

# Spectrum of Rayleigh scattering of light in a nonequilibrium gas

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The spectrum of Rayleigh scattering of light in a molecular gas is theoretically investigated for three forms of stationary disequilibrium: a temperature gradient, a macroscopic-velocity gradient, and a difference between the rotational and translational gas temperatures. The calculation is based in the kinetic method of determining the fluctuations in a nonequilibrium gas. The calculated scattering spectra for temperature and velocity gradients differ from the corresponding published ones mainly in that they contain asymmetric additions if the spectrum is polarized and account is taken of the changes in the depolarized part of the spectrum. These changes are of the same order for the temperature and velocity gradients as the effects in a polarized spectrum. The effect of the third form of disequilibrium on the scattering spectrum is considered for the first time ever.

## 1. INTRODUCTION

Theoretical and experimental research into the statistical properties of nonequilibrium media has greatly increased of late (see, e.g., Ref. 1). A feature of the theoretical studies is a large number of procedures (the hydrodynamic method,<sup>2–7</sup> the kinetic method,<sup>8,9</sup> the nonlinear-response method,<sup>10–13</sup> and some of their variants<sup>14,15</sup>), which lead, however, to ambiguous results.

A critical review of these studies is in our opinion of interest in itself and is not the subject of the present article. We note only that back in 1970 Gantsevich, Gurevich, and Katilyus<sup>16</sup> have derived all the fundamental equations needed to calculate fluctuations in a nonequilibrium state.

Historically, the question of Rayleigh scattering of light in a nonuniformly heated crystal was first considered by Mandel'shtam<sup>17</sup> and quantitative by Leontovich<sup>19</sup> very long ago and was expounded in detail in Fabelinskii's book.<sup>19</sup> The difference predicted by Leontovich<sup>18</sup> between the intensities of the Brillouin components under conditions of a temperature gradient was found to be too small to be observed in experiment.<sup>19</sup> Asymmetry in doublet intensities in a temperature gradient became observable experimentally only recently, in 1980 and 1984, first in a liquid (water<sup>20,21</sup>) and later in a solid (fused quartz<sup>22</sup>).

The effect was first observed qualitatively in a 1980 study of scattering of light by non-uniformly heated water, by Beysens, Garrabos, and Zalcser,<sup>21</sup> but was quantitatively about one-third the value predicted by the theory.<sup>21</sup> Later Kifte, Clouter, and Penney<sup>24</sup> improved in 1984 the quantitative agreement between theory and experiment for water, and observed for the first time asymmetry of the scattering spectrum in fused quartz under temperature-gradient conditions. The results for fused quartz are still approximate, in view of the low scattered-light intensity which was recorded in these experiments at very small scattering angles,  $\theta \lesssim 1^\circ$ .

We calculate here the spectrum of Rayleigh scattering of light in a molecular gas under three types of disequilibrium: 1) temperature gradients; 2) macroscopic-velocity gradient; 3) difference between the rotational and translational gas temperatures. The calculation is based on equations derived by Gantsevich, Gurevich, and Katilyus.<sup>16,23</sup> We show that the changes produced in the scattering spectrum of a

molecular gas by the first two types of disequilibrium occur, generally speaking, in both the polarized and depolarized components of the scattering spectrum. This result differs from previously known ones<sup>6–9</sup> first, in that account is taken of the changes occurring in the depolarized component of the scattering spectrum and having the same orders in the temperature gradients and velocity gradients as the changes in the polarized spectrum, and heretofore not taken into account. Second, besides the known changes of the intensities of the polarized-triplet components, increments asymmetric in frequency appear in the spectrum (see Fig. 1 below). The effect exerted by the third type of inhomogeneity, due to the difference between the rotational and translational gas temperatures, was heretofore, to our knowledge, not considered in the literature. Note that the two effects are not included in the usual hydrodynamic approach to the calculation of a scattering spectrum, and contain terms of higher order of smallness in the hydrodynamic parameter  $l/\lambda$ , where  $l$  is the gas-molecule mean free path and  $\lambda$  is the wavelength of the light.

## 2. CALCULATION OF THE SCATTERING SPECTRUM IN A NONEQUILIBRIUM GAS

The calculation of the scattering spectrum in a nonequilibrium gas by the kinetic method developed in Refs. 16 and 23 consists of three stages: 1) determination of the function  $\bar{f}$  that describes the stationary nonequilibrium state of the gas; 2) determination of the equal-time correlator of the fluctuations of the distribution function  $f$  relative to the nonequilibrium stationary function  $\bar{f}$ ; 3) solution of the kinetic equation for the fluctuation correlator with the initial condition obtained from stage 2.

For a stationary nonequilibrium state with constant gradients of the temperature or of the velocity, the kinetic equation for  $\bar{f}$  (Ref. 21) can be represented in the form

$$\frac{m}{T} \left( v_i v_k - \frac{1}{3} \delta_{ik} v^2 \right) V_{ik} + \frac{E(Q) - c_p T}{T^2} \mathbf{v} \nabla T = I(\bar{f}), \quad (1)$$

where  $\bar{f} = f_0(1 + \bar{\chi})$ ,  $\bar{\chi} \ll 1$ . It is assumed here that the deviations of the function  $f$  from the equilibrium Boltzmann distribution  $f_0$  are small, therefore the collision integral  $I$  in Eq. (1) is written in linearized form.<sup>23</sup> The function  $f = f(Q)$

pertains to a diatomic molecular gas with translational and rotational degrees of freedom, so that the quantity  $Q = (\mathbf{v} \cdot \mathbf{M})$  contains the velocity  $\mathbf{v}$  and the angular momentum  $\mathbf{M}$  of the molecule. The quantity  $E(Q) = mv^2/2 + IM^2/2$  is the total energy of the molecule, where  $m$  and  $I$  are the mass and the moment of inertia of the molecule;  $c_p$  is the specific heat of the molecule at constant pressure. The parameters  $V$  and  $T$  determine the macroscopic values of the velocity and temperature of the gas, and  $V_{ik} = 1/2(\partial V_i/\partial x_k + \partial V_k/\partial x_i)$ . Summation over repeated indices is implied. Note that the left-hand side of (1) is the spatial derivative of a function  $f_0(Q, \mathbf{R})$  that is in local equilibrium and depends on  $\mathbf{R}$  via the dependences of the quantities  $\mathbf{V} = \mathbf{V}(\mathbf{R})$  and  $T = T(\mathbf{R})$  on the spatial coordinates:

$$f_0^{-1} \mathbf{v} \frac{\partial f_0}{\partial \mathbf{R}} = \frac{m}{T} \left( v_i v_k - \frac{1}{3} \delta_{ik} v^2 \right) V_{ik} + \frac{E(Q) - c_p T}{T^2} \mathbf{v} \nabla T. \quad (1')$$

The solution of the integral equation (1) for the function  $\bar{\chi}$  can be formally written in the form

$$\bar{\chi} = \frac{m}{T} V_{ik} \hat{I}^{-1} \left( v_i v_k - \frac{1}{3} \delta_{ik} v^2 \right) + \frac{\partial T}{\partial x_i} \hat{I}^{-1} \left[ v_i \frac{E(Q) - c_p T}{T} \right] \frac{1}{T}. \quad (2)$$

Here the operator  $\hat{I}^{-1}$  is so defined that when acting on eigenfunctions of the operator  $\hat{I}$  with nonzero eigenvalues it is an ordinary inverse operator, but when acting on the five hydrodynamic modes with zero eigenvalues it yields zero.

For a nonequilibrium gas, the equal-time fluctuation correlator  $\delta f = f - \bar{f}$  of the distribution function is connected with the two-particle distribution function  $\bar{f}_{12}(\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2, Q_1, Q_2)$  even in the case of an ideal gas<sup>16,23</sup>

$$\langle \delta f(\mathbf{r}, Q_1) \delta f(0, Q_2) \rangle_{t_1=t_2=0} = \bar{f}_{12}(\mathbf{r}, Q_1, Q_2) - \bar{f}(\mathbf{r}, Q_1) \bar{f}(0, Q_2) + \bar{f}(0, Q_1) \delta(\mathbf{r}) \delta(Q_1 - Q_2). \quad (3)$$

Note that the distribution function  $f$  is normalized here to one particle. The two-particle correlation function

$$\varphi(\mathbf{r}, Q_1, Q_2) = \bar{f}_{12}(\mathbf{r}, Q_1, Q_2) - \bar{f}(\mathbf{r}, Q_1) \bar{f}(0, Q_2)$$

is zero in an equilibrium ideal gas. In the presence of a deviation, stationary in time, of the distribution function  $\bar{f}$  from the equilibrium function  $f_0$ , the pair collisions between particles lead to the onset of a nonzero stationary function  $\varphi$ . The equation for  $\varphi$  at small deviations from equilibrium is of the form

$$(\mathbf{v}_1 - \mathbf{v}_2) \partial \bar{\varphi} / \partial \mathbf{r} - \hat{I}_1 \bar{\varphi} - \hat{I}_2 \bar{\varphi} = \delta(\mathbf{r}) \hat{I}_{12} \bar{\chi}, \quad (4)$$

where  $\bar{\varphi} = f_0(Q_1) f_0(Q_2) \bar{\varphi}$ , and the collision operator  $\hat{I}_{12}$  is given by

$$\hat{I}_{12} \bar{\chi} = N \int w(Q_1, Q_2; Q_1', Q_2') \times [\bar{\chi}(Q_1') + \bar{\chi}(Q_2') - \bar{\chi}(Q_1) - \bar{\chi}(Q_2)] dQ_1' dQ_2',$$

where  $N$  is the gas density,  $w$  the probability of the transition  $Q_1' Q_2' \rightarrow Q_1 Q_2$ , in the collision, differs from the usual Boltzmann collision operator  $I_1$  in that there is no additional integration over  $dQ_2$ .

To solve Eq. (4) we expand the function  $\bar{\varphi}$  in the basis of the orthonormal eigenfunctions of the operator  $\hat{I}_1 + \hat{I}_2$ , i.e.,

$$\bar{\varphi}(\mathbf{r}, Q_1, Q_2) = \sum_{\alpha\alpha'} a_{\alpha\alpha'}(\mathbf{r}) \chi_\alpha(Q_1) \chi_{\alpha'}(Q_2),$$

and transform to the Fourier representation of the function  $\bar{\varphi}$  with respect to the coordinate  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ :

$$\bar{\varphi}(\mathbf{q}, Q_1, Q_2) = \int e^{-i\mathbf{q}\mathbf{r}} \varphi(\mathbf{r}, Q_1, Q_2) d\mathbf{r},$$

$$a_{\alpha\alpha'}(\mathbf{q}) = \int e^{-i\mathbf{q}\mathbf{r}} a_{\alpha\alpha'}(\mathbf{r}, Q_1, Q_2) d\mathbf{r}.$$

As a result, Eq. (4) reduces to a system of equations for the coefficient functions  $a_{\alpha\alpha'}(\mathbf{q})$ :

$$i\mathbf{q}(\mathbf{v}_{\alpha\alpha'} - \mathbf{v}_{\alpha_1\alpha_1'}) a_{\alpha\alpha'} + (\mathbf{v}_\alpha + \mathbf{v}_{\alpha_1}) a_{\alpha\alpha_1} = (\hat{I}_{12} \bar{\chi})_{\alpha\alpha_1}, \quad (5)$$

where  $-\mathbf{v}_\alpha$  are the eigenvalues of the operator  $\hat{I}$  and correspond to the eigenfunctions  $\chi_\alpha$ :

$$\mathbf{v}_{\alpha\alpha'} = \int \chi_\alpha^*(Q) \chi_{\alpha'}(Q) \mathbf{v} f_0(Q) dQ, \\ (\hat{I}_{12} \bar{\chi})_{\alpha\alpha_1} = \int \chi_\alpha^*(Q_1) \chi_{\alpha_1}(Q_2) \hat{I}_{12} \bar{\chi} f_0(Q_1) f_0(Q_2) dQ_1 dQ_2.$$

We continue to seek the solution of the system (5) under the condition  $qv \ll v$ , which is equivalent in the light-scattering problem to the condition  $l \ll \lambda$  for applicability of hydrodynamics. It is precisely under these conditions that the triplet of the polarized light scattering is resolved. In this case, the solution of the system (5) breaks up into three classes:

1. The functions  $\chi_\alpha$  and  $\chi_{\alpha_1}$  are hydrodynamic.
2.  $\chi_\alpha$  is hydrodynamic and  $\chi_{\alpha_1}$  is non-hydrodynamic.
3. Both functions  $\chi_\alpha$  and  $\chi_{\alpha_1}$  are non-hydrodynamic.

Recall that the five hydrodynamic functions  $\chi_i$  and the corresponding eigenvalues  $\lambda_i$  of the operator  $i\mathbf{q} \cdot \mathbf{v} + \hat{I}$  have the following actual form<sup>24,25</sup>:

$$\chi_1 = \left( \frac{c_v}{2c_p} \right)^{1/2} \left[ 1 - \left( \frac{c_p}{c_v} \right)^{1/2} \frac{v_x}{v_0} + c_v^{-1/2} \frac{E - \bar{E}}{\Delta E} \right], \\ \lambda_1 = -i\mathbf{q} \mathbf{u}_{ac} + \gamma_1, \\ \chi_2 = \left( \frac{c_v}{2c_p} \right)^{1/2} \left[ 1 + \left( \frac{c_p}{c_v} \right)^{1/2} \frac{v_x}{v_0} + c_v^{-1/2} \frac{E - \bar{E}}{\Delta E} \right], \\ \lambda_2 = i\mathbf{q} \mathbf{u}_{ac} + \gamma_2, \quad (6)$$

$$\chi_3 = v_y/v_0, \quad \lambda_3 = \gamma_3,$$

$$\chi_4 = v_z/v_0, \quad \lambda_4 = \gamma_4,$$

$$\chi_5 = \left( \frac{c_v}{c_p} \right)^{1/2} \left[ c_v^{-1/2} - \frac{E - \bar{E}}{\Delta E} \right] \quad \lambda_5 = \gamma_5.$$

To be definite, the  $x$  axis is directed here along the vector  $\mathbf{q}$ ,

$$v_0 = (T/m)^{1/2}, \quad \bar{E} = c_v T, \quad \Delta E = c_v^{1/2} T, \quad \mathbf{u}_{ac} = (c_p/c_v)^{1/2} v_0,$$

and  $c_v$  is the specific heat of the molecule at constant volume. It is convenient to express the widths  $\gamma_i$  of the hydrodynamic modes in the form

$$\gamma_1 = \gamma_2 = (q^2/2\rho) [4/3\eta + \zeta + \kappa m(1/c_v - 1/c_p)], \\ \gamma_3 = \gamma_4 = q^2\eta/\rho, \quad \gamma_5 = q^2 m\kappa/\rho c_p, \quad (7)$$

where  $\eta$  and  $\zeta$  are the shear and bulk viscosity coefficients,  $\kappa$

is the thermal conductivity coefficient, and  $\rho = mN$  is the gas density ( $\text{g/cm}^3$ ).

If both functions are hydrodynamic, the solution of the system (5) is

$$a_{ik} = (\hat{I}_{12}\bar{\chi})_{ik} / (\lambda_i + \lambda_k^*), \quad i, k = 1 \dots 5. \quad (8a)$$

For the second class of functions we have

$$a_{i\alpha} = \frac{(\hat{I}_{12}\bar{\chi})_{i\alpha}}{\lambda_i + \nu_\alpha}, \quad a_{\alpha i} = \frac{(\hat{I}_{12}\bar{\chi})_{\alpha i}}{\lambda_i^* + \nu_\alpha}, \quad i = 1, \dots, 5, \quad \alpha > 5. \quad (8b)$$

For the last class of nonhydrodynamic functions we obtain

$$a_{\alpha\alpha'} = a_{\alpha'\alpha} = (\hat{I}_{12}\bar{\chi})_{\alpha\alpha'} / (\nu_\alpha + \nu_{\alpha'}). \quad (8c)$$

The foregoing expressions enable us to calculate the two-particle correlation function  $\varphi$  and thereby determine the equal-time correlator of the fluctuations in a nonequilibrium gas. This correlator is the initial condition for the kinetic equation for the fluctuation correlator of the one-particle distribution function. The Fourier transform  $\Phi$  of the fluctuation correlator with respect to the coordinate and the time is

$$\Phi(\omega, \mathbf{q}, \mathbf{R}, Q_1, Q_2) = \int_0^\infty e^{-i(\omega t - \mathbf{q}\mathbf{r})} \langle \bar{\chi}(t, \mathbf{r}_1, Q_1) \bar{\chi}(0, \mathbf{r}_2, Q_2) \rangle dt d\mathbf{r},$$

where

$$\delta f = f - \bar{f} = f_0 \bar{\chi}, \quad \mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2,$$

satisfies, at small deviations from equilibrium, the equation

$$-i\omega \Phi + [i\mathbf{q}\mathbf{v}_1 + \frac{1}{2}f_0^{-1}(Q_1)\mathbf{v}_1 \partial f_0(Q_1, \mathbf{R}) / \partial \mathbf{R}] \Phi - \hat{I} \Phi = \bar{\varphi}(\mathbf{q}, Q_1, Q_2) + f_0^{-1}(Q_1) [1 + \bar{\chi}(Q_1)] \delta(Q_1 - Q_2). \quad (9)$$

We have used here the relation  $\mathbf{v}_1 \partial / \partial \mathbf{r}_1 = \mathbf{v}_1 \partial / \partial \mathbf{r} + 1/2 \mathbf{v}_1 \partial / \partial \mathbf{R}$ , and the quantity  $\mathbf{v}_1 \partial f_0 / \partial \mathbf{R}$  can be expressed in terms of the gradients of the parameters  $\mathbf{V}$  and  $T$  in accordance with relation (1').

The form of the Rayleigh-scattering spectrum  $J(\omega, \mathbf{q})$  is expressed in terms of  $\Phi(\omega, \mathbf{q}, Q_1, Q_2)$  in the following manner<sup>1)</sup>:

$$J(\omega, \mathbf{q}) = N \text{Re} \int dQ_1 dQ_2 B^*(Q_1) \Phi(\omega, \mathbf{q}, Q_1, Q_2) \times B(Q_2) f_0(Q_1) f_0(Q_2), \quad (10)$$

where

$$B(Q) = e_{1s} \alpha_{st}(Q) e_{2t}, \quad \alpha_{st}(Q) = \alpha_0 \delta_{st} + \alpha_2 (m_s m_t^{-1/3} \delta_{st}),$$

$$\mathbf{m} = \mathbf{M}/M;$$

$\omega = \omega_2 - \omega_1$  and  $\mathbf{q} = \mathbf{k}_2 - \mathbf{k}_1$  are the differences of the frequencies and the wave vectors of the scattered and incident waves;  $\alpha_{st}(Q)$  is the molecule polarizability tensor and contains a scalar ( $\propto \alpha_0$ ) and symmetric ( $\propto \alpha_2$ ) part;  $\mathbf{e}_1$  and  $\mathbf{e}_2$  are the polarization unit vectors of the incident and scattered waves.

Following the developed procedure of solving Eqs. (9) and (10),<sup>26</sup> we transform from  $\Phi$  to a new unknown function

$$\Psi(\omega, \mathbf{q}, Q_1) = \int B(Q_2) f_0(Q_2) \Phi dQ_2$$

and expand the solution in the basis of the eigenfunctions of the operator  $\hat{I}_1$ , i.e.,

$$\Psi(\omega, \mathbf{q}, Q_1) = \sum_\alpha b_\alpha(\omega, \mathbf{q}) \chi_\alpha(Q_1).$$

If the conditions  $qv \ll \nu$  are met, the equations for the coefficients  $b_\alpha$  are given by

$$-i(\omega + \Omega_j) b_j + (\gamma_j + \Delta\gamma_j) b_j = B_j + C_j - i(\Delta B_j + \Delta C_j), \quad j = 1, \dots, 5,$$

$$(-i\omega + \nu_\alpha + \Delta\nu_\alpha) b_\alpha + \sum_{j \leq 5} i q v_{\alpha j} b_j = B_\alpha + C_\alpha, \quad \alpha > 5,$$

$$\Omega_1 = q u_{ac}, \quad \Omega_2 = -q u_{ac}, \quad \Omega_j = 0, \quad j = 3, \dots, 5,$$

$$\Delta\gamma_j = \frac{1}{2} \left\langle \chi_j \left| f_0^{-1} \mathbf{v}_1 \frac{\partial f_0}{\partial \mathbf{R}} \right| \chi_j \right\rangle, \quad j = 1, \dots, 5,$$

$$\Delta\nu_\alpha = \left\langle \chi_\alpha \left| f_0^{-1} \mathbf{v}_1 \frac{\partial f_0}{\partial \mathbf{R}} \right| \chi_\alpha \right\rangle, \quad \alpha > 5, \quad (11)$$

$$B_i = \int \chi_i^*(Q) B(Q) f_0(Q) dQ = \langle \chi_i | B(Q) \rangle,$$

$$C_i = \langle \chi_i | C(Q) \rangle, \quad i \geq 1,$$

$$C(Q) = \bar{\chi}(Q) B(Q) + \sum_{\alpha\alpha'} \chi_\alpha(Q) a_{\alpha\alpha'} B_{\alpha'}(Q),$$

$$\Delta B_j = \langle \chi_j | \mathbf{q}\mathbf{v} | \hat{I}^{-1} B \rangle, \quad \Delta C_j = \langle \chi_j | \mathbf{q}\mathbf{v} | \hat{I}^{-1} C \rangle.$$

Note that we have retained in both the left- and right-hand sides of the system (11) terms that are linear in the spatial gradients; the former contribute to the spectrum width, and the latter to its integrated intensity. In this representation, the scattering spectrum is given by

$$J(\omega, \mathbf{q}) = N \text{Re} \sum_\alpha B_\alpha^* b_\alpha.$$

The solution of the system (11) leads to the following expression for the scattering spectrum:

$$J(\omega, \mathbf{q}) = N \text{Re} \sum_{j=1,2,5} \frac{B_j^* (B_j + C_j - i\Delta B_j - i\Delta C_j)}{-i(\omega + \Omega_j) + (\gamma_j + \Delta\gamma_j)} + N \text{Re} \sum_{\alpha>5} \frac{B_\alpha^* (B_\alpha + C_\alpha)}{-i\omega + (\nu_\alpha + \Delta\nu_\alpha)} - N \text{Re} \sum_{j \leq 5} \frac{\Delta B_j^* (\Delta B_j + \Delta C_j)}{-i(\omega + \Omega_j) + (\gamma_j + \Delta\gamma_j)}. \quad (12)$$

As seen from (12), the scattering spectrum consists of a narrow polarized triplet (first term) with widths  $\gamma_j$ , and a broad depolarized spectrum (with width of the order of  $\nu_\alpha$ ), on which a fine structure (third term) is superimposed. It is expedient to continue the analysis of the spectrum separately for the three disequilibrium cases, viz., in the presence of a temperature gradient, of a velocity gradient, and a difference between the rotational and translational temperatures.

### 3. SCATTERING SPECTRUM IN THE PRESENCE OF TEMPERATURE GRADIENT

Consider a gas with a constant temperature gradient. In this case we obtain for the equilibrium single-particle function, using (2) and (6), the expression

$$\bar{\chi} = -c_p \frac{\partial T}{\partial x_i} \hat{I}^{-1}(v_i \chi_s) \frac{1}{T}. \quad (13)$$

Substituting the obtained  $\bar{\chi}$  in (8), we calculate the coefficients  $a$  that determine the two-particle correlation function  $\varphi$ :

$$\begin{aligned}
a_{11} &= -a_{22} = (\hat{I}_{12}\bar{\chi})_{11}/2\gamma_1, & a_{55} &= 0, \\
a_{15} &= a_{25} = -(\hat{I}_{12}\bar{\chi})_{15}/iqu_{ac}, & a_{51} &= a_{52} = a_{15}^*, & a_{12} &= a_{21} = 0, \\
a_{1\alpha} &= a_{\alpha 1}^* = (\hat{I}_{12}\bar{\chi})_{1\alpha}/(-iqu_{ac} + v_\alpha), & & & & (14) \\
a_{2\alpha} &= a_{\alpha 2}^* = -(\hat{I}_{12}\bar{\chi})_{1\alpha}/(iqu_{ac} + v_\alpha), & a_{\alpha\alpha} &= 0.
\end{aligned}$$

We have calculated here only those coefficients  $a$  which contribute to the scattering spectrum. In particular, since  $B_3 = B_4 = 0$ , the spectrum does not contain the coefficients  $a_{3\alpha}$  and  $a_{4\alpha}$ . These coefficients were chosen with allowance for the following circumstances: 1) the depolarization scattering is determined by a tensor of second rank in  $\mathbf{M}$  [Eq. (10)]; 2) the function  $\bar{\chi}$  is vector nonhydrodynamic mode [see Eq. (13) and the definition of the operator  $\hat{I}^{-1}$ ]; 3) the operators  $\hat{I}_{12}$ ,  $\hat{I}$ , and  $\hat{I}^{-1}$  are scalar.

Using the coefficients  $a$ , we calculate the values of  $C_j$  and  $\Delta C_j$  accurate to terms linear in the small parameters  $qu_{ac}/v$ , and also the width corrections  $\Delta\gamma_j$  which account for the changes in the spectrum and are proportional to the temperature gradient:

$$\begin{aligned}
C_1 &= \frac{(\hat{I}_{12}\bar{\chi})_{11}B_1}{2\gamma_1} - \frac{(\hat{I}_{12}\bar{\chi})_{15}B_5}{iqu_{ac}}, & (\hat{I}_{12}\bar{\chi})_{11} &= \frac{u_{ac}}{T} (e_q \nabla T), \\
C_2 &= -\frac{(\hat{I}_{12}\bar{\chi})_{11}B_1}{2\gamma_1} - \frac{(\hat{I}_{12}\bar{\chi})_{15}B_5}{iqu_{ac}}, & (\hat{I}_{12}\bar{\chi})_{15} &= -\left(\frac{c_v}{2}\right)^{1/2}, \\
C_3 &= 2(\hat{I}_{12}\bar{\chi})_{15}B_1/iqu_{ac}, & C_\alpha &= 0, & \Delta C_j &= 0, & j &= 1, \dots, 4, \\
\Delta\gamma_1 &= -\Delta\gamma_2 & & & & & & (15)
\end{aligned}$$

$$= \left\langle \chi_1 \left| \frac{1}{2} \frac{E - c_p T}{T} v \frac{\nabla T}{T} \right| \chi_1 \right\rangle = -\frac{u_{ac}}{2T} (e_q \nabla T),$$

$$\Delta\gamma_3 = \Delta\gamma_4 = \Delta\gamma_5 = 0, \quad \Delta v_\alpha = 0.$$

The expression for the polarized components of the scattering spectrum in the presence of a constant temperature gradient takes thus in the indicated approximation the form

$$\begin{aligned}
J^{pol}(\omega, \mathbf{q}) &= \frac{NB_1^2(1+\varepsilon')\Gamma_1}{(\omega + qu_{ac})^2 + \Gamma_1^2} + \frac{NB_1^2(1-\varepsilon')\Gamma_2}{(\omega - qu_{ac})^2 + \Gamma_2^2} + \frac{NB_5^2\gamma_5}{\omega^2 + \gamma_5^2} \\
&+ \frac{NB_1(\Delta B_1 + \varepsilon''B_5)(\omega + qu_{ac})}{(\omega + qu_{ac})^2 + \Gamma_1^2} - \frac{NB_1(\Delta B_1 - \varepsilon''B_5)(\omega - qu_{ac})}{(\omega - qu_{ac})^2 + \Gamma_2^2} \\
&- 2NB_5B_1\varepsilon'' \frac{\omega}{\omega^2 + \gamma_5^2}, & & (16)
\end{aligned}$$

$$\Gamma_1 = \gamma_1(1 - \varepsilon'), \quad \Gamma_2 = \gamma_1(1 + \varepsilon'),$$

$$\varepsilon' = \frac{u_{ac}}{T} \frac{(e_q \nabla T)}{2\gamma_1}, \quad \varepsilon'' = \frac{2\gamma_1}{qu_{ac}} \left(\frac{c_v}{2}\right)^{1/2} \varepsilon', \quad \left| \frac{\varepsilon''}{\varepsilon'} \right| \ll 1.$$

The main changes in the polarization spectrum of the scattering, as seen from (16), reduce to the appearance of a difference between the integrated intensities and the widths of the Brillouin components, proportional to the parameter  $\varepsilon'$ , and of small asymmetric increments to the spectrum, proportional to the parameter  $\varepsilon''$ . If we put  $\varepsilon'' = 0$  in (16) and expand in powers of the parameter  $\varepsilon'$  accurate to first-order terms, we obtain the known expression most frequently discussed in the literature (see, e.g., Refs. 7 and 8). Note that neither the cited papers nor the present one take into account the inhomogeneous line broadening due to the temperature dependence of the sound velocity.

The asymmetry in the Brillouin components consists of two terms. The first, proportional to  $\Delta B_1$ , characterizes the connection between the translational and rotational degrees of freedom of molecule collisions in a gas.<sup>26</sup> The second, proportional to  $\varepsilon''B_5$ , is due to the temperature gradient. Their ratio is of the order of  $\Delta B_1/\varepsilon''B_5 \sim \alpha_2/\alpha_0\varepsilon'$ . In the case of spherically symmetric molecules  $\alpha_2 = 0$  and  $\Delta B = 0$ , i.e., the asymmetry is due only to the temperature gradient. For simple diatomic molecule we have  $\alpha_2/\alpha_0 \sim 1 - 10^{-1}$  and  $\Delta B_1/\varepsilon''B_5 \sim 10^{-1}/\varepsilon'$ . More detailed estimates of the parameters  $\varepsilon'$  and  $\varepsilon''$  will be given below.

In the linear approximation in the temperature gradient, the depolarized scattering spectrum reduces, using (15), to the form

$$\begin{aligned}
J^{dep}(\omega, \mathbf{q}) &= N \sum_{\alpha>5} \frac{|B_\alpha|^2 v_\alpha}{\omega^2 + v_\alpha^2} - N \frac{(\Delta B_3^2 + \Delta B_4^2)\gamma_3}{\omega^2 + \gamma_3^2} \\
&- \frac{|\Delta B_1|^2 \Gamma_1}{(\omega + qu_{ac})^2 + \Gamma_1^2} - \frac{|\Delta B_1|^2 \Gamma_2}{(\omega - qu_{ac})^2 + \Gamma_2^2}. & & (17)
\end{aligned}$$

It can be seen from (17) that the presence of a temperature gradient leads to a difference, proportional to the parameter  $\varepsilon'$ , between the contrasts of the dips in the fine structure at the Brillouin frequencies. The dip at the undisplaced frequency and the broad part of the spectrum with width  $\sim v_\alpha$  [the first two terms of (17)] are not sensitive to the temperature gradient in the discussed approximation in the parameter  $qu_{ac}/v$ . Thus, the presence of a temperature gradient is manifested in the  $HH$  component of the depolarized light scattering, for in this case the fine structure consists of two dips at Brillouin frequencies, and is not manifested in the  $VH$  component, where a dip occurs only at the undisplaced frequency.<sup>26</sup>

#### 4. SCATTERING SPECTRUM IN THE PRESENCE OF A VELOCITY GRADIENT

For a constant velocity gradient in a gas, the small increment to the single-particle distribution function is of the form

$$\bar{\chi} = (m/T) V_{ik} \hat{I}^{-1} (v_i v_k - 1/3 \delta_{ik} v^2). \quad (18)$$

Using (8) and (11), we calculate the values of  $a$ ,  $C$ , and  $\Delta\gamma$  which describe the increments, linear in the velocity gradient, to the polarized scattering spectrum:

$$a_{11} = \frac{(\hat{I}_{12}\bar{\chi})_{11}}{2\gamma_1} = a_{22}, \quad a_{12} = a_{21}^* = \frac{(\hat{I}_{12}\bar{\chi})_{11}}{2iqu_{ac}},$$

$$a_{15} = a_{25} = a_{55} = 0,$$

$$\begin{aligned}
C_1 = C_2^* &= \frac{(\hat{I}_{12}\bar{\chi})_{11}B_1}{2\gamma_1} + \frac{(\hat{I}_{12}\bar{\chi})_{15}B_5}{2iqu_{ac}}, \\
(\hat{I}_{12}\bar{\chi})_{11} &= -\bar{V}_{ik} e_{qi} e_{qh}, \quad \bar{V}_{ik} = V_{ik}^{-1/3} \delta_{ik} \sum_{\alpha} V_{\alpha\alpha}, & & (19)
\end{aligned}$$

$$\Delta\gamma_1 = \Delta\gamma_2 = \langle \chi_1 | 1/2 V_{ik} (v_i v_k / v_0^2 - 1/3 \delta_{ik}) | \chi_1 \rangle = 1/2 \bar{V}_{ik} e_{qi} e_{qh},$$

$$\Delta\gamma_5 = 0, \quad \Delta\gamma_3 = \bar{V}_{ik} e_{yi} e_{yh}, \quad \Delta\gamma_4 = \bar{V}_{ik} e_{zi} e_{zh},$$

where the unit vectors  $e_y$  and  $e_z$  are perpendicular to  $e_q$  and their choice is determined by the relation  $\bar{V}_{ik} (e_{yi} e_{zk} + e_{zi} e_{yk}) = 0$ . Satisfaction of this condition ensures diagonalization of the operator  $1/2 V_{ik} (v_i v_k - 1/3 \delta_{ik} v^2)$  in the ba-

sis of the functions  $\chi_3$  and  $\chi_4$ . Introducing the notation

$$\varepsilon_1' = -\nabla_{ik} e_{qi} e_{qk} / 2\gamma_1, \quad \varepsilon'' = \gamma_1 \varepsilon_1' / qu_{ac},$$

we obtain the following expression for the intensities  $J^{\text{pol}}$  and  $J^{\text{dep}}$  of the polarized and depolarized spectra:

$$J^{\text{pol}}(\omega, q) = NB_1^2(1 + \varepsilon_1') \left\{ \frac{\Gamma_1}{(\omega + qu_{ac})^2 + \Gamma_1^2} + \frac{\Gamma_2}{(\omega - qu_{ac})^2 + \Gamma_2^2} \right\} + \frac{NB_5^2 \gamma_5}{\omega^2 + \gamma_5^2} + NB_1(\Delta B_1 + \varepsilon_1'' B_1) \times \left\{ \frac{\omega + qu_{ac}}{(\omega + qu_{ac})^2 + \Gamma_1^2} - \frac{\omega - qu_{ac}}{(\omega - qu_{ac})^2 + \Gamma_2^2} \right\}, \quad (20)$$

$$J^{\text{dep}}(\omega, q) = N \sum_{\alpha > 5} \frac{|B_\alpha|^2 \nu_\alpha}{\omega^2 + \nu_\alpha^2} - N \frac{|\Delta B_3|^2 \Gamma_3}{\omega^2 + \Gamma_3^2} - N \frac{|\Delta B_4|^2 \Gamma_4}{\omega^2 + \Gamma_4^2} - N \frac{|\Delta B_1|^2 \Gamma_1}{(\omega + qu_{ac})^2 + \Gamma_1^2} - N \frac{|\Delta B_2|^2 \Gamma_2}{(\omega - qu_{ac})^2 + \Gamma_2^2}, \quad (21)$$

where

$$\Gamma_1 = \gamma_1(1 + \varepsilon_1') = \Gamma_2, \quad \Gamma_3 = \gamma_3 + \Delta\gamma_3, \quad \Gamma_4 = \gamma_4 + \Delta\gamma_4.$$

The coefficients  $\Delta B$  satisfy the following polarization relations<sup>26</sup>:

$$\Delta B_1 = -\Delta B_2 \infty 2e_{1z} e_{2x}^{-1} / e_1 e_2,$$

$$\Delta B_5 \infty e_{1z} e_{2y} + e_{1y} e_{2z}, \quad \Delta B_4 \infty e_{1z} e_{2z} + e_{1z} e_{2x},$$

where  $e_1$  and  $e_2$  are the unit vectors of the polarizations of the incident and reflected waves.

It follows from (20) that the gas disequilibrium due to the velocity gradient alters the total intensity of the doublet components in the polarization spectrum, i.e., violates the Landau-Placzek relations in the gas, and leads to small asymmetric increments to the Brillouin frequencies (see Fig. 1c below). In contrast to the case with a temperature gradient, however, in this case the scattering spectrum remains symmetric with respect to the substitution  $\omega \rightarrow -\omega$ , i.e., about the point  $\omega = 0$ . In order of magnitude, the parameters  $\varepsilon_1'$  and  $\varepsilon_1''$  are given by

$$\varepsilon_1' \sim 1/4 |\nabla V| / \gamma_1, \quad \varepsilon_1'' = \varepsilon_1' \gamma_1 / qu_{ac}.$$

In the depolarization scattering spectrum (21) a disequilibrium in the form of a velocity gradient alters the quantities  $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$  that determine the widths and contrasts of the fine structure of the depolarized spectrum. In the  $HH$  components of the depolarized-scattering spectrum, the contrasts of the narrow dips at the Brillouin frequencies are changed, and in this case the contrasts of both dips change in like fashion, in contrast to the temperature gradient, where the dip-contrast changes were of opposite sign.

In the  $VH$  component of the spectrum, in the presence of a velocity gradient, the fine structure at the undisplaced frequency is in the general case a superposition of two Lorentz profiles with different widths  $\Gamma_3$  and  $\Gamma_4$  and with different intensities. Recall that in the equilibrium case this fine structure is a dip in the form of a single Lorentz profile of width  $\gamma_3 = \gamma_4$  (Ref. 26). When depolarized scattering is observed at small angles, however, the coefficients  $\Delta B_3$  and  $\Delta B_4$  vanish, whereas the dips at the Brillouin frequencies remain

$\Delta B_1 \neq 0, \Delta B_2 \neq 0$  (see the polarization relations given above for  $\Delta B$ ).

## 5. SCATTERING SPECTRUM IN THE PRESENCE OF A DIFFERENCE BETWEEN THE ROTATIONAL AND TRANSLATIONAL TEMPERATURES OF THE GAS

The disequilibrium considered can be produced in a gas, for example, by exposing it to light of frequency close to that of the frequency of the rotational transition in the gas, i.e., having a frequency on the order of  $2B_{\text{rot}} j$ , where  $B_{\text{rot}}$  is the rotational constant of the molecule and  $j$  is the rotational quantum number.

In a real situation, light absorption by a gas produces in the latter, naturally, stationary thermal flows directed away from the walls of the working vessel. This leads inevitably to spatial gradients of the gas temperature, and hence to the spatial inhomogeneity of the distribution function, discussed above in detail. Thus, light absorption by the bulk of the gas can be an effective method of producing large temperature gradients and is already used in experiment.<sup>27</sup> The main difference, in principle, between effects connected with temperature gradients and spatially homogeneous effects due to a difference between the rotational and translational temperatures is that in the former case the changes in the scattering spectrum are asymmetric with respect to  $\omega = 0$ , and in the latter they are symmetric. Therefore, eliminating the symmetric component of the spectrum, we obtain only effects connected with the difference between the rotational and translational temperatures  $T_{\text{rot}}$  and  $T_{\text{tr}}$  (see Fig. 1).

Consider light absorption that is uniform in the volume and the ensuing rise of  $T_{\text{rot}}$  of the gas relative to  $T_{\text{tr}}$ . In this case

$$\bar{f} \infty \exp(-E_{\text{tr}}/T_{\text{tr}}) \exp(-E_{\text{rot}}/T_{\text{rot}}),$$

where  $E_{\text{tr}}$  and  $E_{\text{rot}}$  are the translational and rotational energies of the molecule. The stationary nonequilibrium increment  $\bar{\chi}$  can then be represented in the form

$$\bar{\chi} = \frac{T_{\text{rot}} - T_{\text{tr}}}{T_{\text{tr}}} \left\{ \frac{E(Q)}{c_v} - \frac{mv^2}{3} \right\} \frac{c_v}{T_{\text{tr}}}. \quad (22)$$

The possibility of introducing two temperatures presupposes rapid relaxation over the rotational and translational degrees of freedom (within times  $t \sim \nu^{-1}$ , where  $\nu$  is the gas-kinetic collision frequency) and a sufficiently slow exchange between them over times  $t \sim \Delta\nu^{-1}$ , with  $\Delta\nu \ll \nu$ .

Calculation of  $a$  and  $C$  leads to the following results:

$$a_{11} = \frac{1}{2\gamma_1} (\dot{I}_{12}\bar{\chi})_{11} = a_{22}, \quad a_{55} = \frac{1}{2\gamma_5} (\dot{I}_{12}\bar{\chi})_{55},$$

$$a_{12} = -\frac{1}{2iqu_{ac}} (\dot{I}_{12}\bar{\chi})_{12} = a_{21}^*,$$

$$a_{15} = -\frac{1}{iqu_{ac}} (\dot{I}_{12}\bar{\chi})_{15} = a_{51}^*, \quad (23)$$

$$C_1 = \frac{1}{2\gamma_1} (\dot{I}_{12}\bar{\chi})_{11} B_1 - \frac{1}{2iqu_{ac}} (\dot{I}_{12}\bar{\chi})_{12} B_1 - \frac{1}{iqu_{ac}} (\dot{I}_{12}\bar{\chi})_{15} B_5 = C_1^*,$$

where

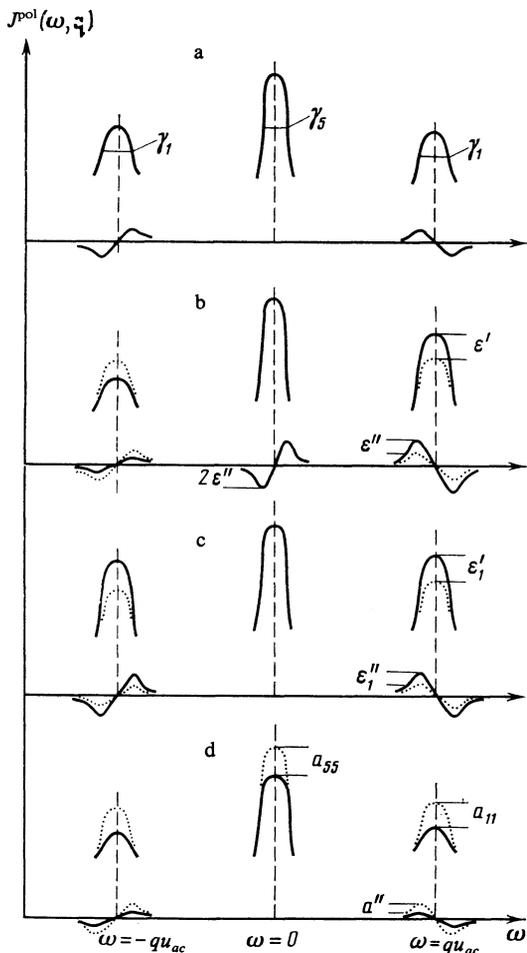


FIG. 1. Polarized component of Rayleigh scattering of light in a molecular gas: a—equilibrium case,  $\gamma_1$  and  $\gamma_5$ —respectively the widths of the Brillouin and central component; b—in the presence of a temperature gradient  $\nabla T, \mathbf{e}_q \nabla T < 0$ ,  $\mathbf{e}_q$ —unit vector in the direction of the scattering wave vector  $\mathbf{q}$ ; c—in the presence of a macroscopic velocity gradient  $\bar{V}_{ik}$  [see (19)],  $\bar{V}_{ik} e_{qi} e_{qk} < 0$ ; d—in the case when the gas rotational temperature  $T_{rot}$  exceeds the translational temperature  $T_{tr}$ ;  $\beta < 0$ . Figs. b, c, and d show for comparison (dotted) the light-scattering profile for the equilibrium gas.

$$\begin{aligned}
 (\hat{I}_{12}\bar{\chi})_{15} &= (2c_v)^{-1/2} (\hat{I}_{12}\bar{\chi})_{55}, & C_5 &= (2\gamma_5)^{-1} (\hat{I}_{12}\bar{\chi})_{55} B_1, \\
 (\hat{I}_{12}\bar{\chi})_{12} &= c_v^{-1} (\hat{I}_{12}\bar{\chi})_{55} - (\hat{I}_{12}\bar{\chi})_{11}, \\
 (\hat{I}_{12}\bar{\chi})_{55} &= -(c_p T^2)^{-1} \langle E^2 | \hat{I} | \bar{\chi} \rangle = \beta \Delta v, \\
 (\hat{I}_{12}\bar{\chi})_{11} &= -(2c_p T^2)^{-1} \langle E^2 | \hat{I} | \bar{\chi} \rangle - (6v_0^2)^{-1} \langle v^2 | \hat{I} | \bar{\chi} \rangle \\
 &= [1/2 \beta^{-1} / 3 \Delta T / T] \Delta v.
 \end{aligned}$$

Here  $\Delta v$  is the average value of the collision operator  $\hat{I}$  in the state  $g\bar{\chi}$  with allowance for the numerical factor  $g$  that ensures the normalization  $\langle g\bar{\chi} | g\bar{\chi} \rangle = 1$ . The coefficient  $\beta$  is of the order of  $\beta \sim \Delta T / T$ , as can be seen from the definition of the function  $\bar{\chi}$  [Eq. (22)]. The sign of  $\beta$  depends on the actual form of the rotational-level excitation function and can be either positive or negative. It can be shown that when sufficiently low rotational levels  $E_j < T$  are excited the coefficient  $\beta$  is negative, and in the region of high excitation energies  $E_j \gg T$  it is positive. In the intermediate region there exists a point where  $\beta = 0$  ( $E_j \sim T$ ). In the present paper we confine ourselves to these general remarks and do not consider the actual form of the excitation function, since it de-

pends strongly on the choice of the molecule and on the parameter of the exciting laser radiation. For the same reason we disregard the corrections to the widths  $\gamma_1$  and  $\gamma_5$ ; this does not affect the changes of the integrated intensity of the spectrum.

The polarized-scattering spectrum takes the form

$$\begin{aligned}
 J^{pol}(\omega, \mathbf{q}) &= NB_1^2 (1 + a_{11}) \left[ \frac{\gamma_1}{(\omega + qu_{ac})^2 + \gamma_1^2} + \frac{\gamma_1}{(\omega - qu_{ac})^2 + \gamma_1^2} \right] \\
 &+ NB_5^2 (1 + a_{55}) \frac{\gamma_5}{\omega^2 + \gamma_5^2} + NB_1 (\Delta B_1 - a'' B_1) \left[ \frac{\omega + qu_{ac}}{(\omega + qu_{ac})^2 + \gamma_1^2} \right. \\
 &\quad \left. - \frac{\omega - qu_{ac}}{(\omega - qu_{ac})^2 + \gamma_1^2} \right], \quad (24)
 \end{aligned}$$

where

$$a_{55} = \frac{\beta \Delta v}{2\gamma_5}, \quad a_{11} = \frac{\Delta v}{2\gamma_1} \left( \frac{1}{2} \beta - \frac{1}{3} \frac{\Delta T}{T} \right), \quad a'' = \frac{\gamma_1}{qu_{ac}} a_{11}.$$

It can be seen from (24) that the changes in the spectrum reduce in this case to the following.

1. The integrated intensity of the central component is changed by an amount  $a_{55} \sim (\Delta T / T) (\Delta v / \gamma_5)$ .

2. Besides the change of the integrated intensity  $a_{11} \sim (\Delta T / T) (\Delta v / \gamma_1)$ , the Brillouin components acquire asymmetrical increments  $a'' \sim (\Delta T / T) (\Delta v / qu_{ac})$  (see Fig. 1d).

## 6. DISCUSSION

The foregoing results (16), (20), and (24) for the profile of the spectrum of polarized Rayleigh scattering of light in a nonequilibrium gas are shown in Fig. 1 for three disequilibrium types: the presence of a temperature gradient (Fig. 1b), a velocity gradient (Fig. 1c), and differences between the rotational and translational gas temperatures (Fig. 1d). Figure 1a shows the form of the spectrum in the equilibrium gas. As seen from the figure, besides the changes in the integrated intensity of the triplet components, the spectrum acquires, for all three types of disequilibrium, asymmetric increments with zero integrated intensity. It must be recognized here that even in the case of an equilibrium gas with rotational degrees of freedom, the polarized scattering contains small asymmetric increments proportional to the parameter  $qu_{ac} / v$  (see Fig. 1). Therefore increments of the same type, due to the disequilibrium and proportional to the parameters  $\epsilon'$  and  $a''$ , can be of the same order of magnitude as the equilibrium asymmetric components. However, the increments due to the disequilibrium reverse sign when the direction of the wave vector  $\mathbf{q}$  is changed, and can thus be in principle separated from the equilibrium ones.

We estimate now the parameters  $\epsilon'$ ,  $\epsilon''$ ,  $a_{11}$ ,  $a''$ , that determine the changes in the spectrum of a nonequilibrium gas. In the presence of a temperature gradient, the spectrum changes are determined by the parameters  $\epsilon'$  and  $\epsilon''$ , exact microscopic expression for which are Eqs. (16). Using these equations, we obtain the following estimates of  $\epsilon'$  and  $\epsilon''$ :

$$\epsilon' = u_{ac} e_q \nabla T / 2\gamma_1 T \sim 1 / L\theta^2 \alpha, \quad \epsilon'' \sim \lambda / L\theta, \quad \alpha = 2\gamma_1 / v_0.$$

Here  $\lambda$  is the mean free path of the incident light,  $\theta$  is the light-scattering angle (assumed to be small),  $L \sim T / |\nabla T|$  is the characteristic length of temperature variation in the gas,

and  $\alpha$  is the reciprocal sound-absorption length at  $180^\circ$  scattering angle. To observe the effect experimentally in gases it is expedient to use the smallest possible scattering angles,  $\theta \ll 1$ . Assuming  $\theta \sim 10^{-2}$  rad  $\approx 0.6^\circ$ ,  $\lambda = 4 \cdot 10^{-5}$  cm,  $L = 5$  cm and using the values of  $\alpha$  for simple gases, we obtain from Ref. 17 (p. 239) the value of  $\epsilon'$  and  $\epsilon''$  listed in the table. It is clear from the table that under the indicated conditions the parameters  $\epsilon'$  are quite large and are observable in experiment. In view of the weak temperature dependence of the refractive index in gases, in contrast to liquids and solids, the scattering angle  $\theta$  can be substantially smaller than the chosen value  $\theta = 10^{-2}$  rad used in experiments on liquids and solids.<sup>18-20</sup> To observe in experiment the spectrum-asymmetry effects connected with the parameter  $\epsilon''$ , it is advantageous to decrease the scattering angle  $\theta$  even more and to lower the gas pressure by 10–100 times. For example, choosing  $\theta \sim 10^{-3}$  rad and  $p \sim 1$  atm we get  $\epsilon' \sim 0.4$ ,  $\epsilon'' \sim 0.01$ . Observation of different intensities in a Brillouin doublet in the presence of a temperature gradient is quite realistic in gases, and observation of more subtle effects connected with the parameter  $\epsilon''$  requires a spectrum-reduction accuracy not worse than 1%.

It must be noted that the greatest difficulty is caused in these experiments by the small amount of light contained in the accessible solid angle, not exceeding  $\theta^2$ , which imposes stringent requirements on the receiver sensitivity. The measured value of  $\epsilon'$  for water<sup>18-20</sup> is  $\epsilon' \sim 0.06$ , and in fused quartz the observed effect was too weak to be measured.

According to the foregoing estimates, the value of  $\epsilon'$  in a gas can be of the same order as in a liquid, or larger (see Table I). It is therefore of great interest to perform such an experiment in a gas, for which the theoretical predictions are fully unambiguous.

Note that besides the changes observed above in the polarized component of the spectrum, effects of the same order in the parameter are present in the depolarized scattering spectrum [see Eq. (17)]. At small scattering angles these effects are manifest in the form of different contrasts of the narrow dips at the Brillouin frequencies, superimposed on the wide depolarized-scattering contour. The dip-depth change due to the temperature gradient is of the same sign as the increments in the polarized doublet (see Fig. 1b).

In the presence of a velocity gradient, the parameters  $\epsilon'_1$  and  $\epsilon''_1$  that govern the change in the spectrum of the non-equilibrium gas, can be estimated in the same manner as in the case of a temperature gradient:

$$\begin{aligned} \epsilon'_1 &= -e_{q1} e_{qh} V_{ih} / 2\gamma_1 \sim 1/L\theta^2 \alpha, \\ \epsilon''_1 &= \gamma_1 \epsilon'_1 / q u_{ac} \sim \lambda / L\theta, \end{aligned}$$

where  $L \sim v_0 / |V_{xy}|$  is the tensor component in the case when the coordinate axis  $x$  is chosen along the velocity  $\mathbf{V}$  and  $y$  along the gradient of  $V_x$ . It can be seen from the estimate that

TABLE I. Values of parameters  $\epsilon'$  and  $\epsilon''$  for several simple gases.

Scattering gas	Pressure atm	$\alpha \cdot 10^{-3} \text{ cm}^{-1}$	$\epsilon'$	$\epsilon'' \cdot 10^3$
N <sub>2</sub>	80	6.4	0.3	0.8
O <sub>2</sub>	80	6.3	0.3	0.8
CO <sub>2</sub>	50	5.8	0.3	0.8
H <sub>2</sub>	100	8.8	0.2	0.8

the effect considered does not occur, i.e.,  $\epsilon'_1 = \epsilon''_1 = 0$ , if  $\mathbf{q}$  is perpendicular to the axis  $x$  or  $y$ , and in particular if  $\mathbf{q}$  is directed along the velocity  $\mathbf{V}$  or is perpendicular to the velocity  $\mathbf{V}$  of the gas as a whole. The maximum effect takes place if  $\mathbf{q}$  is in the  $xy$  plane at an angle  $45^\circ$  to these axes. Assuming by way of estimate  $\theta \sim 10^{-3}$ , a characteristic transverse cell dimension  $d \sim 1$  cm, a gas pressure  $p \sim 1$  atm, and a velocity gradient  $\partial V_x / \partial y \sim 10^{-2} v_0 / d$ , we get  $\epsilon'_1 \sim 0.01$ ,  $\epsilon''_1 \sim 10^{-4}$ . The estimate for the gradient was chosen with allowance for the condition that the gas flow be laminar, i.e.,  $R < 10^3$ , where  $R$  is the Reynolds number. This shows that it is much more difficult to observe the effect in this case than in the case of a temperature gradient.

In the depolarized part of the spectrum, at small scattering angles, the presence of a velocity gradient leads to a small change (proportional to  $\epsilon'_1$ ) of the contrast of the narrow dips at the Brillouin frequencies. The fine structure of the spectrum at the undisplaced frequency vanishes in the case of small-angle light scattering.

We proceed now to the third type of gas disequilibrium due to the difference between the rotational and translational gas temperatures. In this case we assume the gas to be uniformly illuminated by the laser at a frequency close to that of the rotational transition of the molecule. To increase the light-absorption probability it is preferable to choose molecules having dipole moments, such as HD, HCl, NO, CO and others. Both the translational and the rotational temperatures can be made stationary by heat removal through the vessel walls. The light source should be a second laser with frequency in the optical band. It is convenient to observe the scattering at small angles, just as in the preceding cases, so as to decrease the value of  $\gamma_1$ , i.e., increase the parameters  $a_{11}$ ,  $a_{55}$ ,  $a''$ , that determine the disequilibrium-induced changes in the scattering spectrum [see (24) and Fig. 1d]. As seen from Fig. 1d, in this case ( $\beta < 0$ ) the intensities of all the components of the triplet decrease ( $\propto a_{11}, a_{55}$ ) and asymmetric additions to the Brillouin doublet ( $\propto a''$ ) appear. The parameters  $a_{11}$ ,  $a_{55}$ ,  $a''$  are given by

$$a_{55} = \frac{\Delta v}{2\gamma_1} \beta, \quad a_{11} = \frac{\Delta v}{2\gamma_1} \left( \frac{1}{2} \beta - \frac{1}{3} \frac{\Delta T}{T} \right), \quad a'' = a_{11} \frac{\gamma_1}{q u_{ac}}.$$

For more specific numerical estimates of these parameters it is convenient to consider the following relations:

$$a_{11} / \epsilon' \approx a'' / \epsilon'' \approx 1/6 (\Delta T / T) (l / L)^{-1}, \quad (25)$$

where  $\epsilon'$  and  $\epsilon''$  are parameters that characterize the changes in the spectrum in the presence of a temperature gradient and were numerically estimated above,  $l$  is the mean free path, and  $L$  is the characteristic length of temperature change in the gas. Putting  $L \sim 5$  cm, we obtain for 1 atm gas pressure the values  $l \sim 10^{-5}$  cm and  $lL \sim 2 \cdot 10^{-6}$ . It can be seen from (25) that the ratio  $a_{11} / \epsilon'$  becomes of the order of unity at a very small deviation  $\Delta T / T \sim 10^{-5}$ . Thus, the change of the doublet intensity under these conditions can serve as a very accurate indicator for the determination of the ratio  $\Delta T / T$ .

To observe the effect in experiment it is expedient to measure the doublet intensity as a function of the exciting-radiation intensity. This dependence (Fig. 2) is linear and its interpolation to zero intensity of the exciting radiation yields the values of the doublet intensities under equilibrium condi-

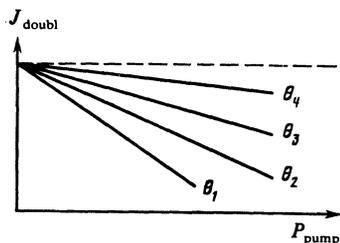


FIG. 2. Integrated intensity of Brillouin doublet vs the external radiation power  $P_{\text{pump}}$  exciting the rotational degrees of freedom.  $\theta_1 < \theta_2 < \theta_3 < \theta_4$ —scattering angles;  $\beta < 0$ .

tions. The slope of the line is inversely proportional to  $q^2$ , and its interpolation to zero intensity of the exciting radiation yields the intensities of the doublet under equilibrium conditions. The slope of the straight line is inversely proportional to  $q^2$ , and the family of curves plotted for different  $q$  (i.e., for different scattering angles  $\theta$ ) converges to one point corresponding to zero pump intensity.

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<sup>1)</sup>We leave out here and below, from all the equations for the intensity, the factor  $2J_0\omega_0^4/9\pi c^4$ , where  $J_0$  is the intensity of the incident light, and consider scattering into a unit volume and into a unit solid angle.

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