Fine structure of the Rayleigh spectrum of the scattering of light in molecular gases

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A review is given of the current data on the fine structure of the Rayleigh scattering spectra of molecular gases and liquids. A microscopic description of the scattering spectrum of a molecular gas is provided by a method based on the Boltzmann transport equation. It is shown that the fine structure of the spectrum is associated with the interaction of rotational and translational degrees of freedom in collisions. The same approach is used in a study of changes in the spectrum of a gas due to the presence of a magnetic field and also due to deviation of the properties from those of an ideal gas.

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1. INTRODUCTION

Investigations of the Rayleigh scattering of light in gases and liquids, whether experimental or theoretical, have been concentrated in the last decade mainly on the fine effects in the scattering spectrum. This trend was started by Starunov, Tiganov, and Fabelinskiï¹ who were the first to observe experimentally the fine structure of the depolarized component of the Rayleigh spectrum of light scattering in liquid nitrobenzene and quinoline. Soon after Stegeman and Stoicheff² also discovered a fine structure in the depolarized spectrum of the scattering by several liquids. These investigations have been continued by many using the latest technology, both lasers and the technique of high spectral resolution.³⁻¹⁸ At present the experimental picture of detailed investigations of the structure of the Rayleigh scattering spectra of liquids looks as follows.

In the depolarized scattering spectra of some liquids consisting of anisotropic molecules there is a small dip at the center of the scattering spectrum which is observed in a certain range of temperatures against the background of a wider Lorentz profile. This applies to the intensity component J_{VH} of the depolarized Rayleigh scattering spectrum, where the subscripts V and H denote (as usual) the directions of the polarization of the incident (V means perpendicular or vertical) and scattered (H means parallel or horizontal) light relative to the scattering plane which is formed by the wave vectors of the incident \mathbf{k}_1 and scattered \mathbf{k}_2 waves. In the case of the $J_{\rm HH}$ component of the depolarized scattered light the unit vectors representing the polarizations of the incident and scattered waves lie in the scattering plane. Typical patterns of the $J_{\rm VH}$ component of the scattering spectrum of



FIG. 1. Scattering $(I_{\rm VH})$ spectrum of triphenyl phosphate recorded at T = 70.2 °C at the scattering angle of $\theta = 90^{\circ}$ ($\lambda = 5145$ Å, $R = h_1/h_2 \approx 0.47$).



FIG. 2. Scattering ($I_{\rm VH}$) spectrum of triphenyl phosphate recorded at T = 41.6 °C for $\theta = 90^{\circ}$.

liquid triphenyl phosphate recorded for different temperatures and for different scattering angles⁸ are shown in Figs. 1-3. For the sake of clarity, the dashed curve in Fig. 1 shows the complete Lorentzian profile extrapolated to the line center from the wide part of the profile in the wings of the line. The dashed curve represents the spectrum which would have been obtained in the absence of a fine structure at the line center ($\omega = 0$). It is clear from Figs. 1–3 that the fine structure disappears as a result of cooling, i.e., on increase in the viscosity (Figs. 1 and 2), or at a fixed temperature because of an increase in the scattering angle θ (see Fig. 3) or of the quantity $q^2 = (4\pi n/\lambda_0)\sin(\theta/2)$, where *n* is the refractive index and λ_0 is the wavelength of the incident light. More precisely, experimental investigations¹⁻¹⁸ have shown that the fine structure in the $J_{\rm VH}$ scattering spectrum manifested by a small dip at the center of a line is observed at relatively low values of the viscosity η ($\eta \sim 10^{-2}$ P), when the following condition is obeyed:

$$\frac{q^2\eta}{\rho\Gamma_0}\ll 1,$$

where η is the shear viscosity, ρ is the mass density (g/cm³), and Γ_0 is the width of the wide part of the spectrum of the depolarized light scattering.

Such a small dip has been observed so far in liquids with molecules with a great variety of shapes: short rods (for example, CS₂ and CO₂ molecules), long rods (MBBA), almost spherical molecules (TPP and pyridine), etc.¹⁷ It is interesting that the dip contrast R at the line center (i.e., the ratio $R = h_1/h_2$ in Fig. 1) is almost independent of the shape of the liquid molecule and is close to $R \approx 0.4$ for all the investigated molecules. Table I gives the values of the dip contrast



FIG. 3. Scattering $(I_{\rm VII})$ spectrum of triphenyl phosphate recorded at T = 25.4 °C for different angles θ ($\lambda = 6328$ Å).

R for various types of molecules. An increase in the viscosity of the liquid (i.e., cooling), when the parameter $q^2 \eta / \rho \Gamma_0$ becomes of the order of unity or greater, destroys the dip in the scattering spectrum. A further increase in the viscosity of the liquid right up to $\eta \sim 10^6$ P, close to the glass-forming range, gives rise in some liquids to two satellites of very low intensity in the $J_{\rm VH}$ scattering spectrum and these satellites are associated with traveling shear waves.¹⁹⁻²² However, we shall not consider highly viscous liquids because the microscopic theory of light scattering considered below applies to dense gases and can provide only a qualitative description of the spectrum in the case of low-viscosity liquids, but is in no way applicable to highly viscous liquids.

The pattern of the $J_{\rm HH}$ component of the Rayleigh scattering spectrum of liquids has been studied much less and is less clear. The most usual feature is the appearance, against the background of a wide profile of the same kind as in the case of the $J_{\rm VH}$ spectrum, of very weak peaks at the Brillouin doublet frequencies $\pm \Omega_{\rm B}$ (Refs. 2, 5, and 8–10). In some cases a fine structure in the form of asymmetric profiles is observed at these frequencies.²³

We have considered so far the structure of a depolarized scattering spectrum of a liquid because the majority of the available experimental investigations of the spectral composition of the scattered light has been carried out on liquids. Experimental studies of the depolarized Rayleigh scattering of light in gases have just begun.^{24–31} In these investigations attention has been concentrated on the profile of the depolarized component of the Rayleigh scattering of light,

TABLE I. Experimental values of R for liquids.

Molecule	R	Ref.	Molecule	R	Ref.
anisaldehyde tolane acetophenone pyridine triphenyl phosphate ethyl benzoate CS ₂ MBBA (isotropic) benzonitrile	$\begin{array}{c} 0,43\pm 0,02\\ 0,39\\ 0,43\pm 0,04\\ 0,35\pm 0,08\\ 0,45\pm 0,05\\ 0,44\pm 0,05\\ 0,35\pm 0,06\\ 0,36\pm 0,02\\ 0,37\pm 0,02 \end{array}$	4 5 6 7,8 9 10 11 12 13	n-hexadecane n-docosane salol pyridine iodopropyne cyanopropyne F ₂ CO ₂	$\begin{array}{c} 0,33\pm0,02\\ 0,38\pm0,02\\ 0,28\pm0,04\\ 0,70\pm0,05\\ 0,20\pm0,05\\ 0,40\pm0,10\\ 0,46\ at\ 70\ K\\ 0,22\ at\ 120\ K\\ 0,20\\ \end{array}$	14 14 15 10 16 16 16 17 17

which in most cases does not reduce to a simple Lorentzian profile. In particular, Keijser *et al.*^{25–27} have shown that for simple molecular gases of N₂, CO₂, HD (but excluding H₂ and D₂) the depolarized scattering line profile differs considerably from the Lorentzian form. The main reason for this difference is the contribution made to the scattering by several *j*-*j* transitions (*j* is the rotational quantum number) each of which has its own damping constant. Consequently, the overall profile represents a superposition of several Lorentzians of different width.³² It should be pointed out that none of the published investigations has revealed a fine structure in the form of a dip at the center of the depolarized scattering line of gases.

A second series of experimental investigations^{29,32–39} has been concerned with the detailed form of a polarized triplet observed at different gas densities, beginning from the lowest pressures (kinetic regime) and ending at high pressures, when the hydrodynamic approximation is valid. No anomalies have been found in the profile of a polarized triplet of the investigated almost spherical symmetric molecules H_2 , CH_4 , SF_6 , He, and Fe.

Very few experimental investigations^{26–32} have been made on asymmetric molecules (for example, CS_2 , CO_2 , N_2 , and others) in which one would expect new effects in the scattering spectrum. However, we shall report later that very careful investigations of the spectral line profile are needed to observe these effects.

The first theoretical prediction of a fine structure in the depolarized scattering spectrum of a liquid was made by Leontovich.40 Leontovich showed that the fine structure in the $J_{\rm VH}$ scattering spectrum appears because of an allowance for the relationship between the strain tensor and low-frequency shear waves. The phenomenological approach to the description of the fine structure was developed fully by Rytov⁴¹ and by Romanov and Solov'ev.⁴² Rytov's theory agrees better with the experimental results than Leontovich's theory because of introduction of a larger number (in most cases two) of tensor relaxation parameters. The theories of Leontovich, of Rytov, and of Romanov and Solov'ev are based on the Maxwellian representation of the viscoelastic behavior of liquids which at high frequencies can be regarded as amorphous solids. Other types of viscoelastic properties of media are considered in Refs. 19-21 and 43.

Numerous phenomenological theories of the scattering of light^{8,17,44-56} reduce to different selections of the relaxation parameters and their relationship to hydrodynamic variables. These parameters are most frequently the molecular orientation tensor and the stress tensor, both related to shear waves.^{45,46} Theoretical investigations^{8,47,48,52,53,56} based on modern statistical physics methods^{57,58} are recently attracting the greatest interest. Application of these methods to the theory of light scattering reduces to microscopic justification of the equations of phenomenological theories. For example, the theory of Pecora and Anderson⁴⁷ based on the Mori method^{44,57,58} is a microscopic analog of the hydrodynamic theory of Volterra,⁴⁵ and the theory of Ailwadi⁴⁸ is a microscopic analog of the theory of Rytov.⁴¹ It seems to us that the most interesting work from the point of view of transition to the kinetic description of the Rayleigh scattering of light is that of Tsay and Kivelson.⁸ The Mori method is used also to obtain the equations of motion in which the slow variables are the molecular orientation tensor D_{ik} and the momentum vector **p**.

For this selection of the variables, which is essentially phenomenological, the parameters of the spectrum including the dip contrast R are expressed in terms of the Liouville operator projected on the subspace of selected variables. However, these expressions are fairly complex and in the case of specific situations there is a need for further simplification. The most important theoretical conclusion is a direct relationship between the depth of the dip and the contribution of the molecular rotation to the shear viscosity of the medium.

Further development of the work of Tsay and Kivelson⁸ based on the use not of the exact Liouville equation, but of a truncated chain of equations for the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) distribution was put forward recently by Cole, Hoffman, and Evans.⁵⁶ They used the same set of variables $\{D_{ik}, \mathbf{p}\}$ as in Ref. 8 and applied the Enskog transport equation for hard ellipsoids to obtain numerical values of the depth of the dip R for a number of molecules. Their calculations showed that: 1) the depth of the dip increases on increase in the gas density and reaches saturation at densities close to those in liquids; 2) the depth of the dip depends weakly on the shape of the molecules. The latter conclusion is supported by the experimental data on liquids¹⁷ (Table I).

It should be pointed out that in all the theoretical papers on the scattering of light, whether phenomenological or statistical, the selection of the relaxation parameters responsible for the scattering of light is somewhat arbitrary, i.e., a phenomenological element remains in the description of the scattering spectrum. On the other hand, the parameters of a medium in the form of a molecular gas are indeed determined by the parameters of the individual molecules such as the polarizability α_{ik} , linear momentum **p**, angular momentum M and others, and the kinetics of the molecular gas is described accurately by the transport equation for the oneparticle distribution function f. Therefore, in developing a theory of the scattering of light in gases we can provide a rigorous microscopic justification for the selection of the "slow variables" and thus avoid the phenomenological indeterminacy of the description.

A microscopic theory of the broadening of spectral lines due to the influence of a buffer gas on one- or two-photon transitions in a molecular gas was developed by Gordon.^{59,60} The transport equation method was used by Hess^{61,62} to describe the spectrum of depolarized Rayleigh scattering in a gas. Hess used a transport equation of the Boltzmann type to describe the profile of the wide depolarized component of the spectrum and related the nature of the spectrum to the gaskinetic characteristics of the medium. A fine structure of the depolarized light spectrum is not predicted by this method because of the limited nature of the distribution function *f*. We shall concentrate our attention on the fine structure of the scattering spectrum. The present authors⁶³ used a transport equation to calculate the spectrum of the Rayleigh scattering of light in a dense diatomic gas. The spectrum had an additional fine structure in the polarized and depolarized components. In particular, the fine structure of the J_{VH} spectrum corresponded to the pattern observed experimentally for low-viscosity liquids and its appearance was due to the contribution of the rotational degrees of freedom to the transport coefficients. All the parameters of the scattering spectrum of a gas, including the transport coefficients, can be expressed in terms of the eigenfunctions and eigenvalues of the Boltzmann collision integral.

The present review will be based on the authors' own paper⁶³ and its development in later papers^{64,65} dealing with the influence of a magnetic field on the Rayleigh scattering spectrum and with changes in the spectrum because the gas is nonideal.

2. KINETIC METHOD FOR THE DESCRIPTION OF THE SPECTRUM OF LIGHT SCATTERING IN A GAS

The usual macroscopic theory of the scattering of light in gases or liquids is based on a calculation of the correlation function of fluctuations of the permittivity of a medium⁶⁶:

$$h_{iklm} = \langle \delta \varepsilon_{ik} (t_1, \mathbf{r}_1) \, \delta \varepsilon_{lm} (t_2, \mathbf{r}_2) \, \rangle, \qquad (1)$$

where $\delta \varepsilon_{ik}(t, \mathbf{r})$ is the deviation of the permittivity of the medium from its equilibrium value ε_{ik} ; the angular brackets $\langle ... \rangle$ denote averaging of fluctuations over a statistical ensemble of averaging over the initial time t_2 for a given value of $t = t_1 - t_2$. In view of the spatial homogeneity of the medium the correlation function h_{iklm} depends only on the difference $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$.

In the case of specific calculations the deviation $\delta \varepsilon_{ik}(t,\mathbf{r})$ is expressed in terms of fluctuations of thermodynamic parameters [for example, the pressure $\delta P(t,\mathbf{r})$ and the entropy $\delta S(t,\mathbf{r})$] and in terms of fluctuations of phenomenologically introduced relaxation parameters $\delta Q_{ik}(t,\mathbf{r})$ (both scalar and tensor) responsible for the scattering of light (see, for example, Ref. 41). The next stage is the solution of the system of linearized hydrodynamic equations (or equations of the theory of elasticity) for fluctuations of thermodynamic parameters and of coupled relaxation equations for fluctuations $\delta Q_{ik}(t,\mathbf{r})$. These equations are supplemented by the relevant initial conditions $(t_2 - t_1 = 0)$, i.e., by the values of simultaneous correlation functions of the selected parameters.

The nature of the scattering spectrum is described by the Fourier transform of the correlation function h_{iklm} :

$$J_{\omega q} \propto 2 \operatorname{Re} e_{1l} e_{2k} e_{1l} e_{2m} \int d\mathbf{r} \int_{0}^{\infty} dt \, h_{iklm} \exp\left(-i\omega t + i\mathbf{qr}\right), (2)$$

where \mathbf{e}_1 and \mathbf{e}_2 are unit vectors of the polarizations of the incident and scattered waves, respectively; $\mathbf{q} = \mathbf{k}_2 - \mathbf{k}_1$ and $\omega = \omega_2 - \omega_1$ are, respectively, the difference between the wave vectors and between frequencies of the scattered and incident waves. The repeated indices in Eq. (2) represent summation.

In this approach the fluctuations of the thermodynamic quantities and scalar relaxation parameters lead to the appearance of a narrow polarized triplet, whereas the fluctuations of the tensor parameters are responsible for the wide depolarized component of the scattering spectrum. The fine structure of the depolarized scattering spectrum appears because of the coupling of the fluctuations of the tensor parameters $\delta Q_{ik}(t,\mathbf{r})$ to the fluctuations of the components of the displacement δu_i or of the velocity $\delta v_i(t,\mathbf{r}) = \delta U_i(t,\mathbf{r})$ in the equations of elasticity or hydrodynamics.^{8,41–47}

The transition to the kinetic description of the scattering of light in a gas is made by replacing the correlation function of fluctuations of the permittivity with the correlation functions of the distribution functions of the gas. The equations for these correlation functions are obtained from the transport equations applicable to the relevant distribution functions.^{67,68} In the simplest case of an ideal gas, the state of which is described well by a single-particle distribution function *f*, the fluctuations of the permittivity reduce to fluctuations of the distribution function δf :

$$\delta \varepsilon_{ik} (t, \mathbf{r}) = 4\pi \int \boldsymbol{\alpha}_{ik} (Q) \, \delta f (t, \mathbf{r}, Q) \, \mathrm{d}Q, \qquad (3)$$

which is a consequence of the well-known relationship applicable to an ideal gas $\varepsilon - 1 = 4\pi N \alpha$ (Ref. 69); here, N (cm^{-3}) is the density of the spatial distribution of the number of particles. which by definition is $N(t,\mathbf{r}) = \int f(t,\mathbf{r},Q) dQ; \alpha_{ik}$ is the polarizability tensor of a single molecule; Q is the set of parameters representing the internal degrees of freedom of a molecule. In the case of a monatomic gas the parameters Q are the components of the velocity of a particle v_i , whereas in the case of polyatomic gases the set Q should include the rotational and vibrational degrees of freedom; $\delta f = f - f_0$ is the deviation of the distribution function from the equilibrium Boltzmann function f_0 .

It follows that the correlation function of the permittivity h_{iklm} reduces in the case of an ideal gas to the correlation function of a single-particle distribution function $\Phi(t,\mathbf{r},Q_1,Q_2)$:

$$\begin{aligned} h_{iklm} &= (4\pi)^2 \int \alpha_{ik} (Q_1) \ \alpha_{lm} (Q_2) \ \Phi (t, \mathbf{r}, Q_1, Q_2) \ dQ_1 dQ_2, \\ (4) \\ \Phi (t, \mathbf{r}, Q_1, Q_2) &= \langle \delta f (t, \mathbf{r}, Q_1) \ \delta f (0, 0, Q_2) \rangle. \end{aligned}$$

3. STRUCTURE OF THE SPECTRUM OF LIGHT SCATTERING IN AN IDEAL GAS

We shall consider an ideal gas consisting of diatomic molecules and allow for the rotational and translational degrees of freedom. We shall assume that the vibrational degrees of freedom are "frozen out," i.e., we shall consider those molecules for which the energy of the vibrational quantum satisfies $\hbar\omega_{vib} \gg T$, where T is the temperature of the gas in energy units. An allowance for vibrations in the kinetic method will be made later when considering the mechanisms of the dispersion of sound.

The rotation of molecules can be described classically, because for the majority of molecules (with the possible exception of hydrogen) the rotation is known to be classical so that $B \ll T$, where B is the rotational constant. In this case the distribution function depends on the following parameters: $f = f(t, \mathbf{r}, \mathbf{n}, Q)$, where **n** is a unit vector directed along the axis of the molecule; the quantity $Q = (\mathbf{p}, \mathbf{M})$ includes the linear momentum **p** and the angular momentum **M** of a molecule, which are canonical conjugates of the variables **r** and **n**, respectively.

It will be now convenient to adopt a new unknown function χ :

$$\chi (t, \mathbf{r}, \mathbf{n}_{1}, Q_{1}) = f_{0}^{-1} (Q_{1}) \int \Phi (t, \mathbf{r}, \mathbf{n}_{1}, \mathbf{n}_{2}, Q_{1}, Q_{2})$$
$$\times e_{1i} \alpha_{ik} (\mathbf{n}_{2}, \mathbf{M}_{2}) e_{2k} d\varphi_{2} dQ_{2}.$$

Here, integration with respect to \mathbf{n}_2 for a fixed \mathbf{M}_2 reduces to integration with respect to the rotation angle φ_2 of the vector \mathbf{n}_2 in a rotation plane perpendicular to the vector \mathbf{M}_2 .

Using the smallness of the fluctuations of the distribution function f relative to the equilibrium value f_0 , we find that χ is described by the following linearized transport equation^{65,68}:

$$\frac{\partial \chi}{\partial t} + \mathbf{v}_1 \frac{\partial \chi}{\partial \mathbf{r}} + [\Omega_1 \mathbf{n}_1] \frac{\partial \chi}{\partial \mathbf{n}_1} + \hat{I}_0 \chi = 0, \qquad (5)$$

where

$$\hat{I}_{0}\chi = -f_{0}^{-1}(Q_{1})\int\left\{-\frac{\partial U_{12}}{\partial \mathbf{r}}\cdot\frac{\partial}{\partial \mathbf{p}_{1}}+\left[\mathbf{n}_{1}\frac{\partial U_{12}}{\partial \mathbf{n}_{1}}\right]\frac{\partial}{\partial \mathbf{M}_{1}}\right\}$$

$$\times f_{0}(Q_{1})f_{0}(Q_{2})$$

$$\times e^{-U_{12}/T}\left[\chi\left(\mathbf{n}_{10},\ Q_{10}\right)+\chi\left(\mathbf{n}_{20},\ Q_{20}\right)\right]\mathrm{d}\mathbf{r}\,\mathrm{d}\varphi_{2},\,\mathrm{d}Q_{2},$$

subject to the initial condition

$$\chi (0, \mathbf{r}, \mathbf{n}_1, Q_1) = e_{1i} \alpha_{ik} (\mathbf{n}_1, \mathbf{M}_1) e_{2k} \delta (r).$$
(6)

The presence of the delta function in the simultaneous correlation function denotes the absence of spatial correlation between simultaneous fluctuations, which corresponds to the approximation of an ideal gas and is associated with the equilibrium nature of the state relative to which the fluctuations are measured.

The operator \hat{I}_0 is the linearized Boltzmann collision operator, which allows additionally for rotation of the vectors \mathbf{n}_1 and \mathbf{n}_2 in collisions (this is known as dephasing⁵⁹); $U_{12} = U_{12}(\mathbf{r}, \mathbf{n}_1, \mathbf{n}_2)$ is the electrostatic interaction potential of the gas molecules; the index "0" denotes the variables \mathbf{n}_{10} , Q_{10} , \mathbf{n}_{20} , and Q_{20} which would have been obtained at the moment t instead of \mathbf{n}_1 , Q_1 , \mathbf{n}_2 , and Q_2 if the particles had been moving freely without interacting with each other. Usually this transformation is described by introducing an operator \hat{S}_{12} (Ref. 68); $\Omega = \mathbf{M}/I$ is the rotation frequency of a molecule and I is its moment of inertia.

The polarizability tensor of a diatomic molecule α_{ik} (**n**,**M**) can be represented in the form

$$\alpha_{ik} (\mathbf{n}, \mathbf{M}) = \alpha_0 \delta_{ik} + \alpha_1 e_{ikj} \frac{M_j}{M_0} + \alpha_2 \left(n_i n_k - \frac{1}{3} \delta_{ik} \right), \quad (7)$$

where $M_0 = (TI)^{1/2}$ and e_{ikj} is an antisymmetric unit tensor.

In this expression the scalar (proportional to α_0) and symmetric (proportional to α_2) parts of the molecular polarizability are related to the geometric structure of the molecule itself, whereas the antisymmetric part (proportional to α_1) appears only for a rotating molecule and for ordinary molecules it is very small: $\alpha_1/\alpha_0 \sim 10^{-4}$ (Ref. 70).

In the Fourier representation Eq. (5), subject to the initial condition (6), has the form

$$i (\mathbf{q}\mathbf{v}_{1} - \boldsymbol{\omega}) \chi_{\boldsymbol{\omega}\boldsymbol{q}} (\mathbf{n}_{1}, Q_{1}) + [\Omega_{1}\mathbf{n}_{1}] \frac{\partial}{\partial \mathbf{n}_{1}} \chi_{\boldsymbol{\omega}\boldsymbol{q}} + \hat{I}_{0} \chi_{\boldsymbol{\omega}\boldsymbol{q}}$$
$$= B (\mathbf{n}_{1}, \mathbf{M}_{1}), \qquad (8)$$
where

nere

 $B(\mathbf{n}, \mathbf{M}) = e_{1i}\alpha_{ik}(\mathbf{n}, \mathbf{M}) e_{2k}.$

The form of the scattering spectrum $J_{\omega q}$ is expressed in terms of $\chi_{\omega q}$ as follows:

$$J_{\boldsymbol{\omega}\boldsymbol{q}} \propto \operatorname{Re} \int B(\mathbf{n}, \mathbf{M}) f_{\boldsymbol{0}}(Q) \chi_{\boldsymbol{\omega}\boldsymbol{q}}(\mathbf{n}, Q) \, \mathrm{d}\boldsymbol{\varphi} \, \mathrm{d}\boldsymbol{Q}. \tag{9}$$

The expressions (8) and (9) describe in classical language the complete scattering spectrum of light in a diatomic gas, including the unshifted Rayleigh component and two rotational Raman components shifted relative to $\omega = 0$ by $\pm 2\overline{\Omega} = \pm 2(T/I)^{1/2}$.

When the Rayleigh and the Raman components are spectrally separated, i.e., when the average rotational frequency of the $\overline{\Omega}$ molecules is higher than the gaskinetic collision frequency $\overline{\Omega} \gg v$ (free rotation condition), the solution of Eq. (8) should be sought in the form of an expansion in terms of eigenfunctions of the operator $[\Omega n]\partial/\partial n$ which are of the form $\Psi_k = \exp(ik\varphi)$, where k is an integer and φ is the angle of rotation of the vector **n** in the rotation plane. The corresponding eigenvalues are $ik\Omega$. In this basis the zeroth harmonic (k = 0) is separated spectrally from all the other harmonics and describes the Rayleigh scattering. The rotational Raman scattering is described by harmonics with $k = \pm 2$ and is manifested in the scattering spectrum because of the symmetric component $\alpha_2[(n_i n_k - (1/3)\delta_{ik}]]$ in the polarizability of a molecule given by Eq. (7). The spectrum of rotational Raman scattering represents two inhomogeneously broadened lines, the structure of which is similar to the structure of a Doppler-broadened line, and the frequency shift is associated with rotation and not with the velocity of a molecule. The width of these lines is equal to Ω as long as the condition $\overline{\Omega} \ge v$ is satisfied. When the density is increased further, so that $\overline{\Omega} \leq v$, the spectrum of the rotational Raman scattering becomes narrower in accordance with the mechanism analogous to the narrowing of Dopplerbroadened lines by collisions. However, we shall not consider these topics in the present paper.

3.1. Rayleigh scattering spectrum

We shall now consider the unshifted Rayleigh component in the spectrum. In this case the function $\chi_{\omega q}$ is independent of the vector \mathbf{n}_1 and Eq. (8) can be integrated with respect to the angle of rotation $d\varphi_1$. Then, the second term describing the shift of the scattering frequency of a molecule because of rotation disappears from the left-hand side of Eq. (8). The integral $\hat{I}_{0\gamma}$ [see Eq. (5)] reduces after integration with respect to $d\varphi_1$ by the familiar procedure⁶⁸ to an ordinary linearized Boltzmann collision integral:

$$\hat{I}_{0}\chi = \int dQ_{2} d^{2}\rho d\phi_{1} d\phi_{2} v_{rel} f_{0} (Q_{2}) \\ \times [\chi (Q_{1}) + \chi (Q_{2}) - \chi (Q_{10}) - \chi (Q_{20})], \quad (10)$$

where ρ is the impact parameter and $v_{rel} = |\mathbf{v}_2 - \mathbf{v}_1|$ is the relative velocity of the colliding particles.

Integration of the right-hand side of Eq. (8) gives

$$\int B(\mathbf{n}, \mathbf{M}) \,\mathrm{d}\boldsymbol{\varphi} = B_0 + B_2\left(\frac{\mathbf{M}}{M}\right), \qquad (11)$$

where

$$B_0 = \alpha_0 (\mathbf{e_1} \mathbf{e_2}), \quad B_2 = -\frac{1}{3} \alpha_2 \left\{ \frac{(\mathbf{e_1} \mathbf{M}) (\mathbf{e_2} \mathbf{M})}{M^2_{ij}} - \frac{1}{3} (\mathbf{e_1} \mathbf{e_2}) \right\}.$$

In the expression for the scattering spectrum (9) the process of integration with respect to $d\varphi_1$ reduces to integration of the quantity $B(\mathbf{n}, \mathbf{M})$ with respect to $d\varphi_1$.

Therefore, the transport equation and the expression for the unshifted Rayleigh scattering of light assume the following final form:

$$i \left(\mathbf{q} \mathbf{v}_1 - \boldsymbol{\omega} \right) \chi_{\boldsymbol{\omega} \boldsymbol{q}} + \hat{I}_0 \chi_{\boldsymbol{\omega} \boldsymbol{q}} = B_0 + B_2 \left(\frac{M_1}{M_1} \right), \tag{8'}$$

$$J_{\omega q} \propto \operatorname{Re} \int (B_0 + B_2) f_0 (Q_1) \chi_{\omega q} (Q_1) dQ_1.$$
 (9')

The nature of the Rayleigh spectrum or the solution of the system (8')-(9') depends strongly on the properties of the collision integral $\hat{I}_{0\gamma}$ [see Eq. (10)]. In Eq. (10) the collision integral is given in terms of the impact parameter ρ of collisions. The quantities Q_{10} and Q_{20} represent colliding particles before impact and Q_1 and Q_2 after impact.

The most convenient from the point of view of the physical interpretation is the expression for the Boltzmann collision integral in terms of the transition probability $w(Q_1,Q_2,Q'_1,Q'_2)$, where $Q'_1 = Q_{10}$ and $Q'_2 = Q_{20}$, which is equivalent to Eq. (10) (Ref. 68). In this form the collision integral becomes⁶⁸:

$$\mathbf{I}_{0}\chi(Q_{\mathbf{i}}) = \int dQ_{2} dQ_{\mathbf{i}}' dQ_{\mathbf{i}}' [\chi(Q_{\mathbf{i}}) + \chi(Q_{2}) - \chi(Q_{\mathbf{i}}) - \chi(Q_{\mathbf{i}})].$$
(10')

It should be noted that the collision integrals (10) and (10') differ in respect of the sign from the generally accepted expressions.⁶⁸ Selection of this sign shows that the operator \hat{I}_0 is positive definite and, consequently, all its eigenvalues are positive.

The symmetry properties of the operator \hat{I}_0 written in the form of Eq. (10') are governed by the symmetry properties of the function $w(Q_1,Q_2,Q_1',Q_2')$. It follows from the symmetry of the equations of mechanics on reversal of the sign of time that the function w has in its most general form the following property (see, for example, Ref. 68):

$$w(Q_{1}, Q_{2}, Q'_{1}, Q'_{2}) = w(Q'^{T}_{1}, Q'^{T}_{2}, Q^{T}_{1}, Q^{T}_{2}), \qquad (12)$$

where $Q^T = \hat{T}Q = (-\mathbf{v}, -\mathbf{M})$, and \hat{T} is the time-reversal operator. If the interaction between gas molecules is invariant under spatial inversion and does not contain terms of the rotational-orbital type, Eq. (12) reduces to the simplest variant of the principle of detailed balancing

$$w(Q_1, Q_2, Q'_1, Q'_2) = w(Q'_1, Q'_2, Q_1, Q^2).$$
(12')

This case corresponds to a gas free of stereoisomers, the molecules of which interact with one another in a purely electrostatic manner. An analysis of the Boltzmann transport equation for gases with rotational degrees of freedom was made by Kagan and Maksimov⁷¹ using the most general form of the principle of detailed balancing of Eq. (12). They found that in this case the collision operator may relate functions with different spatial and temporal parity, so that a number of interesting effects can be observed particularly in the case of stereoisometry. For example, the presence of a temperature gradient creates an average angular momentum, i.e., it causes the gas to rotate. For this reason a change in the transport coefficients on application of an external field may be in the form of a reduction or an increase, whereas Eq. (12')predicts only a reduction in the transport coefficients on application of the field.

The simplest case of the principle of detailed balancing (12') corresponds to the case when the collision operator is self-adjointi.e., $\int \varphi^*(Q) f_0(Q) \hat{I}_0 \psi(Q) dQ = \int \psi^*(Q) f_0(Q) I_0 \varphi(Q) dQ$ or $\langle \varphi | \hat{I}_0 | \psi \rangle = \langle \psi | \hat{I}_0 | \varphi \rangle$, where φ and ψ are arbitrary functions of Q.

In the case of this operator we can, as is known, construct an orthonormal basis of eigenfunctions and then seek a solution of Eq. (8') in this basis.

It is known (see, for example, Refs. 58, 59, and 68), that among the eigenfunctions of \hat{I}_0 there are five functions with zero eigenvalues which correspond to five laws of conservation of the following quantities in collisions: the number of particles, three components of the momentum mv_x , mv_y , and mv_z , and the energy \mathcal{E} , where \mathcal{E} is understood to be the sum of the rotational and translational energies.

We can easily show that the functions $\chi = 1$, $m\mathbf{v}$, \mathcal{E} cause the collision integral of Eq. (10') to vanish. In the case of a sufficiently dense gas, when the mean free path obeys $l \ll \lambda = 2\pi/q$, the principal term in Eq. (8') is the collisional term and it is then convenient to solve this equation using perturbation theory with a parameter $qv/v \sim l/\lambda \ll 1$. Then, in the first order of perturbation theory, out of five functions with zero eigenvalues we can derive such linear combinations in which the operator of free motion $i\mathbf{q}\cdot\mathbf{v}$ is diagonal. If the x axis in the selected coordinate system is directed along \mathbf{q} , the corresponding eigenfunctions and eigenvalues of the operator $i\mathbf{q}\cdot\mathbf{v} + \hat{I}_0$ can be written as follows^{57,58}:

$$\chi_{1} = \left(\frac{c_{v}}{2c_{p}}\right)^{1/2} \left[1 - \left(\frac{c_{p}}{c_{v}}\right)^{1/2} \frac{v_{x}}{v_{0}} + c_{v}^{-1/2} \frac{\mathscr{E} - \widetilde{\mathscr{E}}}{\Delta \mathscr{E}}\right],$$

$$\lambda_{1} = -iqv_{0} \left(\frac{c_{p}}{c_{v}}\right)^{1/2},$$

$$\chi_{2} = \left(\frac{c_{v}}{2c_{p}}\right)^{1/2} \left[1 + \left(\frac{c_{p}}{c_{v}}\right)^{1/2} \frac{v_{x}}{v_{0}} + c_{v}^{-1/2} \frac{\mathscr{E} - \widetilde{\mathscr{E}}}{\Delta \mathscr{E}}\right],$$

$$\lambda_{2} = iqv_{0} \left(\frac{c_{p}}{c_{v}}\right)^{1/2},$$

$$\chi_{3} = \frac{v_{y}}{v_{0}}, \quad \lambda_{3} = 0,$$

$$\chi_{4} = \frac{v_{z}}{v_{0}}, \quad \lambda_{4} = 0,$$

$$\chi_{5} = \left(\frac{c_{v}}{c_{v}}\right)^{1/2} \left(c_{v}^{-1/2} - \frac{\mathscr{E} - \widetilde{\mathscr{E}}}{\Delta \mathscr{E}}\right), \quad \lambda_{5} = 0,$$
(13)

where $v_0 = (T/m)^{1/2}$ is the thermal velocity of a molecule; $\overline{\mathscr{C}} = c_v T$ and $\Delta \mathscr{C} = (c_v)^{1/2} T$ are the average energy and the scatter of this energy for a molecule; c_v and c_p are the specific heats of a molecule at constant volume and pressure, respectively, calculated allowing for the rotational and translational degrees of freedom.

These five functions form a set of hydrodynamic modes, of which the functions χ_1 and χ_2 correspond to acoustic modes, the functions χ_3 and χ_4 to shear modes, and the function χ_5 to a heat conduction mode.

It is clear from the system (13) that acoustic waves travel in a gas at the velocity of sound $u_{ac} = (c_p/c_v)^{1/2}v_0$ and the other three modes do not propagate. The finite decay time of hydrodynamic modes proportional to q^2 is obtained in the second order of perturbation theory.^{57,58}

We shall seek the solution of Eq. (8') as an expansion in eigenfunctions of the operator \hat{I}_0 :

$$\chi_{\boldsymbol{\omega}\boldsymbol{q}}(Q) = \sum_{\alpha=1}^{\infty} a_{\alpha}(\boldsymbol{\omega}, \boldsymbol{q}) \chi_{\alpha}(Q),$$

where $\chi_{\alpha}(Q)$ with $\alpha > 5$ are eigenfunctions with nonzero eigenvalues, i.e., they are called nonhydrodynamic modes. We can go over from Eqs. (8') and (9') to Eqs. (14) and (15) for the coefficients a_{α} :

$$-i (\omega + qu_{ac}) a_{1} + i \sum_{\alpha > 5} (qv_{x})_{1\alpha} a_{\alpha} = B_{0} \left(\frac{c_{v}}{2c_{p}}\right)^{1/2},$$

$$-i (\omega - qu_{ac}) a_{2} + i \sum_{\alpha > 5} (qv_{x})_{2\alpha} a_{\alpha} = B_{0} \left(\frac{c_{v}}{2c_{p}}\right)^{1/2},$$

$$-i \omega a_{3} + i \sum_{\alpha > 5} (qv_{x})_{3\alpha} a_{\alpha} = 0,$$

$$-i \omega a_{4} + i \sum_{\alpha > 5} (qv_{x})_{4\alpha} a_{\alpha} = 0,$$

$$-i \omega a_{5} + i \sum_{\alpha > 5} (qv_{x})_{5\alpha} a_{\alpha} = B_{0}c_{v}^{-1/2},$$

$$(-i\omega + v_{\alpha}) a_{\alpha} + i \sum_{\alpha'} (qv)_{\alpha\alpha'} a_{\alpha'} = B_{2\alpha},$$

(14)

where

$$a > 5,$$

$$J_{\omega q} \propto \operatorname{Re} \left[B_0 \left(\frac{c_v}{2c_p} \right)^{1/2} (a_1 + a_2) + B_0 c_v^{-1/2} a_5 \right] + \operatorname{Re} \sum_{\alpha > 5} B_{2\alpha}^* a_\alpha, \qquad (15)$$

$$(qv_x)_{\alpha \alpha'} = \int \chi_{\alpha}^* f_0 qv_x \chi_{\alpha'} \, \mathrm{d}Q$$

is a matrix element of the operator qv_x between the states χ_{α} and $\chi_{\alpha'}$, and

$$B_{2\alpha} = \langle \chi_{\alpha} | B_{2} \rangle \equiv \int \chi_{\alpha}^{*} f_{0} B_{2} \, \mathrm{d}Q$$

It follows from the system of equations (14) that the solutions for the functions $a_1(\omega,\mathbf{q})$, $a_2(\omega,\mathbf{q})$, and $a_5(\omega,\mathbf{q})$ describe the familiar scalar scattering triplet, whereas the integrated intensities of these components obey the Landau-Placzek relationship

 $\frac{J_{\text{doubl}}}{J_{\text{tot}}} = \frac{c_{v}}{c_{p}} ,$

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where J_{doubl} is the integral intensity of the Brillouin doublet and J_{tot} is the integral intensity of the whole triplet.

It is clear from Eq. (14) that the symmetric part of the polarizability tensor or the function B_2 governing the depolarized part of the scattering spectrum does not contribute to the integral density of the triplet, whereas the hydrodynamic modes are independent of the direction of the vector **M**. On the other hand, it follows from the orthogonality of the functions 1 and χ_{α} , where $\alpha > 5$, that the scalar part of the polarizability tensor (or the function B_0) does not affect the integral intensity of the wide depolarized component of the operator. Therefore, two terms in the expression for the intensity given by Eq. (15) integrated with respect to the frequencies correspond to the scalar and symmetric types of scattering.

However, the scalar and symmetric scattering spectra are not independent, since the equations for the coefficients $a_1, ..., a_5$ of the system (14) are linked to the equations for a_{α} , where $\alpha > 5$, by the matrix elements of the operator *i***q**•**v**.

In solving the system (14) by perturbation theory in respect of the parameter qv/v we can simplify the equations with $\alpha > 5$ by dropping the terms $(qv_x)_{\alpha\alpha}a_{\alpha}$ compared with $v_{\alpha}a_{\alpha}$ and solving them for the coefficients a_{α} :

$$a_{\alpha} = \frac{B_{2\alpha}}{-i\omega + v_{\alpha}} - i \sum_{\beta \leqslant 5} \frac{(qv_{\alpha})_{\alpha\beta} a_{\beta}}{v_{\alpha}}.$$
 (16)

Substituting this expression in the first five equations (for the hydrodynamic mode) of the system (14), we obtain

$$-i (\omega + \Omega_j) a_j + \Gamma_j a_j = B_j - i\Delta B_j, \quad j = 1, \ldots, 5,$$
(17)

where $\Omega_1 = qu_{\rm ac}$, $\Omega_2 = -qu_{\rm ac}$, and $\Omega_{3,4,5} = 0$. The widths of the hydrodynamic modes Γ_j obtained in the second order of perturbation theory are

$$\Gamma_{j} = \sum_{\alpha > 5} v_{\alpha}^{-1} (qv_{x})_{j\alpha} (qv_{x})_{\alpha j}, \qquad (18)$$

$$\Delta B_{j} = \sum_{\alpha > 5} v_{\alpha}^{-1} (qv_{x})_{j\alpha} B_{2\alpha},$$

$$B_{1} = B_{2} = B_{0} \left(\frac{c_{v}}{2c_{p}}\right)^{1/2}, \quad B_{3} = B_{4} = 0, \quad B_{5} = B_{0} \cdot c_{v}^{-1/2}.$$

The quantities in the above expressions have the values $\Gamma_1 = \Gamma_2$, $\Gamma_3 = \Gamma_4$, $-\Delta B_1 = \Delta B_2$, $\Delta B_5 = 0$ because of the symmetry properties of the operator \hat{I}_0 under time reversal and under rotation. It should be noted that the contribution to the quantities ΔB_j representing the "spectral mixing" of the scalar and symmetric scattering is made only by the symmetric part of the polarizability of a molecule α_2 because of the orthogonality of the functions 1 and χ_{α} , where $\alpha > 5$.

The quantities Γ_j and ΔB_j can be described in a form which is equivalent to that given by Eq. (18), but this time in terms of the inverse operator \hat{I}_0^{-1} (see, for example, Refs. 57 and 58):

$$\Gamma_{j} = \langle \chi_{j} q v_{x} | \hat{I}_{0}^{-1} | q v_{x} \chi_{j} \rangle, \quad \Delta B_{j} = \langle \chi_{j} q v_{x} | \hat{I}_{0}^{-1} | B_{2} \rangle, \quad (19)$$

which is convenient to use in the derivation of the dependences of the spectral characteristics on the polarizations of the incident and scattered waves.

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It should be noted that the widths of the modes Γ_j , where $j \leq 5$, can be expressed—in accordance with the ordinary hydrodynamic theory—in terms of the transport coefficients such as the shear viscosity η , the second (bulk or dilatational) viscosity ζ , and the thermal conductivity \varkappa (Refs. 57, 58, 66):

$$\Gamma_{1} = \frac{q^{2}}{2\rho} \left[\frac{4}{3} \eta + \zeta + \varkappa m \left(\frac{1}{c_{v}} - \frac{1}{c_{p}} \right) \right],$$

$$\Gamma_{3} = \frac{q^{2}}{\rho} \eta, \quad \Gamma_{5} = \frac{q^{2}m}{\rho c_{p}} \varkappa;$$
(20)

here $\rho = mN$ is the density of the investigated gas.

The comparison of the expressions in Eq. (20) with those in Eq. (18) enables us to express the transport coefficients in terms of the eigenfunctions of the Boltzmann collision integral:

$$\begin{aligned} \kappa &= \frac{\rho}{mT^{2}} \left\langle v_{x} \left(\mathscr{E} - c_{y}T \right) \left| \hat{I}_{0}^{-1} \right| v_{x} \left(\mathscr{E} - c_{y}T \right) \right\rangle, \\ \eta &= \frac{\rho m}{T} \left\langle v_{x}v_{y} \left| \hat{I}_{0}^{-1} \right| v_{x}v_{y} \right\rangle, \\ \zeta &= \frac{\rho}{mT} \left\langle \frac{mv^{2}}{3} - \frac{\mathscr{E}}{c_{t}} \left| \hat{I}_{0}^{-1} \right| \frac{mv^{2}}{3} - \frac{\mathscr{E}}{c_{v}} \right\rangle. \end{aligned}$$
(21)

It is clear from the above formulas that the second viscosity ζ represents the contribution of the scalar nonhydrodynamic modes to the attenuation of sound in a gas, the thermal conductivity \varkappa represents the vector modes, and the shear viscosity η represents the contribution of the secondrank tensor modes. The advantage of this form of the transport coefficients is that it can be used to separate explicitly the contributions of the various degrees of freedom. Relationships of this kind for the transport coefficients of a monatomic gas (without rotation) were first obtained in Refs. 57 and 58.

The general solution of the system of equations (16)-(18) yields the following expression for the Rayleigh scattering spectrum:

$$J_{\omega q} = J_{0}(\omega, q) + J_{2}(\omega, q),$$

$$J_{0}(\omega, q) = \frac{c_{\upsilon}}{2c_{p}} B_{0}^{2} \left[\frac{\Gamma_{1}}{(\omega + qu_{ac})^{2} + \Gamma_{1}^{2}} + \frac{\Gamma_{I}}{(\omega - qu_{ac})^{2} + \Gamma_{1}^{2}} + \frac{2}{c_{\upsilon}} \frac{\Gamma_{5}}{\omega^{2} + \Gamma_{5}^{2}} \right] + \left(\frac{c_{\upsilon}}{2c_{p}}\right)^{1/2} B_{0} \Delta B_{1} \left[\frac{\omega + qu_{ac}}{(\omega + qu_{ac})^{2} + \Gamma_{5}^{2}} - \frac{\omega - qu_{ac}}{(\omega - qu_{ac})^{2} + \Gamma_{1}^{2}} \right], \quad (22)$$

$$J_{2}(\omega, q) = \sum_{\alpha > 5} \frac{(B_{2\alpha})^{2} v_{\alpha}}{\omega^{2} + v_{\alpha}^{2}} - (\Delta B_{3}^{2} + \Delta B_{4}^{2}) \frac{\Gamma_{3}}{\omega^{2} + \Gamma_{3}^{2}} - (\Delta B_{1})^{2} \left[\frac{\Gamma_{1}}{(\omega + qu_{ac})^{2} + \Gamma_{1}^{2}} + \frac{\Gamma_{1}}{(\omega - qu_{ac})^{2} + \Gamma_{1}^{2}} \right].$$

Here, $J_0(\omega, \mathbf{q})$ describes the narrow polarized part of the Rayleigh scattering spectrum, which consists of the familiar triplet and small asymmetric corrections at the frequencies of the Brillouin doublet $\Omega_{\rm B} = qu_{\rm ac}$ of intensity proportional to $B_0\Delta B_1$, i.e., $\alpha_0\alpha_2$. The signs of these corrections are opposite for the Stokes and anti-Stokes components.

When the polarizations of the incident and scattered waves are orthogonal, so that $\mathbf{e}_1 \cdot \mathbf{e}_2 = 0$ and $B_0 = 0$, we find

that $J_0(\omega, \mathbf{q}) = 0$ and the depolarized scattering spectrum is described by the function $J_2(\omega, \mathbf{q})$. It is clear from the expression in Eq. (22) for $J_2(\omega, \mathbf{q})$ that in the depolarized scattering spectrum there is a background of a wide profile of width $\sim v_\alpha$ and narrow dips at the frequencies of the acoustic components $\omega = \Omega_B$ and at the line center because of the mixing of the acoustic (χ_1 and χ_2) and shear (χ_3 and χ_4) modes with the nonhydrodynamic modes χ_α .

The dependences of the intensities of the dips on the polarizations of the incident \mathbf{e}_1 and scattered \mathbf{e}_2 waves are obtained from Eq. (19) when an allowance is made for the spherical symmetry of the operator \hat{I}_0^{-1} ;

$$\Delta B_1 \propto 2e_{1x}e_{2x} - \frac{2}{3} (e_1e_2),$$

$$\Delta B_3 \propto e_{1x}e_{2y} + e_{1y}e_{2x},$$

$$\Delta B_4 \propto e_{1x}e_{2z} + e_{1z}e_{2x}.$$

Consequently, the intensity of the dips in the depolarized scattering spectrum in the $\mathbf{e}_1 \cdot \mathbf{e}_2 = 0$ case is given by

$$\Delta B_{1}^{2} = \Delta B_{2}^{2} \propto e_{1x}^{2} e_{2x}^{2},$$

$$(\Delta B_{3})^{2} + (\Delta B_{4})^{2} \propto (e_{1x}^{2} + e_{2x}^{2}) (1 - e_{1x}^{2} - e_{2x}^{2}).$$
(23)

Therefore, if the polarizations \mathbf{e}_1 and \mathbf{e}_2 lie in the scattering plane defined by the wave vectors \mathbf{k}_1 and \mathbf{k}_2 , the fine structure of the depolarized scattering spectrum consists of two narrow dips at the shifted frequencies $\omega = \pm \Omega_{\rm B}$. This case corresponds to the HH component of the depolarized scattering spectrum.

In the case of the VH scattering the fine structure consists of a single dip at the unshifted frequency $\omega = 0$. This case corresponds to the fine structure in the depolarized scattering spectrum of low-viscosity liquids first discovered by Fabelinskiĩ *et al.*¹ and then confirmed by many others.²⁻¹⁸ This fine structure is shown in Fig. 1.

It is worth considering specifically the case of a small departure from the condition $\mathbf{e}_1 \cdot \mathbf{e}_2 = 0$. In this case we find that in the HH polarization there is a background profile described by the function $J_2(\omega, \mathbf{q})$, as well as a spectral structure described by the function $J_0(\omega, \mathbf{q})$ [see Eq. (22)]. In this case the fine structure in the depolarized scattering spectrum is supplemented by a triplet and asymmetric corrections at the Brillouin frequencies $\omega = \pm \Omega_{\rm B}$. In particular, we may encounter the case illustrated in Fig. 2 corresponding to $\Delta B_1^2 = B_0^2 c_v / 2c_p$, when the fine structure at the Brillouin frequencies is in the form of purely asymmetric profiles governed by the second term in the expression for $J_0(\omega, \mathbf{q})$.



FIG. 4. Scattering (I_{VII}) spectrum recorded for a slight deviation from orthogonality $\mathbf{e}_1 \cdot \mathbf{e}_2 \neq 0$; $B_{\perp}^2 = B_{\perp 0}^2 c_i / 2c_p$.

An analogous departure from the orthogonality for the VH polarization $(\Delta B_3^2 + \Delta B_4^2 = B_0^2/c_p)$ results in disappearance of a dip at the line center and the fine structure profile at the shifted frequencies becomes a superposition of a peak and an asymmetric profile, in accordance with Eq. (22). It should be pointed out that the case shown in Fig. 4 corresponds to the following estimate of the deviation from the orthogonality: $(\mathbf{e_1} \cdot \mathbf{e_2}) \sim (qv/v)\alpha_2/\alpha_0 \leqslant 1$. Hence, it follows that as the gas density increases, the orthogonality condition must be satisfied by the gas more and more rigorously in order to observe the fine structure.

3.2. Theory of perturbations based on the anisotropy of the interaction potential

Usually in the case of simple molecules collisions accompanied by a change in velocity occur more frequently than collisions accompanied by a change in the rotational momentum, i.e., the anisotropic part of the potential is relatively small compared with the isotropic part.^{72,73} In this approximation the collision integral \hat{I}_0 can be divided into two terms:

$$\hat{I}_0 = \hat{I} + \Delta \hat{I}, \qquad (24)$$

where \hat{I} refers to the isotropic part of the potential, i.e., it describes only the change in the velocity in collisions, and the small correction $\Delta \hat{I}$ associated with the anisotropic part of the potential represents collisions accompanied by changes in the rotational momentum of the molecules. The characteristic frequencies of these operators will be denoted by v and Δv , respectively, and we shall assume that the condition $qv \ll \Delta v \ll v$ is satisfied.

An analysis of the transport equation with the collision operator of the (24) type was made by Kagan and Maksimov in Ref. 74. It follows from this analysis that the set of eigenfunctions of the operator can be divided into three classes:

a) χ^v_{α} are the functions which depend only on the velocity **v**;

b) χ_{α}^{M} are the functions dependent only on the angular momentum **M**;

c) χ_{α}^{Mv} are the functions dependent both on v and on M.

The angular dependences of these functions on the vectors \mathbf{v} and \mathbf{M} can be represented by bipolar harmonics or spherical polynomials:

$$\chi_{\alpha} \propto \sum_{m=m_1+m_2} \left(l_1 l_2 lm \left| l_1 m_1 l_2 m_2 \right\rangle Y_{l_1 m_1} \left(\frac{\mathbf{v}}{v} \right) Y_{l_2 m_2} \left(\frac{\mathbf{M}}{\mathbf{M}} \right) \right),$$

where Y_{lm} is a spherical harmonic and $(l_1 l_2 lm | l_1 m_1 l_2 m_2)$ is a Clebsch-Gordan coefficient.

The eigenvalues of the functions χ_{α}^{v} are of the order of v, the eigenvalues of the functions χ_{α}^{M} are of the order of Δv , whereas the functions χ_{α}^{Mv} have eigenvalues of the order of vand of Δv .

Using these properties, we shall analyze the main parameters of the Rayleigh light scattering spectrum. The depolarized light scattering spectrum considered in the zeroth approximation of perturbation theory in terms of the parameter $\Delta v/v$ can be described by a single eigenfunction

 $\chi_{\alpha} = Y_{2m} (\mathbf{M}/\mathbf{M})$ with the eigenvalue $\Delta v = 0$. The finite width of the depolarized spectrum is obtained in the next order of perturbation theory by solving the secular equation in the degenerate space of the functions χ_{α}^{M} .

Let us assume that $\chi_{\alpha}^{M} = c_{\alpha}(M) Y_{2m}(M/M)$ is the eigenfunction of the operator ΔI with the eigenvalue Δv_{α} obtained from the secular equation. Then, the depolarized scattering profile is a superposition of Lorentzian profiles of widths Δv_{α} with intensities proportional to $|\langle c_{\alpha} | 1 \rangle|^{2}$. It then follows from the normalization condition that $\sum_{\alpha} |\langle c_{\alpha} | 1 \rangle|^{2} = 1 = \langle c_{\alpha} | c_{\alpha} \rangle$. As already pointed out in the Introduction, there have been several theoretical and experimental investigations²⁴⁻³² in which calculations and measurements were made of the deviation of the line profile of

mental investigations²⁴⁻³² in which calculations and measurements were made of the deviation of the line profile of the depolarized Rayleigh scattering from the pure Lorentzian profile for gases of simple molecules.

The coefficients ΔB_j considered in the first order of perturbation theory in respect of the parameter $\Delta \nu/\nu$ are given by the following expressions which allow for the admixture, to the eigenfunctions χ_{α}^{M} , of the functions χ_{α}^{v} :

$$\Delta B_{j} = -\sum_{\alpha\alpha'} \frac{\langle \chi_{j} q v_{\alpha} | \chi_{\alpha'}^{v} \rangle}{v_{\alpha'}} \frac{\langle \chi_{\alpha'}^{v} | \Delta T | \chi_{\alpha}^{M} \rangle}{\Delta v_{\alpha}} \langle \chi_{\alpha}^{M} | B_{2} \rangle.$$
(25)

We can see from Eq. (25) that the coefficients ΔB_j are independent of the parameter $\Delta v/v$, but are proportional to the hydrodynamic small parameter qv/v. Hence, it follows that the integral intensity of the dip in the depolarized scattering, proportional to ΔB_j^2 , is also independent of the parameter $\Delta v/v$, i.e., it is independent of the degree of anisotropy of the potential of the interaction between molecules.

The following results are obtained for the widths of the hydrodynamic modes (or of the transport coefficients) from perturbation theory.

In the first order of perturbation theory the width Γ_5 or the thermal conductivity is independent of the rotational degrees of freedom of a molecule, because the spatial inversion invariance of the operator ΔI means that this operator cannot link the polar **v** and axial **M** vectors. Consequently, the expression for Γ_5 becomes

$$\Gamma_{5} = \sum_{\alpha > 5} \frac{|\langle \chi_{5} q v_{\alpha} | \chi_{\alpha}^{\nu} \rangle|^{2}}{\nu_{\alpha} (l = 1)}, \qquad (26)$$

where the condition l = 1 in the parentheses of the denominator means that the summation should be carried out over the vectors of the nonhydrodynamic functions. Nonzero corrections to Γ_5 (or to the thermal conductivity \varkappa) because of the molecular rotation appear only in the second order of perturbation theory in respect of the parameter $\Delta v/v$ (Ref. 74). In spite of the smallness of these corrections, which in the case of nitrogen amount to $\Delta \varkappa/\varkappa \approx 10^{-2}$, they are experimentally detectable from the change in the thermal conductivity of gases on application of external fields⁷⁵⁻⁸¹ and will be discussed in detail in the next chapter.

The expression for the width Γ_3 (or the shear viscosity coefficient) obtained in the first order of perturbation theory is

$$\Gamma_{3} = \sum_{\alpha > 5} \frac{|\langle \chi_{3}qv_{\lambda} | \chi_{\alpha}^{*} \rangle|^{2}}{|v_{\alpha}(l=2)|} + \sum_{\alpha > 5} \frac{1}{\Delta v_{\alpha}(l=2)} \left| \sum_{\alpha' > 5} \langle \chi_{3}qv_{x} | \chi_{\alpha'}^{v} \rangle v_{\alpha'}^{-1} \langle \chi_{\alpha'}^{v} | \Delta I | \chi_{\alpha}^{M} \rangle|^{2}.$$

$$(27)$$

The notation (l = 2) corresponds to summation over the tensor nonhydrodynamic functions of the second rank. The first term on the right-hand side of Eq. (27), equal to $\eta(v)$, is entirely due to the contribution of the translational degrees of freedom to the shear viscosity, whereas the second $(\Delta \eta)$ allows for the contribution of the rotational degrees of freedom and is of the order of $\Delta v/v$ compared with the first term.

A comparison of Eqs. (25) and (27) makes it possible to estimate the contrast or depth of the dip at the unshifted frequency from perturbation theory:

$$R(\omega = 0) = \frac{\Delta B_3^2 + \Delta B_4^2}{\Delta B_2^2} \frac{\Delta v}{\Gamma_3} \sim \frac{\Delta \eta}{\eta(v)} \sim \frac{\Delta v}{v}.$$
 (28)

Using the explicit expression (13) for the hydrodynamic functions χ_i , where i = 1, ..., 5 we can express the width of the acoustic mode Γ_1 in terms of the widths Γ_3 and Γ_5 and in terms of the second viscosity ζ . Retaining in ζ the principal terms (in the first order of perturbation theory), we obtain

$$\Gamma_{1} = \frac{1}{2c_{0}} \Gamma_{5} + \frac{2}{3} \Gamma_{3} + \frac{q^{2}}{\rho} \zeta, \qquad (29)$$

$$\zeta = \sum_{\alpha>5} \frac{|\langle \chi_1 q v_x | \chi_\alpha \rangle|^2}{\Delta v_\alpha \ (l=0)}.$$
 (30)

In Eq. (30) for the second viscosity ζ we sum only over the correct scalar (l = 0) nonhydrodynamic functions in the zeroth order approximation, which in the first order of perturbation theory relax at a frequency Δv_{α} . This expression for ζ differs from the familiar definition of Eq. (21) (see, for example, Ref. 68) only in respect of the form in which it is expressed. A comparison of Eqs. (26), (27), (29), and (30) shows that the main contribution to the attenuation of sound comes from the term with the second viscosity ζ if the condition $\Delta v \ll v$ is obeyed. Using this result, we obtain the following estimate of the contrast of the dips at the shifted frequencies:

$$R(\omega = \Omega_{\rm B}) = \frac{\Delta B_1^2}{B_2^2} \frac{\Delta \nu}{\Gamma_1} \sim \frac{\Delta \eta}{\zeta} \sim \left(\frac{\Delta \nu}{\nu}\right)^2. \tag{31}$$

Therefore, the contrast of the fine structure in the VH and HH scattering cases is independent of the density of the gas and represents the relative contribution of the rotational degrees of freedom to the shear viscosity. The precision of this conclusion is limited only by the validity of the Boltzmann transport equation in the case of a gas with the rotational degrees of freedom. Within this framework, the description provided above is purely microscopic and does not contain phenomenological elements known to occur in the published statistical theories, including those based on the Mori method.^{8,47,48,52,53,56}

It follows from the above that interpretation of the observed fine structure of dense gases is simpler and more certain than in the case of liquids. Consequently, it would be very interesting to carry out experiments designed to detect the fine structure of gases. For example, in the case of such molecules as N₂O or CO₂, the anisotropy of the potential is sufficiently strong, $\Delta \nu / \nu \sim 0.8$ (Refs. 72 and 73), so that we can expect a higher contrast of the fine structure.

We shall conclude this chapter by analyzing the Rayleigh scattering spectrum of a gas obtained by the kinetic method from the point of view of the general symmetry properties of the scattering tensor $h_{iklm} (\omega, \mathbf{q})$ allowing for the spatial dispersion of the medium.⁴⁴ It is known⁴⁴ that in the case of an isotropic medium the spectral dependence of the scattering tensor $h_{iklm} (\omega, \mathbf{q})$ obtained allowing for the spatial dispersion is given by five independent functions $\sigma_1(\omega, q^2), ..., \sigma_5(\omega, q^2)$:

$$f_{ihlm} (\omega, \mathbf{q}) = \sigma_1 \delta_{ik} \delta_{lm} + \sigma_2 \mu_{ihlm} + \sigma_8 (\delta_{ik} \pi_{lm} + \delta_{lm} \pi_{ik}) + \sigma_4 \pi_{ik} \pi_{lm} + \sigma_5 \mathbf{v}_{ihlm}, \qquad (32)$$

where

$$\pi_{ik} = q_l q_k - \frac{1}{3} q^2 \delta_{ik},$$

$$\mu_{lklm} = \frac{1}{2} \left(\delta_{ll} \delta_{km} + \delta_{im} \delta_{kl} \right) - \frac{1}{3} \delta_{ik} \delta_{lm},$$

$$\nu_{iklm} = \frac{1}{4} \left(\delta_{ll} q_k q_m + \delta_{im} q_k q_l + \delta_{km} q_l q_l + \delta_{kl} q_l q_m \right)$$

$$- q_l q_k q_l q_m q^{-2}.$$

We can determine all five functions $\sigma_1, ..., \sigma_5$ for a gas in the case when $\nu, \Delta \nu \gg qv$ if we know simply the spectral dependences of three components of the scattered light: $J_{VV}(\omega, \mathbf{q}), J_{VH}(\omega, \mathbf{q})$, and $J_{HH}(\omega, \mathbf{q})$. It is known⁴⁴ that these functions are related to the functions $\sigma_1, ..., \sigma_5$ by the



FIG. 5. Structure of the Rayleigh scattering spectrum of an ideal gas.

following expressions:

$$J_{\rm VV}(\omega, q) = \sigma_1 + \frac{2}{3} \sigma_2 - \frac{2}{3} q^2 \sigma_3 + \frac{1}{9} q^4 \sigma_4, \qquad (33)$$
$$J_{\rm HH}(\omega, q) = \frac{1}{2} \sigma_1 + \frac{1}{4} q^4 \sigma_4, \quad J_{\rm VH}(\omega, q) = \frac{1}{2} \sigma_2 + \frac{1}{8} q^2 \sigma_5.$$

The frequency integrals of the functions $\sigma_{3,4,5}$ vanish.

A comparison of the expressions (33) and (22) makes it possible to determine all five functions $\sigma_1, ..., \sigma_5$. It is found that the function $\sigma_1(\omega, \mathbf{q})$ describes the polarized scattering triplet; the function $\sigma_2(\omega, \mathbf{q})$ represents the wide part of the depolarized scattering spectrum, the width of which is of the order of Δv . The functions $\sigma_4(\omega, \mathbf{q})$ and $\sigma_5(\omega, \mathbf{q})$ determine the fine structure in the depolarized scattering spectrum, whereas the function $\sigma_3(\omega, \mathbf{q})$ describes asymmetric corrections to the polarized scattering spectrum at the shifted frequencies. Figure 5 shows the complete picture allowing for the fine structure. It should be noted that the integral intensity of the dips in the depolarized spectrum does not vanish because we have ignored the frequency dispersion of the quantities ΔB_i , i.e., the terms $i\omega$ in the denominators $(i\omega + v_{\alpha})^{-1}$. When an allowance is made for this frequency dependence, the integral intensity of the fine structure vanishes identically because the negative contribution of the dips in the narrow frequency range $\omega \sim q u_{\rm ac}$ is compensated by positive corrections at frequencies $\omega \sim \Delta v$.

4. SPECTRUM OF THE RAYLEIGH SCATTERING OF LIGHT OF A BOLTZMANN GAS IN A STRONG MAGNETIC FIELD

We shall now calculate the spectrum of the Rayleigh light scattering in a gas consisting of anisotropic diatomic molecules subjected to an external sufficiently strong magnetic field. We shall show that the structure of the spectrum, both polarized and particularly depolarized, is very sensitive to the presence of a magnetic field. This is due to partial freezing of the rotational degrees of freedom of molecules by a magnetic field.^{71,74,82,83} In their turn the rotational degrees of freedom are manifested actively in the structure of the scattering spectrum (see Sec. 3), both in the polarized component via the dependences of the transport coefficients on the rotational degrees of freedom, and in the depolarized component of the spectrum, the width of which is governed by collisions that alter the rotational moment of the molecules. Moreover, in the depolarized part of the scattered light there is a fine structure in the form of three narrow dips (at the unshifted frequency and at the Brillouin frequencies), the intensities of which are governed by the collisional coupling of the translational and rotational degrees of freedom, and the width of a dip at the unshifted frequency is determined solely by the shear viscosity η . Therefore, the dependence of the width of a dip at the unshifted frequency on the magnetic field direction makes it possible to study directly the changes in the shear viscosity as a result of application of a magnetic field.

After the first theoretical paper of Kagan and Maksimov,⁸³ in which it was shown that the magnetic and electric fields affect the gas transport coefficients via the rotational degrees of freedom, a large series of investigations of this interesting effect has been published.^{74–82} The dependences of the transport coefficients on external electric and magnetic fields have been studied under conditions of nonequilibrium gases and in most of the experiments the attention has been concentrated on the thermal conductivity at various gas pressures.⁷⁵⁻⁸³

Precision investigations of the structure of the Rayleigh scattering spectrum of a gas subjected to a magnetic field, which have become possible recently because of the use of lasers and high-resolution techniques,¹⁹ can provide information on the magnetic-field dependences of all the transport coefficients, icluding the shear and second viscosities, which are difficult to study under nonequilibrium gas conditions.

All the parameters of the scattering spectrum of a gas in a magnetic field (including the transport coefficients) can be expressed in terms of eigenfunctions and eigenvalues of the linearized Boltzmann collision integral. In the approximation of a small deviation of the interaction potential of gas molecules from the isotropic law the angular dependences of the spectral characteristics of the scattering make it possible to determine explicitly the contribution of the translational and rotational degrees of freedom to all the transport coefficients.

4.1. Structure of the depolarized component of the spectrum

When a magnetic field **H** is applied, molecules begin to interact with the field because a rotating molecule has a magnetic moment μ , which is given by $\mu = \gamma \mathbf{M}$, where the gyromagnetic ratio γ depends on the internal structure of a diatomic molecule.⁷⁴ In the case of paramagnetic molecules we have $\gamma \approx \mu_{\rm B}/\hbar$, where $\mu_{\rm B}$ is the Bohr magneton amounting to 0.93×10^{-20} erg/Oe. For the majority of molecules the ground state is nondegenerate and the spin is zero: they are nonparamagnetic molecules. In this case the magnetic moment of a molecule is associated with the rotation of the nucleus and the gyromagnetic ratio is governed by the nuclear magneton (for example, in the case of nitrogen we have $\gamma = 0.25\mu_{\rm n}/\hbar$, where $\mu_{\rm n}$ is the nuclear magneton amounting to 5.05×10^{-24} erg/Oe).

In the presence of a magnetic field the left-hand side of the transport equation (8') should be supplemented by the term γ [**MH**] $\partial \chi / \partial$ **M**, describing the precession of the magnetic moment of a molecule in an external field, so that this equation becomes

$$i (\mathbf{q}\mathbf{v} - \mathbf{v}) \chi_{\mathbf{w}g} + \gamma [\mathbf{M}\mathbf{H}] \frac{\partial}{\partial \mathbf{M}} \chi_{\omega g} + \hat{I}_0 \chi_{\omega g} = B_0 + B_2. (34)$$

The eigenfunctions of the operator γ [**MH**] ∂/∂ **M** are spherical harmonics Y_{lm}^{H} (**M**/*M*) with the quantization axis *z* directed along **H**. The corresponding purely imaginary eigenvalues are *im* γ *H*.

In this chapter we shall consider mainly the case of a sufficiently strong magnetic field satisfying the inequalities

$$T \gg \gamma H \gg \nu \gg q v. \tag{35}$$

In the case of paramagnetic molecules (such as oxygen) these inequalities are satisfied for the following values of the parameters: $H > 5 \times 10^2$ Oe, $p \approx 1$ atm, $\gamma H / T \sim 5 \times 10^{-4}$ or

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 $H > 5 \times 10^3$ Oe, $p \approx 10$ atm, $\gamma H / T \sim 5 \times 10^{-3}$; in the case of nonparamagnetic (such as nitrogen) molecules, we have $H > 10^6$ Oe, $p \approx 1$ atm, $\gamma H / T \sim 10^{-4}$.

When the inequalities of Eq. (35) are satisfied, the main term in the transport equation (34) is that containing the magnetic field: γ [**MH**] $\partial \chi_{coq} / \partial$ **M**. When only this term is allowed for, the depolarized scattering spectrum ($\mathbf{e_1} \cdot \mathbf{e_2} = 0$) represents five resolved components located at frequencies $\omega = 0$ (m = 0), $\omega = \pm \gamma H$ (m = ± 1), $\omega = \pm 2\gamma H$ (m = ± 2). The integrated intensity of each component depends on the magnetic field direction as follows:

$$J (m = 0) \propto 4 (\mathbf{he}_{1})^{2} (\mathbf{he}_{2})^{2},$$

$$J (m = \pm 1) \propto \frac{2}{3} [(\mathbf{he}_{1})^{2} + (\mathbf{he}_{2})^{2} - 4 (\mathbf{he}_{1})^{2} (\mathbf{he}_{2})^{2}],$$

$$J (m = \pm 2) \propto \frac{2}{3} [1 - (\mathbf{he}_{1})^{2}] [1 - (\mathbf{he}_{2})^{2}], \quad h = \frac{\mathbf{H}}{\mathbf{H}}.$$
(36)

Naturally, the total integrated intensity of all five components is independent of the magnetic field **H** [as is easily demonstrated by summing all the components in Eq. (36)], but is governed by the square of the symmetric component α_2^2 of the polarizability tensor. Figure 6 illustrates the spectrum of depolarized scattering of light for certain relationships between the vectors **h**, **e**₁, and **e**₂.



FIG. 6. Depolarized Rayleigh light scattering spectrum of diatomic gases in a strong magnetic field $\gamma H \gg \Delta \nu$. Here, γH is the precession frequency of the rotational momentum about the direction of the magnetic field and $\Delta \nu$ is the width of the depolarized component of the scattering spectrum. a) Vector **h** parallel to one of the vectors \mathbf{e}_1 and \mathbf{e}_2 ; b) vector **h** in the plane of the vectors \mathbf{e}_1 and \mathbf{e}_2 oriented at an angle of 45°; c) vector **h** perpendicular to the vectors \mathbf{e}_1 and \mathbf{e}_2 ; d) nature of the spectrum in the absence of a magnetic field ($\mathbf{H} = 0$).

An allowance for the collisional term in the transport equation gives rise to a finite width of each component of the depolarized scattering equal to Δv_m :

$$\Delta \mathbf{v}_{m} = \left\langle Y_{2m}^{\mathrm{H}} \left(\frac{\mathbf{M}}{M} \right) | \hat{I}_{0} | Y_{2m}^{\mathrm{H}} \left(\frac{\mathbf{M}}{M} \right) \right\rangle.$$
(37)

We recall that $\Delta v_m < v$ is related only to the anisotropic part of the interaction potential of the molecules.

We shall now consider the fine structure of the scattering spectrum associated with an allowance for terms $i\mathbf{q}\cdot\mathbf{v}$ in Eq. (34). The operator $\gamma[\mathbf{MH}]\partial/\partial \mathbf{M}$ splits the whole space of the functions χ_{α} into five subspaces, each of which corresponds to a specific eigenvalue $im\gamma H$, where $m = 0, \pm 1$, ± 2 . These subspaces are spectrally independent, because they are not coupled by collisions because of the condition $\nu \ll \gamma H$. In such a strong magnetic field we can calculate the fine structure of the spectrum simply by solving Eq. (34) in the subspace of the functions with zero eigenvalue. Any function from the zeroth subclass can be represented in the form:

$$\chi(\mathbf{v}, \mathbf{M}) = \sum_{l} a_{l}(\mathbf{v}, \mathbf{M}) Y_{l0}^{\mathrm{H}}\left(\frac{\mathrm{M}}{\mathrm{M}}\right) \mathbf{o}$$
(38)

It should be noted that the restriction of the complete set of functions to the subclass (38) is physically equivalent to a transition from a variable **M** precessing in a magnetic field to the average between collisions $\langle \mathbf{M} \rangle = (\mathbf{M}\mathbf{h})\mathbf{h}$. The situation is fully analogous to the splitting of purely rotational Raman scattering from the Rayleigh component, when a transition is made from a description by means of the vectors **M** and **n** to the average (over a rotation period) description using only the angular momentum vector **M** [see Eqs. (10) and (11), and Eqs. (8') and (9')].

When Eq. (34) is solved in the subspace of Eq. (38), the collisional operator is $\tilde{I}_0 = \hat{P}\hat{I}_0\hat{P}_0$, where \hat{P} is the operator describing projection to the space of the functions (38). The eigenfunctions I_0 can be selected in the form:

$$\chi_{am} = \sum_{l, s} \varphi_{am}^{ls}(v, M) Y_{sm}^{\rm H}\left(\frac{v}{v}\right) Y_{l0}^{\rm H}\left(\frac{M}{M}\right), \qquad (39)$$

where $\varphi_{am}^{k}(v,M)$ are real functions. Since the operator \tilde{I}_{0} is real, the functions χ_{am} and χ_{a-m} are related by $\chi_{am}^{*} = (-1)^{m} \chi_{a-m}$ and the corresponding eigenvalues are $v_{am} = v_{a-m}$. Further calculations in the selected space (38) are practically fully analogous to the calculations in the absence of a magnetic field (see Sec. 3). It should be noted that in the problem with a magnetic field the most convenient coordinate system is that in which the x axis is directed along the vector **q**, the y axis lies in the plane of the vectors **q** and **H**, and the z axis is perpendicular to this plane. We shall denote the corresponding unit vectors by

$$\mathbf{e}_{\mathbf{x}} = \frac{\mathbf{q}}{q}, \quad \mathbf{e}_{\mathbf{y}} = [[\mathbf{e}_{\mathbf{x}}\mathbf{b}]\mathbf{e}_{\mathbf{x}}], \quad \mathbf{e}_{\mathbf{z}} = [\mathbf{e}_{\mathbf{x}}\mathbf{b}]. \tag{40}$$

Equation (34) is then expanded in terms of the basis of the eigenfunctions of the collision operator \tilde{I}_0 using the coordinate system (40).

It therefore follows that in calculation of the fine structure of the spectrum in a magnetic field we can use the system of equations (8') in which the nonhydrodynamic modes are taken from the subspace (38), whereas summation in the range $\alpha > 5$ has to be understood as summation in the space (38).

It should be noted that the operator \tilde{I}_0 has axial symmetry relative to the vector **h**, in contrast to the spherical symmetry of the total operator \hat{I}_0 . Consequently, the parameters of the scattering spectrum depend on the angle between the scattering vector **q** and the direction of the magnetic field **h**. In particular, in the presence of a magnetic field the quantities Γ_3 and Γ_4 are not identical and in the selected coordinate system (40) the modes χ_3 and χ_4 are not coupled.

4.2. Dependence of the spectral characteristics of the polarized scattering on a magnetic field

It is known^{57,58} that the widths of the narrow components of the scattering spectrum are governed by the damping of the hydrodynamic modes and can be expressed in terms of the transport coefficients (shear and second viscosities, and thermal conductivity). In the presence of a magnetic field these coefficients become anisotropic and, therefore, they are described by tensor quantities.

We shall begin our analysis starting with the quantity Γ_5 which is determined only by the thermal conductivity tensor

$$\Gamma_{5} = \sum_{ij} q_{i}q_{j}\varkappa_{ij} \frac{m}{\rho c_{p}},$$

where ρ is the gas density (g/cm³) and

$$\mathbf{x}_{ij} = \frac{\rho}{mT^2} \sum_{\boldsymbol{\alpha} > 5, k} \mathbf{v}_{\boldsymbol{\alpha}\boldsymbol{k}}^{-1} \langle \boldsymbol{v}_i \left(\boldsymbol{\mathcal{E}} - \boldsymbol{c}_p T \right) | \boldsymbol{\chi}_{\boldsymbol{\alpha}\boldsymbol{k}} \rangle \langle \boldsymbol{\chi}_{\boldsymbol{\alpha}\boldsymbol{k}} | \boldsymbol{v}_j \left(\boldsymbol{\mathcal{E}} - \boldsymbol{c}_p T \right) \rangle.$$
(41)

Substituting in Eq. (41) the explicit expressions for the eigenfunctions $\chi_{\alpha h}$ from Eq. (38) and separating the angular dependence on the velocity **v**, we obtain

$$\begin{aligned} \varkappa_{ij} &= \sum_{k=0, \pm 1} \left\langle \frac{v_i}{v} \middle| Y_{1k}^{\mathrm{H}} \left(\frac{v}{v} \right) \right\rangle \left\langle Y_{1k}^{\mathrm{H}} \left(\frac{v}{v} \right) \middle| \frac{v_j}{v} \right\rangle C_k, \\ C_k &= \frac{1}{3} \sum_{\alpha > 5} \frac{\rho}{mT^2} v_{\alpha k}^{-1} \left| \langle v \left(\mathcal{E} - c_p T \right) | \varphi_{\alpha k}^{102} \rangle |^2 \geqslant 0. \end{aligned}$$
(42)

Since the coefficients $\varphi_{\alpha k}^{10}$ and the eigenvalues $v_{\alpha k}$ depend only on the modulus k, the constants C_k in Eq. (42) have the property $C_k = C_{-k}$. Using this property, we find the following expression for \varkappa_{ii} :

$$x_{ij} = x \delta_{ij} + x_1 h_i h_j, \quad x = C_1, \quad x_1 = C_0 - C_1.$$
 (43)

The antisymmetric part of the thermal conductivity tensor appears in the moderately strong fields⁷⁴ when $\gamma H \propto \nu$, but we can see from Eq. (41) that it makes no contribution to Γ_5 . Using the explicit form of the dependence of the thermal conductivity tensor on the magentic field of Eq. (43), we shall determine the corresponding dependence for the width of the central component of a polarized triplet Γ_5 :

$$\Gamma_{\mathbf{5}} = \frac{m}{\rho c_p} q^2 \left(\mathbf{x} + \mathbf{x}_{\mathbf{i}} \cos^2 \theta \right), \quad \cos \theta = \mathbf{h} \mathbf{e}_{\mathbf{x}}. \tag{44}$$

It follows from the above expression that the width Γ_5

depends on the angle θ between the direction of the magnetic field and the scattering vector **q**. Variation of the angle θ makes it possible to separate experimentally the isotropic and anisotropic parts of the width Γ_5 and thus determine the coefficients \varkappa and \varkappa_1 representing the thermal conductivity tensor. It was shown by Kagan and Maksimov⁷⁴ that in the case of a weakly anisotropic potential characterized by $\Delta \nu /$ $\nu \ll 1$ the ratio of these coefficients obeys $\pi_1/\pi \propto (\Delta \nu/\nu)^2$, i.e., the ratio of the anisotropic part of the line width Γ_5 to its isotropic part is of the order of $(\Delta v/v)^2$. Experimental investigations of the thermal conductivity of gases in external fields involving measurements of a heat flux in the presence of a temperature gradient are reported in Refs. 75-81. In most cases the thermal conductivity of gases decreases on application of a magnetic field and becomes an anisotropic function of the direction of this field. These changes in the thermal conductivity (for example, in the case of nitrogen) amount to a few percent.84

We shall now consider the quantities Γ_3 and Γ_4 which determine the width of shear modes. These coefficients are related to the shear viscosity tensor η_{ijkl} by the following expressions:

$$\Gamma_{s} = \frac{1}{\rho} \sum_{ijkl} q_{j}q_{k}\eta_{ijkl}e_{yl}e_{yl},$$

$$\Gamma_{4} = \frac{1}{\rho} \sum_{ijkl} q_{j}q_{k}\eta_{ijkl}e_{zi}e_{zi},$$
(45)

where

$$\begin{split} \eta_{ijkl} &= \frac{\rho m}{T} \sum_{\alpha > 5, \ k'} v_{\alpha k'}^{-1} \left\langle v_i v_j - \frac{1}{3} v^2 \delta_{ij} | \chi_{\alpha k'} \right\rangle \\ &\times \left\langle \chi_{\alpha k'} | \ | v_k v_l - \frac{1}{3} v^2 \delta_{kl} \right\rangle. \end{split}$$

Separating in Eq. (45) the explicit angular dependence on the velocity v, we obtain

$$\eta_{i\,jkl} = \sum_{k'=0, \pm 1, \pm 2} \left\langle \frac{v_i v_j}{v^2} - \frac{1}{3} \,\delta_{i\,j} \left| Y_{2k'}^{i} \left(\frac{\mathbf{v}}{v} \right) \right\rangle \right\rangle \\ \times \left\langle Y_{2k'}^{\mathrm{H}} \left(\frac{\mathbf{v}}{v} \right) \left| \frac{v_k v_l}{v^2} - \frac{1}{3} \,\delta_{kl} \right\rangle d_{k'}, \\ d_{k'} = \frac{4}{3} \cdot \left(\frac{1}{15} \right)^2 \sum_{\alpha > 5} \frac{\rho m}{T} \frac{|\langle v^2 | \varphi_{\alpha k}^{20} \rangle|^2}{v_{\alpha k'}}.$$

$$(46)$$

Using the property of the coefficients $d_k = d_{-k}$, we can represent the tensor η_{ijkl} in the following form^{74,82,83}:

$$\begin{aligned} \eta_{ijkl} &= \eta \left(\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} - \frac{2}{3} \delta_{ij} \delta_{kl} \right) \\ &+ \eta_1 \left(h_i h_k \delta_{jl} + h_i h_l \delta_{jk} + h_j h_l \delta_{ik} \right) \\ &+ h_j h_k \delta_{0l} - 4 h_i h_j h_k h_l \right) + \eta_2 \left(\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} - \delta_{ij} \delta_{kl} \right) \\ &+ h_i h_j \delta_{kl} + h_l h_k \delta_{lj} \\ &+ h_i h_j h_k h_l - h_i h_k \delta_{jl} - h_i h_l \delta_{jk} - h_j h_k \delta_{il} - h_j h_l \delta_{ik} \right), \\ \eta &= \sum_{k=0}^{\infty} \sum_{i=1}^{\infty} d_k, \quad \eta_1 = d_1 - d_0, \quad \eta_2 = d_2 - d_0. \end{aligned}$$
(47)

In the zeroth order approximation the coefficient η in Eq. (47) is identical with the scalar viscosity in the absence

of a magnetic field, whereas η_1 and η_2 vanish. (The coefficients d_k are then equal to one another.) The anisotropic part of the viscosity tensor appears because zeroth order eigenfunctions of the type $\chi_{\alpha 0} \propto Y_{20}^{\rm H} (M/M)$ acquire admixtures in the form of the functions $\chi_{\alpha 0} \propto Y_{20}^{\rm H}$ (v/v). This gives rise to a correction to the coefficient d_0 and the correction is of the first order in $\Delta v/v$. Corrections to the coefficients $d_{k\neq 0}$ appear only in the second order of perturbation theory in respect of the parameter $\Delta v/v$. Consequently, in the first order of perturbation theory the coefficients η_1 and η_2 are equal and are of the order of $\eta \Delta v / v$. In the absence of a magnetic field the viscosity tensor includes contributions of additional terms because zeroth order eigenfunctions of the type $Y_{2m}^{\rm H}$ (M/M), where $m \neq 0$, acquire admixtures in the form of the functions $Y_{2m}^{\rm H}(\mathbf{v}/v)$. This contribution is again of the order of $\eta \Delta v / v$.

Since for elements of the tensor η_{ijij} the above contribution is positive, we can say that the application of a magnetic field reduces the tensor component η_{ijij} by an amount of the order of $\eta \Delta v/v$ and thus reduces the widths Γ_3 and Γ_4 by $\Gamma_3 \Delta v/v$.

It should be noted that the observed changes in the widths Γ_3 and Γ_4 on application of a magnetic field are greater than the change in the width Γ_5 , because the former appear in a lower order of perturbation theory in respect of the parameter $\Delta v/v$. This is due to the fact that, because of invariance of the collision operator under spatial inversion, the operator \hat{I}_0 couples the functions $Y_{lm}(\mathbf{v}/v)$ and $Y_{lm}(\mathbf{M}/M)$ only if l is even. Therefore, in the case of the thermal conductivity (l=1), such a matrix element vanishes, whereas for the shear viscosity (l=2) it differs from zero. Consequently, the change in the shear viscosity in a magnetic field is proportional to $\Delta v/v$, whereas the change in the thermal conductivity is proportional to $(\Delta v/v)^2$.

Using the expressions for η_{ijkl} from Eq. (47), we can now calculate Γ_3 and Γ_4 :

$$\Gamma_{3} = \frac{q^{2}}{\rho} \left[\eta + \eta_{1} + \left(\frac{1}{4} \eta_{2} - \eta_{1} \right) \sin^{2} 2\theta \right], \qquad (48)$$

$$\Gamma_{4} = \frac{q^{2}}{\rho} \left[\eta + \eta_{1} + (\eta_{2} - \eta_{1}) \sin^{2} \theta \right], \cos \theta = \mathbf{h} \mathbf{e}_{\mathbf{x}}, \sin \theta = \mathbf{h} \mathbf{e}_{\mathbf{y}}.$$

Equations (18), (19), and (39) show that in the presence of a magnetic field the depths of the dips at the unshifted frequency ($\omega = 0$) in the depolarized scattering spectrum are described by

$$\Delta B_{\mathbf{s}}^{\mathbf{a}} \propto (\mathbf{he}_{z})^{2} (\mathbf{hq})^{2} (\mathbf{he}_{i})^{2} (\mathbf{he}_{2})^{2} = 0,$$
(49)
$$\Delta B_{\mathbf{s}}^{\mathbf{a}} \propto (\mathbf{he}_{y})^{2} (\mathbf{hq})^{2} (\mathbf{he}_{i})^{2} (\mathbf{he}_{2})^{2} \propto (\mathbf{he}_{i})^{2} (\mathbf{he}_{2})^{2} \sin^{2} 2\theta.$$

It is clear from Eq. (49) that the dip in the unpolarized spectrum appears only for the mode χ_3 and its maximum depth corresponds to the angle $\theta = 45^\circ$. The dip disappears in the case when **h** is parallel or perpendicular to **q**. The dip contrast *R* in the presence of the field is

$$R(\omega=0) \propto \frac{\Delta\eta}{\eta(v)} \sin^2 2\theta.$$

The dependence of the depth of a dip on the polarizations of the incident and scattered waves [Eq. (49)] is the same as for the intensity of the main component of the depolarized

scattering [see Eq. (36)]. Therefore, the contrast of the dip at the unshifted frequency is the same for the depolarized VH and HH scattering components, whereas in the absence of a magnetic field there is no dip for the HH component.

An investigation of the dependence of the width of the dip on the direction of the magnetic field makes it possible to separate the isotropic and anisotropic parts in the expression for the width of the dip Γ_3 . According to perturbation theory in respect of the parameter $\Delta \nu/\nu$ (accurate to the first order) this is sufficiently accurate for a complete description of all the components of the viscosity tensor. In fact, in this case we have $\eta_1 = \eta_2 = -\Delta \eta$, where $\Delta \eta > 0$ is the change in η due to the rotational degrees of freedom $\eta = \eta(v) + \Delta \eta$, and the width of the dip Γ_3 is described by the following simple expression

$$\Gamma_{3} = \frac{q^{2}}{\rho} \left[\eta \left(\nu \right) + \frac{3}{4} \Delta \eta \cdot \sin^{2} 2\theta \right].$$
(50)

For comparison, in the absence of the field the same quantity is

$$\Gamma_{\mathbf{3}}(\mathbf{H}=0)=\frac{q^{\mathbf{2}}}{\rho}\left[\eta\left(v\right)+\Delta\eta\right].$$

Therefore, the part of the width of the dip independent of the angle θ determines the part of the viscosity which depends only on the translational degrees of freedom. The anisotropic part of the width Γ_3 can be used to find the positive correction $\Delta \eta$, so that all three viscosity coefficients can be obtained ($\eta_1 = \eta_2 = -\Delta \eta$, $\eta = \eta(v) + \Delta \eta$) and thus describe completely the magnetic-field dependence of the viscosity tensor. We shall now consider the dependence of the width of an acoustic mode Γ_1 on the magnetic field. Using Eqs. (18) and (39), we can represent Γ_1 in the form

$$\Gamma_{i} = \sum_{ij} \frac{1}{2\rho} q_{i} q_{j} \xi_{ij},$$

$$\xi_{ij} = 2\rho \sum_{\alpha > 5, \ k} v_{\alpha k}^{-i} \langle \chi_{i} v_{i} | \chi_{\alpha k} \rangle \langle \chi_{\alpha k} | \chi_{i} v_{j} \rangle.$$
(51)

Using the explicit form of the function χ_1 from Eq. (13), we can separate in Eq. (51) the terms associated with the thermal conductivity and viscosity tensors, which are \varkappa_{ij} and η_{ijk} , respectively. In this way we obtain

$$\xi_{ij} = (\varkappa \delta_{ij} + \varkappa_1 h_i h_j) m \left(\frac{1}{c_v} - \frac{1}{c_p}\right) + \eta_{ixjx} + \delta_{ix} \delta_{jx} \zeta + \zeta_1 \left[h_i h_j \left(\delta_{ix} + \delta_{jx}\right) - \frac{2}{3} \delta_{ix} \delta_{jx}\right], \quad (52)$$

where

$$\zeta = \frac{\rho m}{T} \sum_{\alpha > 5} \frac{1}{9} \operatorname{v}_{\alpha 0}^{-1} |\langle v^2 | \varphi_{\alpha 0}^{00} \rangle|^2$$

is the usual second viscosity describing the kinetic energy dissipation independent of the magnetic field direction, whereas

$$\zeta_{i} = \frac{\rho m}{T} \cdot \frac{2}{5} \sum_{\alpha > 5} \frac{1}{9} \nu_{\alpha 0}^{-1} \langle \nu^{2} | \varphi_{\alpha 0}^{00} \rangle \langle \varphi_{\alpha 0}^{20} | \nu^{2} \rangle$$

is the second viscosity describing the effects which are anisotropic in respect of the magnetic field. Using Eqs. (51)–(52), we obtain the following final expression for the width Γ_1 of acoustic modes in the presence of a strong magnetic field:

$$\Gamma_{i} = \frac{mq^{2}}{2c_{p}c_{0}\rho} (\varkappa + \varkappa_{1}\cos^{2}\theta) + \frac{q^{2}}{2\rho} \zeta + \frac{q^{2}}{2\rho} \zeta_{1} \left(\cos^{2}\theta - \frac{1}{3}\right) + \frac{q^{2}}{2\rho} \left(\frac{4}{3}\eta + \eta_{1}\sin^{2}2\theta + \frac{4}{3}\eta_{2}\sin^{4}\theta\right).$$
(53)

It is clear from Eq. (53) that the width Γ_1 includes contributions from the isotropic and anisotropic components of the thermal conductivity, from the shear viscosity, and also the terms associated with the second viscosity. Estimates of all the transport coefficients occurring in Eq. (53) give the following results:

$$\varkappa$$
, $\eta \sim \frac{\Delta \nu}{\nu} \zeta$, ζ_i , η_i , $\eta_2 \sim \left(\frac{\Delta \nu}{\nu}\right)^2 \zeta$, $\varkappa_i \sim \left(\frac{\Delta \nu}{\nu}\right)^3 \zeta$.

It is clear from this estimate that within the perturbation theory framework the main contribution to the dependence of the width of an acoustic mode (or the attenuation of sound) on the magnetic field direction comes from the shear and second viscosities η_1 , η_2 , and ζ_1 . As in the case of the widths Γ_3 and Γ_5 , the width of an acoustic mode Γ_1 decreases on application of a magnetic field by an amount $\sim \Delta v/v\Gamma_1$ because of a corresponding reduction in ζ . The dependences of Γ_1 , Γ_3 , and Γ_5 on the magnetic field direction are shown in Fig. 7.

The contrast of the dips at the shifted frequencies in the



FIG. 7. Dependences of the values of Γ_5 , Γ_3 , and Γ_1 on the angle θ between the direction of the magnetic field and the scattering vector \mathbf{q} : a) $\varkappa = \varkappa_1$ is the thermal conductivity in the case when **H** is perpendicular to a gradient of the temperature $T \text{ and } \varkappa + \varkappa_1 = \varkappa_{\parallel}$ is the thermal conductivity in the case when **H** is perpendicular to the shear viscosity associated with the translational and rotational degrees of freedom, respectively; c) ζ_1 is the anisotropic part of the second (bulk or dilatational) viscosity.

presence of a magnetic field is

$$R(\omega = \Omega_{\rm B}) \sim \frac{\Delta \eta}{\zeta} \left(\cos^2 \theta - \frac{1}{3} \right)^2$$
(54)

and it is independent of the polarizations of the incident and scattered waves. It is clear from Eq. (54) that the quantity $R(\omega = \Omega_{\rm B})$ is maximal if **h** is parallel or perpendicular to **q**, i.e., it is maximal when there is no dip at all at the center.

4.3. Influence of effects even in respect of a magnetic field on the structure of the scattering spectrum

It is known that the application of a magnetic field gives rise to terms odd in respect of the field in the transport coefficients⁷⁴ and these terms disappear in the limit of sufficiently strong fields $\gamma H \gg \nu$. We can easily demonstrate [see Eqs. (41) and (51)] that the widths of the Rayleigh Γ_5 and Brillouin Γ_1 components of the polarized scattering are insensitive to these effects. In the scattering spectrum the odd effects may appear only in the fine structure of the depolarized part of the scattering at the unshifted frequency.

In the case of moderately strong magnetic fields $(\gamma H \sim \Delta \nu)$ the shear viscosity tensor η_{ijkl} is characterized by five independent components.⁷⁴ These components can be the complex quantities d_k , where $k = 0, \pm 1, \pm 2$ and the expansion (46) for these components satisfies the relationship $(d_k)^* = d_{-k}$ (Ref. 74). The values of d_0 , Re d_1 , and Re d_2 represent the effects which are even in respect of the field, whereas Im d_1 and Im d_2 represent the odd effects. These terms appear most clearly in the spectrum in the case when the magnetic field is directed along the scattering vector $(\mathbf{h} \| \mathbf{q})$. In this case the solution of the secular equation for the modes χ_3 and χ_4 gives two complex-conjugate eigenvalues:

$$\lambda_{1} = \frac{q^{2}}{\rho} \left[\operatorname{Re} d_{1} + i \left(\operatorname{Im} d_{1} + \frac{1}{\sqrt{2}} \operatorname{Im} d_{2} \right) \right] = \Gamma + i\Delta,$$

$$\lambda_{2} = \frac{q^{3}}{\rho} \left[\operatorname{Re} d_{1} - i \left(\operatorname{Im} d_{1} + \frac{1}{2} \operatorname{Im} d_{2} \right) \right] = \Gamma - i\Delta.$$
(55)

The existence of two complex-conjugate eigenvalues means that the fine structure of the depolarized part of the scattering has two dips with identical widths Γ displaced relative to the unshifted frequency by an amount Δ . The order of the ratio of Δ and Γ is as follows:

$$\frac{\Delta}{\Gamma} \sim \left(\frac{\Delta \nu}{\nu}\right)^2 \frac{\xi^3}{1+\xi^3}, \quad \xi = \frac{\gamma H}{\Delta \nu}.$$

4.0

Therefore, determination of the value of Δ from the splitting in the spectrum makes it possible to find Im $d_1 + (1/2)$ Im d_2 and thus estimate the contribution of the odd effects to the shear viscosity tensor. In the case when $\mathbf{h} || \mathbf{q}$ the depolarized scattering spectrum in a magnetic field consists of four components at frequencies $\pm \gamma H$ and $\pm 2\gamma H$ for the VH polarization of the scattering and of three components at frequencies $\pm 2\gamma H$ and $\pm 2\gamma H$ for the VH polarization of the scattering and of three components at frequencies $\pm 2\gamma H$ and $\omega = 0$ for the HH scattering. The splitting of the fine structure pointed out above should appear for the VH scattering polarization, because the fine structure in the $\mathbf{h} || \mathbf{q}$ case appears solely because shear waves χ_3 and χ_4 are admixed to functions of the Y_{1k} (M/M) type that contribute to the depolarized scattering at the frequencies $\pm \gamma H$. The intensities of the two split



FIG. 8. Fine structure of the I_{VH} component of the depolarized scattering spectrum in a magnetic field satisfying $\gamma H \sim \Delta \nu(\mathbf{h} || \mathbf{q})$. Here, 2Δ is the splitting between the shear modes χ_3 and χ_4 due to the effects which are odd in respect of the magnetic field.

profiles are the same. A qualitative appearance of the spectrum expected for this case is shown in Fig. 8. In the HH polarization case the fine structure does not appear at all because there are no components of the polarized spectrum at the frequencies $\pm \gamma H$. It should be pointed out that the spectrum is symmetric relative to the frequency $\omega = 0$. Therefore, reversal of the direction of the magnetic field, equivalent to the reversal $\omega \rightarrow -\omega$, does not alter the spectrum.

5. DISPERSION OF SOUND AND ALLOWANCE FOR VIBRATIONAL DEGREES OF FREEDOM

An analysis of the Rayleigh scattering spectrum is made above subject to the condition $qv \ll \Delta v, v$, where v and Δv are the frequencies of the collisions representing relaxation in respect of the translational and rotational degrees of freedom, respectively. This condition implies the absence of the dispersion of sound, because the frequency of sound in a medium which is governed by the parameter qv is much less than the relaxation frequencies v and Δv . All other relaxation frequencies Δv_h exhibited by a medium (for example, those associated with the conversion of the vibrational or electronic energy into the translational energy) are assumed to be very low compared with the frequency of sound: $\Delta v_k \ll qv$. Therefore, only the translational and rotational degrees of freedom can participate in the formation of hydrodynamic modes in a medium, particularly of acoustic modes.

If one of the relaxation frequencies Δv_k approaches the frequency of sound, i.e., if $\Delta v_k \sim qv$, the situation changes radically. It seems that a new degree of freedom characterized by a frequency Δv_k is activated in the formation of hydrodynamic modes. For example, the velocity of sound in an ideal gas on transition (on the gas density scale) through a dispersion region $\Delta v_k \sim qv$ changes from $u_- = v_0 (c_p^-/c_v^-)^{1/2}$ to $u_+ = v_0 (c_p^+/c_v^+)^{1/2}$, where c_p^- and c_v^- are the specific heats of the gas at constant pressure and constant volume deduced ignoring the k th degree of freedom, whereas c_p^+ and c_v^+ are the corresponding specific heats found allowing for the k th degree of freedom.

In describing the dispersion region in the kinetic approach it is necessary to supplement the set of quantities $Q = (\mathbf{p}, \mathbf{M})$ by new parameters which describe the activated degrees of freedom and are averaged over the appropriate period of motion. In the case of the vibational degrees of

freedom of a diatomic molecule this parameter is the vibrational energy $\mathscr{C}_v > 0$. The scalar parameter \mathscr{C}_v can be treated classically or by quantum theory. In the latter case the integration with respect to dQ is understood to be summation over the energy levels \mathscr{C}_v .

By way of example, we shall consider in greater detail the dispersion of sound due to activation of the vibrational degrees of freedom in a diatomic molecule. In this case in the transport equation for the correlation function of the oneparticle distribution function the collisional term can be separated into two components $\hat{I}_0 = \hat{I} + \Delta \hat{I}_k$, the first of which describes collisions without a change in the vibrational energy \mathscr{C}_v and the second those accompanied by a change in \mathscr{C}_v . The characteristic frequencies of the operators \hat{I} and $\Delta \hat{I}_k$ are Δv and Δv_k , respectively, and they satisfy the inequality $\Delta v \ge \Delta v_k$. It follows from this inequality that the operator $\Delta \hat{I}_k$ together with the operator $i\mathbf{q}\cdot\mathbf{v}$ can be regarded as a small correction to \hat{I} and we can use perturbation theory in terms of the parameter $(i\mathbf{q}\cdot\mathbf{v} + \Delta v_k)/\Delta v$.

In the zeroth order approximation of perturbation theory the space of the eigenfunctions of the operator \hat{I} splits into hydrodynamic eigenfunctions without allowance for the vibrations $\chi_i(\mathbf{v}, M)$, where i = 1, ..., 5, and the vibrational eigenfunctions $\chi_v(\mathscr{C}_v)$ dependent only on \mathscr{C}_v .

The functions $\chi_i(\mathbf{v}, \mathbf{M})$ and $\chi_v(\mathscr{C}_v)$ represent the zeroth order subspace in which the eigenfunctions of the operator \hat{I} vanish.

In constructing the correct hydrodynamic modes in the first order of perturbation theory in respect of the parameter $(i\mathbf{q}\cdot\mathbf{v} + \Delta v_k)/\Delta v$ it is necessary to solve the secular equation and to find the corresponding eigenvalues in the zeroth subspace. The simplest case of a secular equation is obtained when the collision frequency accompanied by resonant transfer of the vibrational energy $\Delta v_{\rm res}$ is many times greater than the collision frequency accompanied by the transfer of a vibrational energy Δv_k to other degrees of freedom (rotational or translational). In this case a vibrational temperature is established in a system quite rapidly (in a time $\tau \sim \Delta v_{\rm res}^{-1}$) and this temperature relaxes relatively slowly (in a time $\tau \sim \Delta v_k^{-1}$) to the equilibrium gas temperature T. From the point of view of the transport equation this description means that among all the vibrational modes the one that plays the dominant role is the mode φ_k $= (\mathscr{C}_v - \overline{\mathscr{C}}_v) / \Delta \mathscr{C}_v$, where $\overline{\mathscr{C}}_v = T$ is the average vibrational energy and $\Delta \mathscr{C}_{v}$ is the dispersion (scatter) of the vibrational energy describing relaxation of the vibrational energy of the system to the equilibrium value \mathcal{B}_{v} .

In deriving the secular equation it is sufficient to consider just one mode φ_k . In this approximation, which corresponds to $\Delta v_{\rm res} \gg \Delta v_k$, the secular equation is of the third order:

$$[\lambda^{2} + (qu_{-})^{2}] \lambda = [\lambda^{2} + (qu_{+})^{2}] \Delta v_{k}, \qquad (56)$$

where u_{-} and u_{+} are the values of the velocity of sound obtained ignoring and allowing for the vibrational degrees of freedom, respectively:

$$\Delta v_{k} = \left[1 + \frac{1}{(c_{v}^{2})^{1/2}}\right]^{2} \langle \varphi_{k} | \Delta \hat{I}_{k} | \varphi_{k} \rangle,$$



FIG. 9. Dispersion of the velocity of sound u_{ac} (a) and of the absorption coefficient of sound Γ_1 (b) due to vibrational degrees of freedom. Here, u_{-} and u_{+} are the velocities of sound deduced ignoring and allowing for the vibrational degrees of freedom; Δv_k is the frequency of transfer of the vibrational energy to other degrees of freedom (translational or rotational); Δv is the frequency of the rotational-translational exchange of energy.

where c_{ν}^{-} is the specific heat of a molecule without allowance for the vibrations.

Equation (56) can be reduced by a simple substitution of the variables $\lambda = -i\Omega$ and $\Delta v_k = 1/\tau$ to the familiar dispersion equation of the Mandel'shtam-Leontovich relaxation theory of propagation of sound in a liquid with one relaxation time τ (Ref. 85). It is known that Eq. (56) has three roots, two of which λ_1 and λ_2 are complex-conjugate and correspond to two traveling acoustic modes, whereas the third root $\lambda_3 \sim \Delta v_k$ is real and it determines the frequency of conversion of the vibrational energy to the translational or rotational forms. Although Eq. (56) is quite familiar in the case of liquids, it would be of interest to consider its solution for a gas when the variable is the gas density. If we solve the secular equation (56), we can obtain an explicit expression of Im $\lambda_1 = -$ Im λ_2 or for the velocity of sound throughout the full range of variation of the gas density. This dependence is shown in Fig. 9a. Calculations of the absorption of sound or of the width of hydrodynamic modes $\operatorname{Re} \lambda_1 = \operatorname{Re} \lambda_2$ showed that in the range of low gas densities corresponding to $\Delta v_k \ll qv$ the second-order corrections $\sim (qv)^2/\Delta v$ exceed the first order corrections Δv_k and determine the widths of acoustic modes. Figure 9b shows the dependence of the width of acoustic modes on the gas density. We can see from this figure there are three characteristic parts of this dependence.

In the range of low densities $(qu_{-})^{2}/\Delta v \gg \Delta v_{k}$ the width of acoustic modes is inversely proportional to the density and is independent of the vibrational process. In this case we can calculate the spectrum ignoring the vibrational degrees of freedom.

In the second part of the dependence in Fig. 9b the attenuation of sound varies linearly with the density

$$\Gamma_{i} = \operatorname{Re} \lambda_{i} = \frac{1}{2} \left(1 - \frac{u_{i}^{2}}{u_{i}^{2}} \right) \Delta v_{k}.$$

This rise continues until $\Delta v_k \leq qu_-$. The maximum value of the width is $(\Gamma_1)_{\max} \approx 2q(u_- - u_+)$, i.e., it is twice the discontinuity of the velocity of sound because of dispersion (Fig. 9a). A further increase in the gas density has the effect that the vibrational mode φ_k becomes nonhydrodynamic, $\Delta v_k \geq qu_-$, and the linear rise changes to a fall in accordance with the law

$$\Gamma_{1} = \frac{1}{2} \left(1 - \frac{u_{+}^{2}}{u_{-}^{2}} \right) \frac{(qu_{-})^{2}}{\Delta v_{k}}.$$

We recall that here, as in region II of Fig. 9b, there is a scale factor

 $\frac{1}{2}\left(1-\frac{u_{+}^{2}}{u_{-}^{2}}\right)$,

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which is known to decrease gradually on activation of an increasing number of degrees of freedom and its value is maximal for the dispersion due to the rotational relaxation. In the case of a diatomic molecule this factor is

$$\frac{1}{2}\left(1-\frac{u_{+}^{2}}{u_{-}^{2}}\right)=0.08$$

•

for the rotational degrees of freedom and 0.04 for the vibrational ones.

It follows from the above analysis that in the dispersion region $\Delta v_k \sim qv$ the width of acoustic modes (or the absorption of sound) depends strongly on three parameters: Δv_k , u_- , and u_+ . Such a simple result is a consequence of inclusion in the secular equation of only the φ_k mode. In general, if we allow for the contribution to the attenuation of sound of all the other vibrational modes, we encounter small corrections of the order of $(\Delta v_k / \Delta v_{res})$ (Ref. 3) to the second viscosity or to the width of an acoustic mode Γ_1 in the region where $\Delta v_k \gg qu_-$. Then, the slope of the linear part of the dependence of Γ_1 on the density (region II in Fig. 9b) is still governed only by the relaxation frequency of the vibrational energy Δv_k .

It therefore follows that deviation of the dispersion law of sound from the simple Mandel'shtam-Leontovich relaxation theory is manifested by the dependence of the absorption of sound on the density of gas in region III of Fig. 9b and it may be significant if the parameter $\Delta v_k / \Delta v_{res}$ approaches unity. This case may be encountered, for example, for molecules which are at high vibrational levels where because of the anharmonicity the probabilities of the vibrational-translational Δv_k and resonance vibrational-vibrational relaxation Δv_{res} processes become of the same order of magnitude.^{73,86} Clearly, the parameter $\Delta v_k / \Delta v_{res}$ is close to unity if the dispersion of sound is related to the rotational degrees of freedom for which the ratio of the rotational-translational and rotational-rotational relaxation frequencies is of the same order of magnitude.^{73,86}

The maximum of the dependence of the absorption of sound on the gas density (Fig. 9b) at gas pressures of the order of atmospheric corresponds to ultrasonic frequencies if the dispersion of sound is due to the vibrational degrees of freedom and changes greatly with the nature of the molecule. For example, in the case of oxygen this frequency is ~ 10 Hz, whereas for the CO₂ molecules it is $\sim 5 \times 10^4$ Hz (Ref. 86). If the dispersion of sound is due to the rotational degrees of freedom, the corresponding frequency is considerably higher. For example, in the case of molecular hydrogen at atmospheric pressure the resonance frequency is $\sim 10^7$ Hz (Ref. 86). In this case the dependence of the ab-



FIG. 10. Dispersion of the transport coefficients \varkappa , η , and ζ due to the rotational degrees of freedom of a molecule. Here, $\Delta \nu$ is the frequency of the rotational-translational energy exchange; u_{-} is the velocity of sound deduced allowing only for the translational degrees of freedom; $\varkappa(v)$ and $\eta(v)$ are the thermal conductivity and the shear viscosity associated solely with the translational degrees of freedom.

sorption of sound on the gas density can be deduced from the width of the Brillouin components and the frequency of sound corresponding to the absorption maximum $\Omega_{\max} \approx qv$ can change because of a change in the scattering angle θ , since $q \approx 2k \sin(\theta/2)$.

Since the widths of hydrodynamic modes are related uniquely to the transport coefficients [see Refs. 57 and 58 and the formulas in Eq. (20)], the dispersion of the widths of these modes can be regarded as the dispersion of the corresponding transport coefficients. In particular, activation of additional vibrational degrees of freedom results in the dispersion of the second viscosity ζ . Then, neither the thermal conductivity nor the shear viscosity show dispersion, because they appear due to the coupling between hydrodynamic modes and nonhydrodynamic modes of the vector and second-rank tensor types, respectively [see Eq. (21)].

However, if the dispersion of sound is due to the rotational degrees of freedom characterized by the vector parameter \mathbf{M} , the dispersion may be exhibited both by the shear viscosity and the thermal conductivity. It should be pointed out that an increase in the thermal conductivity in this case is hindered by the selection rules relating to the spatial parity. This case is illustrated in Fig. 10.

6. CHARACTERISTICS OF THE RAYLEIGH SPECTRUM OF LIGHT SCATTERING IN A NONIDEAL GAS

The description of the Rayleigh light scattering spectrum given in preceding sections is based on the Boltzmann transport equation, which is valid in the case of an ideal gas. Essentially the concept of an ideal gas implies the following restrictions: 1) collisions are binary or they can be described in the impact approximation; 2) gas molecules are free to rotate. The first restriction is satisfied if $\tau_c \ll \tau = 1/\nu$, where τ_c is the collision time, τ is the time between collisions, and ν is the frequency of gaskinetic collisions (sec⁻¹). This condition can be rewritten in the form $\tau_c / \tau \sim Nd^3 \ll 1$, where d is

the range of the molecular forces and N is the density of the particles in the gas (cm^{-3}) . The small parameter Nd³ is usually called the gaseous state parameter.

We can easily demonstrate that when the second restriction relating to free rotation of molecules in a gas is obeyed, the angular velocity of rotation of a molecule Ω must be higher than the collision frequency v. Since $\Omega \sim 1/\tau_c$, this condition reduces to the previous one $\tau_c v \ll 1$ or we have $Nd^3 \ll 1$. In the case of simple molecular gases we have $d \sim 10^{-7}$, which gives the following familiar restriction on the gas density associated with the impact approximation: $N < 10^{21}$ cm⁻³ or the gas pressure at room temperature p < 30 atm (Ref. 87).

When the gas pressure is increased ($p \sim 100$ atm), the effects associated with the mutual correlation of particles or deviation of the gas from its ideal behavior begin to be felt. The spectral composition of the scattered light depends on the nature of the equation describing the kinetics of a nonideal gas. In the first order of the gaseous state parameter Nd^3 the corrections to the transport equation are known to reduce to an allowance for nonlocal pair and local triple collisions.^{68,88,89} The contribution of triple collisions simply increases slightly the eigenvalues of the Boltzmann collision operator, because these collisions do not disturb the local laws of conservation of the number of particles and their momentum and energy. More interesting results for the spectrum are obtained when nonlocal corrections to the collision integral are considered.

It is shown in Refs. 65, 88, and 89 that the linearized transport equation for the function $\chi_{\omega q}$ is

$$i (\mathbf{q}\mathbf{v}_{1} - \omega) \chi_{\omega q} + (\hat{I}_{0} + \Delta \hat{I}_{0}) \chi_{\omega q} + \hat{I}_{2} i (\mathbf{q}\mathbf{v}_{1} - \omega) \chi_{\omega q} + i \mathbf{q} \hat{I}_{1} \chi_{\omega q}$$

= $B_{0} + B_{1} (\mathbf{M}) + B_{2} \left(\frac{\mathbf{M}}{\mathbf{M}}\right),$ (57)

where

$$\begin{split} B_0 &= \alpha_0 \; (\mathbf{e_1 e_2}), \\ B_1 &= \alpha_1 \; \left([\mathbf{e_1 e_2}] \frac{M}{M_0} \right) \; , \\ B_2 &= \; -\frac{1}{3} \; \alpha_2 \; \left\{ \frac{(\mathbf{M e_1}) \; (\mathbf{M e_2})}{M^2} - \frac{1}{3} \; (\mathbf{e_1 e_2}) \right\} \; , \end{split}$$

and α_1 is the antisymmetric part of the polarizability tensor. We have retained here the antisymmetric component of the scattering of light; \hat{I}_0 is the Boltzmann collision operator; $\Delta \hat{I}_0$ is the correction of the order of Nd³ to the Boltzmann integral due to triple collisions; the nonlocal part of the collision integral $i\mathbf{q} \cdot \mathbf{I}_1$ is in fact a correction of the order of Nd³ to the nonlocal free motion operator $i\mathbf{q}\cdot\mathbf{v}$. The operator $i\mathbf{q}\cdot\mathbf{I}_{1}$ violates the local laws of conservation of energy and momentum: $\langle \mathscr{C} | i \mathbf{q} \hat{\mathbf{I}}_1 \neq 0, \langle v | i \mathbf{q} \hat{\mathbf{I}}_1 \neq 0, \text{ but conserves the number of} \rangle$ particles $\langle 1 | i q \hat{I}_1 = 0$. The operator \hat{I}_2 is related to the finite nature of the collision time (of the order of Nd³ on I_0) and violates only the local law of conservation of energy $\langle \mathscr{C} | I_2 \neq 0$, but conserves momentum and the number of particles $\langle \mathbf{v} | \hat{I}_2 = \langle 1 | \hat{I}_2 = 0$. The most interesting qualitative difference between Eq. (57) and the equation for an ideal gas is that the nonlocal correction $i\mathbf{q}\cdot\hat{\mathbf{I}}_1$ couples shear modes $\chi_3 = v_v / v_0$ and $\chi_4 = v_z / v_0$ to the modes Y_{1m} (M/M) describing the antisymmetric scattering. An explicit calculation of the normal and inverse matrix elements of the operator $i\mathbf{q}\cdot\hat{\mathbf{I}}_1$ gives the relationships

$$\left\langle \frac{v_y}{v_0} |i\mathbf{q}\hat{\mathbf{I}}_1| \frac{M_z}{M_0} \varphi_\alpha(M) \right\rangle$$

$$= -iq \left(\frac{I}{m} \right)^{1/2} \left\langle \frac{M_z}{M_0} |\hat{I}_0| \frac{M_z}{M_0} \varphi_\alpha(M) \right\rangle$$

$$= -2 \left\langle \frac{M_z}{M_0} \varphi_\alpha(M) |i\mathbf{q}\hat{\mathbf{I}}_1| \frac{v_y}{v_0} \right\rangle,$$

$$\left\langle \frac{v_z}{v_0} |i\mathbf{q}\hat{\mathbf{I}}_1| \frac{M_y}{M_0} \varphi_\alpha(M) \right\rangle$$

$$= iq \left(\frac{I}{m} \right) \left\langle \frac{M_y}{M_0} |\hat{I}_0| \frac{M_y}{M_0} \varphi_\alpha(M) \right\rangle$$

$$= -2 \left\langle \frac{M_y}{M_0} \varphi_\alpha(M) |i\mathbf{q}\hat{\mathbf{I}}_1| \frac{v_z}{v_0} \right\rangle.$$

$$(58)$$

These relationships are consequences of the law of conservation of the total angular momentum $\mathbf{M} + [\mathbf{rp}]$ written in the form of matrix elements of the total collision operator in the Fourier representation in respect of 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 obeyed rigorously only when we allow for the nonlocal nature of the collision integral was considered by Kagan and Maksimov.⁹⁰ They allowed for a new integral of motion and supplemented the usual equations of hydrodynamics with an equation for the total angular momentum.

Since the normal and inverse matrix elements of Eq. (58) are purely imaginary and have opposite signs, it follows that the fine structure appears in the antisymmetric scattering and it is manifested by a narrow peak of width Γ_3 and intensity I_a :

$$\Delta_{B_3^a} = \sum_{\alpha > 5} v_{\alpha}^{-1} \left(q \hat{I}_{1\alpha} \right)_{3\alpha} B_{1\alpha} = -q \left(\frac{I}{m} \right)^{1/2} \left\langle \frac{M_z}{M_0} \middle| B_1(\mathbf{M}) \right\rangle,$$

$$\Delta B_4^a = q \left(\frac{I}{m} \right)^{1/2} \left\langle \frac{M_y}{M_0} \middle| B_1(\mathbf{M}) \right\rangle, \qquad (59)$$

$$I_a \propto (\Delta B_3^a)^2 + (\Delta B_4^a)^2 \propto \alpha_1^2 q^2 \frac{I}{m} \{ [\mathbf{e}_1 \mathbf{e}_2]^2 - ([\mathbf{e}_1 \mathbf{e}_2] \mathbf{e}_x)^2 \},$$

where I and m are the moment of inertia and the mass of a molecule.

Physically the appearance of a peak is associated with the process of relaxation of vortices in a dense gas, i.e., conversion of the orbital momentum of the vortices [**rp**] into the internal angular momentum M. In the Boltzmann approximation the orbital angular momentum is conserved.

The contrast of a peak (relative to the wide antisymmetric part of the scattering) is a small quantity of the order of $\sim (Nd^3)^2$ and it rises significantly only on approach to the liquid state.

One should seek this peak in the HH polarization of the depolarized scattering, when at the unshifted frequency there is no contribution due to the fine structure of the symmetric scattering. This case is represented in Fig. 11. Experimental observations of antisymmetric scattering of molecules are usually very difficult because of the smallness of the relevant scattering cross section $(\alpha_1/\alpha_{10})^2 \sim 10^{-8}$ (Ref. 91). However, as demonstrated by Baranova and Zel'dovich in Ref. 91 this cross section may be increased greatly to val-



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FIG. 11. Depolarized (HH) spectrum of light scattering in a nonideal gas: 1) peak in the antisymmetric component of the spectrum associated with the exchange of angular momentum between the internal M and orbital [rp] momenta; 2) dips in the symmetric component of the spectrum due to the contribution of the rotational degrees of freedom to the shear viscosity η .

ues $(\alpha_1/\alpha_0)^2 \sim 10^{-2}$ by approaching an electronic absorption band of molecules.

Other changes in the scattering spectrum due to the nonideal nature of the gas are manifested as follows. Firstly, the dependence of the velocity of sound on the gas density gives rise to a similar density dependence of the splitting of a Brillouin doublet. The relative change in the doublet frequency is proportional to the paramter Nd^{3} . The dependence of the velocity of sound u_{ac} on the gas density in the absence of dispersion is described by the virial coefficient

$$B(T) = \int (1 - e^{-U_{12}/T}) \, \mathrm{d}\mathbf{r} \, \mathrm{d}o_{n_1} \, \mathrm{d}o_{n_2},$$

where U_{12} is the potential of interaction of molecules in the gas:

$$u_{ac} = v_0 \left(\frac{c_p}{c_v}\right)^{1/2} \left(1 + NB + \frac{NT}{c_p} \frac{\mathrm{d}B}{\mathrm{d}T} + \frac{N}{2c_p c_v} \frac{\mathrm{d}T^2}{\mathrm{d}T} \frac{\mathrm{d}B}{\mathrm{d}T}\right).$$
(60)

In the case of a van der Waals gas we have B(T) = b - (a/T) and the relative shift of the doublet frequency is

$$\frac{\Delta\Omega}{\Omega} = N\left(b - \frac{c_v}{c_p} \frac{a}{T}\right).$$

For example, in the case of the N_2 molecule variation of temperature alters the virial coefficient from $B(T = 300 \text{ K}) = -1 \times 10^{-23} \text{ cm}^3 \text{ to } B(T = 1000 \text{ K}) = 5 \times 10^{-23} \text{ cm}^3$, and in the case of H_2 the change is from $B(T = 50 \text{ K}) = -7 \times 10^{-23} \text{ cm}^3$ to $B(T = 1000 \text{ K}) = 3 \times 10^{-23} \text{ cm}^3$ (Ref. 92). Hence, it is clear that the shift of the doublet frequency (or the dispersion of the velocity of sound) can be positive or negative, depending on the actual temperature. An estimate of the order of magnitude of the ratio $\Delta\Omega/\Omega$ for simple molecules gives $\Delta\Omega/\Omega \sim 10^{-3}$ when the gas pressure is altered by one atmosphere, which is readily observed when modern laser spectroscopy methods are used.⁹³

Secondly, the contrast of narrow dips in the spectrum of the depolarized scattering is a function of the gas density.

Using Eq. (57), we can obtain expressions for the contrast of the dips $R(\omega = 0)$ and $R(\omega = \Omega_B)$ (Ref. 65) which in the subsequent analysis can be represented conveniently in the following simple form using perturbation theory in respect of the parameter $\Delta v/v$:

$$R(\omega = 0) = \frac{\Delta B_3^2 + \Delta B_4^2}{B_2^2} \frac{\Delta v}{\Gamma_9} \sim \frac{\Delta v + (\Delta \hat{I}_0)_{MM}}{v + \langle \Delta \hat{I}_0 \rangle_{vv}} (1 + 2NB(T)),$$

$$R(\omega = \Omega_B) = \frac{\Delta B_1^2}{B_2^2} \frac{\Delta v}{\Gamma_1} \sim \frac{\Delta v + \langle \Delta \hat{I}_0 \rangle_{MM}}{v + \langle \Delta \hat{I}_0 \rangle_{DD}} R(\omega = 0);$$
(61)

here, $\langle \Delta \hat{I}_0 \rangle_{\rm MM}$ and $\langle \Delta \hat{I}_0 \rangle_{vv}$ are positive corrections to the collision frequencies Δv and v, respectively, and they are due to triple collisions; B(T) is the virial coefficient. It should be noted that the expressions in Eq. (61) represent an estimate of the order of magnitude of the contrast so that we have omitted numerical factors of the order of unity, which follow from a more rigorous microscopic expression for R. A correction proportional to the virial coefficient B(T) is associated with the operators \hat{I}_1 and \hat{I}_2 , which allow for the spatial and temporal nonlocality of double collisions. In the case of a van der Waals gas we have B = b - (a/T), where the parameter b is proportional to the molecular volume d^3 and

$$a \propto \int_{d}^{\infty} |U_{12}| \, \mathrm{dr} \, \mathrm{d}o_{\mathbf{n_1}} \, \mathrm{d}o_{\mathbf{n_2}}$$

is governed by the long-range part of the potential. Then, at high temperatures when $U_{12}/T \ll 1$ the main role in the interaction potential is played by the repulsion region $B \approx b$. which increases the contrast $R(\omega = 0)$ on increase in the gas density N. If we ignore the contribution of triple collisions, this case corresponds to models of the Enskog type.⁵⁸ Specific numerical calculations of $R(\omega = 0)$ carried out using the Enskog model for hard ellipsoids were given by Cole, Hoffman, and Evans.⁵⁶ As already mentioned in the Introduction, these authors found that the dip depth is independent of the shape of the molecule and that this depth rises linearly with the gas density. In our view, the contrast of a dip in this model does depend on the shape of the molecule via the parameter $\Delta v/v$. (In particular, in the case of weakly anisotropic molecules, we have $\Delta \nu / \nu \rightarrow 0$, i.e., the contrast of the dip is small.)

In the region of sufficiently low gas temperatures, when $U_{12}/T \sim 1$ and the main role is played by the long-range part of the potential, the virial coefficient B(T) may become negative: $B(T) \approx -a/T$. This reduces the dip contrast on increase in the gas density.

The contribution of triple collisions which effectively reduces to redefinition of the collision frequencies Δv and vis manifested directly in the gas-density dependence of the ratio of the dip contrasts $R(\omega = \Omega_{\rm B}/R(\omega = 0))$ and, therefore, can be found experimentally.

7. CONCLUSIONS

The above kinetic approach to the calculation of the light scattering spectrum of molecular gases is very promising because it makes it possible to provide a completely microscopic description of the structure of the spectrum. In particular, in the case of the Boltzmann gas it is possible to calculate completely the fine structure of the Rayleigh scattering spectrum in the polarized and depolarized components, i.e., to find all the components of the scattering tensor (Fig. 5). Within the framework of this method it is convenient to allow for the influence of external fields, particularly of the magnetic field \mathbf{H} , on the internal degrees of freedom of molecules. In the case of rotating molecules the application of a magnetic field gives rise to a dependence of the parameters of the spectrum on the intensity and direction of \mathbf{H} , which makes it possible to identify the contribution of the rotational degrees of freedom to all the transport coefficients (Fig. 7).

The application of the kinetic method to the description of the dispersion of sound provides a criterion of validity of the Mandel'shtam-Leontovich phenomenological theory. An allowance for corrections due to the nonideal nature of a gas gives rise to a narrow peak in the antisymmetric component of light scattering, associated with the exchange of the angular momentum between the translational and rotational degrees of freedom. The parameters of the spectrum of a nonideal gas can be expressed in terms of the virial coefficient B(T).

We shall conclude by noting that the kinetic approach is used above only for the unshifted pure Rayleigh scattering subject to the simplest assumptions on the structure of the collision integral and on the simultaneous correlation function of the distribution, namely, the collision operator is regarded as self-adjoint and the simultaneous correlation function applies to an equilibrium ideal gas. Dropping of the first assumption makes it possible, for example, to study a gas consisting of stereoisomeric molecules.⁷¹ An allowance for the nonideal nature of the gas in the case of simultaneous correlation functions renormalizes the polarizability, which no longer reduces to the polarizability of a single molecule and this corresponds to the Lorentz-Lorenz effect for the permittivity of a medium.⁶⁹ These corrections alter the integrated intensity of the scattered light. The same method can be used to study the rotational Raman scattering spectrum of gases. One can expect interesting features in the spectrum associated with the interference between hydrodynamic and nonhydrodynamic modes if one considers a nonequilibrium gas in which single nonhydrodynamic modes are excited externally. For example, an external laser can be used to increase considerably the vibrational temperatures of a gas, which corresponds to the excitation of a vibrational mode φ_k , the flow of a gas along a tube can be used to excite shear modes, etc.

The published theoretical calculations of the scattering spectrum for a nonequilibrium medium, associated with the presence of temperature and velocity gradients, give ambiguous results^{94–97} and the available experimental results are still few and far between. We know of only two studies of the polarized scattering spectrum in the presence of a temperature gradient in water and in fused quartz.^{98,99}

All these features of the scattering spectrum of a gas can be readily observed by modern laser spectroscopy methods and experimental investigations in this field would in our opinion provide very interesting results.

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