considered in Refs. 24 and 25, and just as in these references it has a purely spectral character and therefore does not manifest itself in the integrated intensities of the scalar and depolarized (symmetrical, with zero trace) types of light scattering.

In the "scalar" spectrum, the effect of a spectral mixing of the functions that describe different types of scattering leads to the appearance of an asymmetrical increment to the usual Lorentz contour of the Mandel'shtam-Brillouin components. The ensuing shift of the maximum of the Mandel'shtam-Brillouin components is equal to $qv_0\,(qv_0/\nu)^2$ [see Eq. (10)].

The fine structure in the depolarized scattering spectrum of a gas [see (11)–(13)] constitutes one dip at the center $\omega = 0$ of the spectrum $I_{xz} = I_{yz}\ (I_{VH} = I_{HV})$ and two dips at the Mandel'shtam-Brillouin frequencies $\pm\,\omega_{\mathrm{MB}}$ in the spectrum $I_{yx}\ (I_{HH})$. This picture agrees with the experimentally observed fine structure in depolarized light scattering in low-viscosity liquids.[2,3] To explain this structure in phenomenological scattering theories it is necessary to take into account the connection between the rotary motion of the liquid molecules and the longitudinal deformations [the fine structure in the $I_{yx}\ (I_{HH})$ spectrum] and with the transverse deformations [in the $I_{yz}\ (I_{HV})$ spectrum]. Such a connection would take into account in the Leontovich theory,[4] which predicted a fine structure in the depolarized spectrum of scattering of liquids, but could not explain the experimental material on the temperature dependence of the fine structure (see the bibliography in Ref. 12). For a quantitative explanation of the fine structure in the Rayleigh line wing, with allowance for the temperature dependences, it is necessary to introduce at least two anisotropy-relaxation times, as was done in the later papers by Rytov,[5] Romanov and Solov'ev,[6] and others. The discussed fine structure in the spectrum of the scattering in the gas is connected with the interaction of the rotational and translational degrees of freedom of the molecules and it is this which leads to the appearance of interference terms in both the scalar spectrum [see Eq. (10)] and in the depolarized one [see (11)]. Naturally, this effect is in no way connected with other properties of the medium, inasmuch as in a gas there is no slow relaxation of the transverse (shear) deformations at any frequency.

In the present paper, the parameters of the fine structure in a gas are expressed in terms of the eigenvalues of the collision operator $\hat{K}$ [see (17)]. It has turned out that the depth of the narrow dips depends very strongly on the ratio of the parameters $\Delta\nu/\nu$, i.e., on the ratio of the collision frequencies $\Delta\nu$, which are connected with the energy exchange between the rotational and translational degrees of freedom, and the frequencies ν of the gas kinetic collisions. The width is proportional to $(\Delta\nu/\nu)^3$ for the central component and to $(\Delta\nu/\nu)^4$ for the Mandel'shtam-Brillouin components. This cause of this difference is that the width of the acoustic components is determined by the quantity $\gamma_1 \sim (qv_0)^2/\Delta\nu$, whereas the width of the central component is given by $\gamma_3 \sim (qv_0)^2/\nu$. For an experimental observation of the discussed fine structure in the depolarized scattering spectrum it is therefore preferable to use molecules whose parameter $\Delta\nu/\nu$ is close to unity, for example, the linear molecules N_2O and CO_2 for which $\Delta\nu/\nu = 0.8$ (Ref. 17).

Since our analysis had led practically to a single characteristic width in a broad part of the spectrum of the unshifted depolarized scattering, it is of interest to compare, on the one hand, expression (17) for the intensity of the fine structure of depolarized scattering in I_{yx} polarization at the frequencies $\omega = \pm\omega_{MB}$, and on the other the corresponding quantity obtained by Leontovich,[4] who used one relaxing tensor parameter. This comparison yields the following expression for the Maxwell constant M (the birefringence constant in a stream) in a dense gas

$$|\Delta B_1|^2 \Big/ \sum_\alpha |B_\alpha|^2 = M^2 q^2 v_0^2 \tag{22}$$

We recall that

$$\Delta B_1 = \sum_\alpha \frac{\langle\chi_2|\mathbf{qv}|\chi_\alpha^v\rangle}{\nu_\alpha^v(L=2)} \sum_{\alpha'} \frac{B_{\alpha'}\langle\chi_\alpha^M|\hat{K}|\chi_\alpha^v\rangle}{\nu_\alpha^v(L=2)},$$

and $\Sigma_\alpha |B_\alpha|^2$ is the integrated intensity of the broad contour of the depolarized scattering.

It can be seen from the obtained equations that the Maxwell constant is of the order of $M \sim \nu^{-2}\Delta\nu$. The microscopic meaning of the constant M, as shown by Eq. (22), is the following. In order for the hydrodynamic modes (in this case we are dealing with acoustic modes described by the functions χ_1 and χ_2) to appear in the depolarized spectrum we need, first an interaction of the hydrodynamic modes with non-hydrodynamic ones, effected by the operator $\mathbf{q}\cdot\mathbf{v}$ and corresponding to allowance for effects of spatial dispersion, and second, transfer of the orientational motion in the space of the velocities $\mathbf{v}$ to the space of the angular momentum $\mathbf{M}$ via the collision operator $\hat{K}$.

In conclusion, it is of interest to analyze the results of the microscopic description of the spectrum in a dense gas, obtained in the present paper, from the viewpoint of the general properties of the scattering tensor with allowance for the spatial dispersion of the medium. In our notation the scattering tensor can be taken to be the fourth-ranked tensor $C_{\alpha\beta\gamma\delta}(\omega,\mathbf{q})$, the contraction of which with the unit vectors of the incident and scattered waves in Eq. (1) yields the scattering spectrum.

It is known that in the case of an isotropic medium[11,26] the spectral dependence of this tensor is given by five independent functions $\sigma_1,\ldots\sigma_5(\omega,q^2)$, in terms of which the components I_{VV}, I_{VH}, and I_{HH} of the scattered light are expressed in the following fashion[11]:

$$\begin{gathered} I_{VV}(\omega,\ q^2) = \sigma_1 + {}^2/_3\sigma_2 - {}^2/_3 q^2\sigma_3 + {}^1/_9 q^4\sigma_4, \\ I_{VH}(\omega,\ q^2) = I_{HV}(\omega,\ q^2) = {}^1/_2\sigma_2 + {}^1/_8 q^2\sigma_5, \\ I_{HH}(\omega,\ q^2) = {}^1/_2\sigma_2 + {}^1/_4 q^4\sigma_4. \end{gathered} \tag{23}$$

The integrals of the functions $\sigma_{3,4,5}$ with respect to the frequencies are equal to zero, while those of σ_1 and σ_2 are of equal order of magnitude. When the condition $\nu \gtrsim \Delta\nu \gg qv_0$ is satisified, the system (23) of three equations is transformed into a system of six equations (in practice, of five since two of them are identical) for the two spectral intervals $\omega \lesssim qv_0$ and $\omega \gg qv_0$. This circumstance, together with the relations for the frequency-integrated quantities $\sigma_1,\ldots,\sigma_5$ make it possible, by comparing (23) with (10) and (11), to determine in the indicated approximation all five scalar functions $\sigma_1,\ldots\sigma_5$.

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[1)] When account is taken of the terms that depend on q, the first term in (6) is no longer pure scalar, since it contains terms proportional to $\alpha_0\alpha_{ik}^*$.

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