Kinetic description of depolarized Rayleigh scattering of light in dense noble gases

T. L. Andreeva and A. V. Malyugin

P. N. Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow

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Calculation is reported of the spectrum of the depolarized scattering of light in a dense noble gas when the scattering is due to the anisotropic polarizability of a pair of particles participating in a collision. The calculation is based on a system of coupled equations for one- and two-particle distribution functions. An allowance for the coupling of fluctuations of the one- and two-particle distribution functions gives rise to a new fine structure in the scattering spectrum. It is shown that the fine structure parameters are governed by the Maxwell constant of the investigated gas.

1. INTRODUCTION

Phenomena associated with a collision-induced anisotropic polarizability $\Delta\alpha_{ij}(\mathbf{r})$ of a pair of interacting particles are currently attracting much attention (see, for example, the reviews in Refs. 1–3). The phenomena include above all the appearance of a spectrum of depolarized scattered light in dense noble gases.[4–7] In spite of a large number of experimental and theoretical investigations of this spectrum, a clear interpretation of the line profile throughout the relevant frequency ranges is still lacking. In most of the investigations a description of the spectrum reduces to a selection of one function $\Delta\alpha(r)$ which is used to calculate the total intensity and the profile of the scattering spectrum.[1–10]

We shall report a calculation of the spectrum of depolarized scattering of light in a noble gas based on a coupled system of equations for one- and two-particle distribution functions. We shall show that near the line center (Fig. 1) a new fine structure appears in the scattering spectrum and the intensity of this structure can be expressed in terms of the Maxwell constant μ of the gas. The contrast R of this fine structure is found to be large, $R\sim 1$, and independent of the gas density. The contrast R can be expressed in terms of the Maxwell μ and Kerr K constants of the investigated noble gas, which in turn are related uniquely to the collision-induced anisotropic polarizability $\Delta\alpha_{ij}(\mathbf{r})$.[6,11,12] Therefore, a complete description of the complex spectrum of the depolarized scattering of light in a dense noble gas requires the knowledge of such physical constants of the medium as the Maxwell and Kerr constants.

2. SYSTEM OF EQUATIONS FOR FLUCTUATIONS OF DISTRIBUTION FUNCTIONS

The depolarized Rayleigh scattering in noble gases is associated with the appearance, during a collision, of an anisotropic polarizability of a pair of interacting particles. In this case the correlation function of the permittivity, which governs the scattering spectrum, can be expressed in terms of the correlation function of a two-particle distribution function[12]:

$$\Phi(\mathbf{R},t)=\langle\delta\varepsilon_{ij}(\mathbf{R},t)\,\delta\varepsilon_{ij}(0,0)\rangle=(2\pi N^2)^2\int\Delta\alpha_{ij}(\mathbf{r})\times\Delta\alpha_{ij}(\mathbf{r}')\langle\delta f_2(t,\mathbf{R},\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})\,\delta f_2(0,0,\mathbf{v}_1',\mathbf{v}_2',\mathbf{r}')\rangle d^4\mathbf{v}\,d\mathbf{r}\,d\mathbf{r}'. \tag{1}$$

Here, $\delta\varepsilon_{ij}(\mathbf{R},t)$ is a fluctuation of the permittivity at a point $\mathbf{R}$ at a moment t; N is the number of particles in 1 cm^3; $\Delta\alpha_{ij}(\mathbf{r})$ is the collision-induced polarizability of a pair of interacting particles; $\mathbf{v}_1$ and $\mathbf{v}_2$ are the particle velocities; $\mathbf{R}=\frac{1}{2}(\mathbf{r}_1+\mathbf{r}_2)$ is the coordinate of the center of mass of the systems; $\mathbf{r}$ is the distance between the particles; $\delta f_2(t,\mathbf{R},\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})$ is a fluctuation of the two-particle distribution function of the interacting particles; $d^4\mathbf{v}=d\mathbf{v}_1d\mathbf{v}_2d\mathbf{v}_1'd\mathbf{v}_2'$. The distribution function $f_2(t,\mathbf{R},\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})$ and also the function $f(t,\mathbf{R},\mathbf{v})$ are normalized to a unit volume as follows:

$$\int f_2(t,\mathbf{R},\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})\,d\mathbf{R}\,d\mathbf{r}\,d\mathbf{v}_1\,d\mathbf{v}_2=V^2,\qquad \int f_1(t,\mathbf{R},\mathbf{v})\,d\mathbf{R}\,d\mathbf{v}=V, \tag{2}$$

where V is the volume of the investigated gas.

The simultaneous correlation function of the permittivity $\langle\delta\varepsilon_{ij}(\mathbf{R},0)\delta\varepsilon_{ij}(0,0)\rangle$ is defined in terms of the equilibrium two particle distribution function

$$f_{20}(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})=f_0(v_1)f_0(v_2)\exp[-U(r)/T],$$

where $f_0(v)$ is the equilibrium Maxwellian distribution

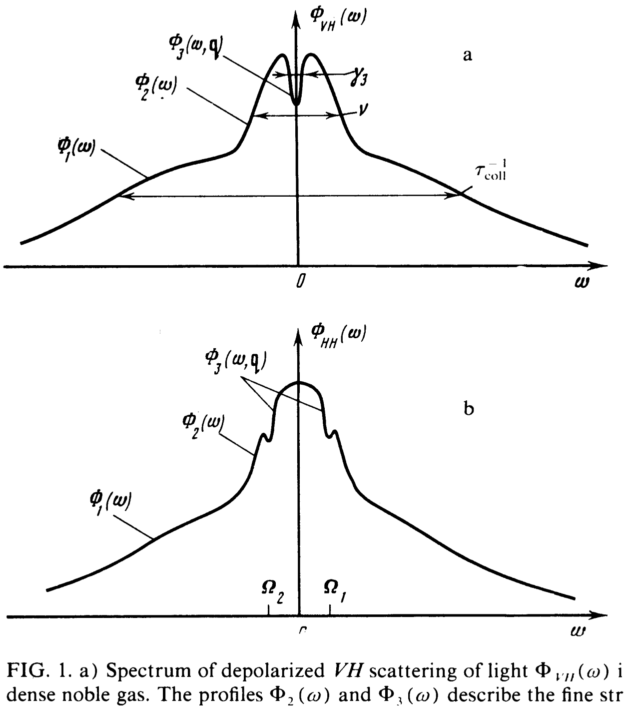

FIG. 1. a) Spectrum of depolarized *VH* scattering of light $\Phi_{VH}(\omega)$ in a dense noble gas. The profiles $\Phi_2(\omega)$ and $\Phi_3(\omega)$ describe the fine structure of the spectrum. b) Spectrum of depolarized *HH* scattering of light $\Phi_{HH}(\omega)$ in a dense noble gas. The fine structure of the spectrum $\Phi_3(\omega,\mathbf{q})$ represents in this case two narrow dips at frequencies of sound $\Omega_{1,2}=\pm qu_s$.

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function of the velocities, $U(r)$ is the potential energy of the interaction of the colliding particles, and T is the gas temperature. The structure of the simultaneous correlation function for an equilibrium gas is symmetric under transposition of the particles 1 and 2, and is given by

$$\begin{aligned}\langle\delta f_2(0,\mathbf{R},\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})\delta f_2(0,0,\mathbf{v}_1',\mathbf{v}_2',\mathbf{r}')\rangle&=N^{-2}\delta(\mathbf{R})\\ \times f_{20}(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})[\delta(\mathbf{v}_1-\mathbf{v}_1')\delta(\mathbf{v}_2-\mathbf{v}_2')\delta(\mathbf{r}-\mathbf{r}')\\ +\delta(\mathbf{v}_1-\mathbf{v}_2')\delta(\mathbf{v}_2-\mathbf{v}_1')\delta(\mathbf{r}+\mathbf{r}')].\end{aligned}\tag{3}$$

The next stage in the calculation of the spectrum requires a space–time equation for a quantity $\langle\delta f_2(t)\delta f_2(0)\rangle$ which is known to be identical with the equation for $f_2(t)$. The equation for the two-particle distribution function obtained ignoring triple collisions reduces to $df_2/dt=0$, i.e., the function f_2 is conserved along the path of motion of the colliding particles in the phase space. A complete description of the structure of the scattering spectrum requires allowance for a system of simultaneous equations for the functions f_2 and f_1, which are obtained from the first two equations of a Bogolyubov chain[14,15]:

$$\frac{\partial f_1}{\partial t}+\mathbf{v}_1\frac{\partial f_1}{\partial\mathbf{R}}=-N\int\frac{\partial U}{\partial\mathbf{r}}\frac{\partial f_2}{\partial\mathbf{p}_1}d\mathbf{v}_2\,d\mathbf{r},\quad\frac{df_2}{dt}=0.\tag{4}$$

The system of equations (4) is usually supplemented by a statement that the pair of colliding particles is statistically independent,[13,14] which in the case of the second equation in the system (4) acts as the initial condition. Therefore, the general solution for f_2 where t exceeds the collision time τ_{coll} can be written in the form

$$f_2(t,\mathbf{R},\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})=f_1(t,\mathbf{R},\mathbf{v}_{10})f_1(t,\mathbf{R},\mathbf{v}_{20}),\tag{5}$$

where $\mathbf{v}_{10}$ and $\mathbf{v}_{20}$ are the velocities of the particles for a collision. Then, these velocities $\mathbf{v}_{10}$ and $\mathbf{v}_{20}$ are functions of $\mathbf{v}_1$, $\mathbf{v}_2$, and $\mathbf{r}$.

We can see from Eqs. (4) and (5) that fluctuations of δf_1 and δf_2 are related, which gives rise to a new structure (see below) in the spectrum of the depolarized scattering of light in a dense gas consisting of isotropic particles. Solving the system of equations (4) for the correlation functions $\langle\delta f_2(t)\delta f_2(0)\rangle$ and $\delta f_1(t)\delta f_2(0)\rangle$ we need the initial condition for the correlation function $\langle\delta f_1(0)\delta f_2(0)\rangle$ which is obtained by analogy with the corresponding condition for the quantities $\langle\delta f_1(0)\delta f_1(0)\rangle$, $\langle\delta f_2(0)\delta f_2(0)\rangle$ (Ref. 16):

$$\begin{aligned}\langle\delta f_1(0,\mathbf{R},\mathbf{v}_1)\delta f_2(0,0,\mathbf{v}_1',\mathbf{v}_2',\mathbf{r}')\rangle&={}^1/_2N^{-1}\delta(\mathbf{R})\\ \times f_{20}(\mathbf{v}_1',\mathbf{v}_2',\mathbf{r}')[\delta(\mathbf{v}_1-\mathbf{v}_1')+\delta(\mathbf{v}_1-\mathbf{v}_2')].\end{aligned}$$

The final kinetic equations for the correlation functions can be written conveniently in terms of new variables F_1 and F_2:

$$\begin{aligned}F_1(t,\mathbf{R},\mathbf{v}_1)&=N^2f_0^{-1}(v_1)\int\langle\delta f_1(t,\mathbf{R},\mathbf{v}_1)\delta f_2(0,0,\mathbf{v}_1',\mathbf{v}_2',\mathbf{r}')\rangle\\ &\quad\times\Delta\alpha_{ij}(\mathbf{r}')d\mathbf{r}'\,d\mathbf{v}_1'\,d\mathbf{v}_2',\\ F_2(t,\mathbf{R},\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})&=N^2\{f_{20}(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})\}^{-1}\int\langle\delta f_2(t,\mathbf{R},\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})\\ &\quad\times\delta f_2(0,0,\mathbf{v}_1',\mathbf{v}_2',\mathbf{r}')\rangle\Delta\alpha_{ij}(\mathbf{r}')d\mathbf{r}'\,d\mathbf{v}_1'\,d\mathbf{v}_2',\end{aligned}$$

so that the system (4) becomes

$$\begin{aligned}&\frac{\partial F_1}{\partial t}+\mathbf{v}_1\frac{\partial F_1}{\partial\mathbf{R}}\\ &=-N[f_0(v_1)]^{-1}\int\frac{\partial U}{\partial\mathbf{r}}\frac{\partial}{\partial\mathbf{p}_1}[f_{20}F_2]d\mathbf{v}_2\,d\mathbf{r},\quad\frac{dF_2}{dt}=0.\end{aligned}\tag{6}$$

The initial conditions are

$$\begin{aligned}F_1(0,\mathbf{R},\mathbf{v}_1)&=0,\\ F_2(0,\mathbf{R},\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})&=\delta(\mathbf{R})\Delta\alpha_{ij}(\mathbf{r}).\end{aligned}$$

We can see from the definition of the function F_1 at the initial moment $t=0$ that it is proportional to the integral

$$F_1\propto\int d\mathbf{r}'\,\Delta\alpha_{ij}(\mathbf{r}')\exp\left[-\frac{U(\mathbf{r}')}{T}\right].$$

In the depolarized scattering case under discussion ($\Delta\alpha_{ij}$ is a symmetric tensor of rank two) in a gas of isotropic molecules [when the potential $U(\mathbf{r}')$ is a function only of the modulus of the distance between the molecules $\mathbf{r}'$], the function F_1 vanishes when the tensor $\Delta\alpha_{ij}(\mathbf{r}')$ is averaged along the directions $\mathbf{r}'$.

The expression for $\Phi(\mathbf{R},t)$, the Fourier component of which $\Phi(\omega,\mathbf{q})$ governs the scattering spectrum, is

$$\Phi(\mathbf{R},t)=(2\pi N)^2\int\Delta\alpha_{ij}(\mathbf{r})f_{20}F_2(t,\mathbf{R},\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})d\mathbf{v}_1\,d\mathbf{v}_2\,d\mathbf{r}\tag{7}$$

($\mathbf{q}$ is the wave vector of the scattered light). We shall transform the system of equations (6) by separating explicitly the solution for F_2:

$$\begin{aligned}F_2(t,\mathbf{R},\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})&=\delta(\mathbf{R})\Delta\alpha_{ij}(\mathbf{r}_0)\\ &\quad+F_1(t,\mathbf{R},\mathbf{v}_{10})+F_1(t,\mathbf{R},\mathbf{v}_{20}),\end{aligned}\tag{8}$$

$$\begin{aligned}\frac{\partial F_1}{\partial t}+\mathbf{v}_1\frac{\partial F_1}{\partial\mathbf{R}}-\hat{I}F_1&=-\delta(\mathbf{R})N\int\frac{\partial U}{\partial\mathbf{r}}\frac{\partial}{\partial\mathbf{p}_1}[f_{20}\Delta\alpha_{ij}(\mathbf{r}_0)]d\mathbf{v}_2\,d\mathbf{r},\\ F_1(0,\mathbf{R},\mathbf{v}_1)&=0.\end{aligned}\tag{9}$$

Here, the vector $\mathbf{r}_0=\mathbf{r}_0(\mathbf{v}_1,\mathbf{v}_2,\mathbf{r})$ is a function of the quantities $\mathbf{v}_1$, $\mathbf{v}_2$, and $\mathbf{r}$ and represents the initial distance between the interacting particles on condition that at a moment t their velocities become equal to $\mathbf{v}_1$ and $\mathbf{v}_2$, and the distance between them becomes $\mathbf{r}$; $\hat{I}$ is the linearized Boltzmann collision integral.[13]

The right-hand side of Eq. (9) is obtained by substituting the first term of Eq. (8) for F_2 into the collision integral (6) and is a source of fluctuation of the one-particle distribution function F_1. We can see from Eq. (9) that the intensity of this source is proportional to Nd^3, where d^3 is the effective volume of the interaction region governed by the potential $U(r)$. The duration of action of the source is determined by the function $\Delta\alpha_{ij}(\mathbf{r}_0)$, which differs from zero for times t of the order of τ_{coll}. The two remaining terms in Eq. (8) correspond to statistical independence of a pair of colliding particles and, on substitution in Eq. (6) for the one-particle distribution function F_1, they usually yield[13] the Boltzmann collision integral $\hat{I}$, the characteristic frequency of which ν is governed by the frequency of gaskinetic collisions.

3. SCATTERING SPECTRUM

We shall now consider the correlation function Φ governing the light scattering spectrum. We can see from Eqs. (7)–(9) that the spectrum has a wide wing (of width of the order of τ_{coll}^{-1}) governed by the first term in Eq. (8) and a narrower structure associated with fluctuations of the one-particle distribution function F_1 [Eq. (9)]. In a study of a narrow part of a spectrum, i.e., of the time $t\gg\tau_{\text{coll}}$ we have to integrate Eq. (9) over a time interval Δt: $\nu^{-1}\gtrsim\Delta t\gg\tau_{\text{coll}}$. Integration of Eq. (9) gives

$$\frac{\partial F_1}{\partial t}+\mathbf{v}_1\frac{\partial F_1}{\partial \mathbf{R}}=\hat{I}F,\quad F_1(\Delta t,\mathbf{R},\mathbf{v}_1)=-N\delta(\mathbf{R})$$

$$\times[f_0(v_1)]^{-1}\int\frac{\partial U}{\partial \mathbf{r}}\frac{\partial}{\partial \mathbf{p}_1}\Big[f_{20}\int_0^{\Delta t}d\tau\Delta\alpha_{ij}(\mathbf{r}_0)\Big]d\mathbf{v}_2\,d\mathbf{r}. \qquad (10)$$

It should be noted that Eq. (10) has a nonzero initial condition which distinguishes it from Eq. (9). This means that the spectrum described by Eq. (10) is located in the spectral range $\omega \lesssim \nu$ and its integrated intensity is given by the function $F_1(\Delta t)$. The total, integrated over the frequencies, contribution to the scattering spectrum associated with the function F_1 vanishes, in accordance with the initial condition for Eq. (9). It therefore follows that the contribution made to the spectrum at low frequencies $\omega \lesssim \nu$ is compensated by a negative contribution to the line wings $\omega \sim \tau_{\text{coll}}^{-1}$. The spectrum described by Eq. (10) includes an even narrower structure of width of the order of γ and this structure is associated with the hydrodynamic modes of the collision operator $\hat{I}$ (Refs. 17–19).

It follows that the general structure of the spectrum can be divided into three regions:

$$\Phi(\omega,\mathbf{q})=\Phi_1(\omega\sim\tau_{\text{coll}}^{-1})+\Phi_2(\omega\sim\nu)+\Phi_3(\omega\sim\gamma,\mathbf{q}).$$

The integrated intensity of the investigated depolarized light scattering is

$$\int d\omega\Phi(\omega)=\int d\omega\Phi_1(\omega),$$

and the contributions of the terms Φ_2 and Φ_3 determine the fine structure of the spectrum and are of purely interference nature.

3.1. High-frequency scattering spectrum

The scattering spectrum at high frequencies $\nu \ll \omega \sim \tau_{\text{coll}}^{-1}$ is governed by a function $\Phi_1(\omega)$, which—according to Eqs. (7) and (9)—is given by

$$\Phi_1(\omega)=4\pi N^2\int_0^\infty dt\cos\omega t\iint\Delta\alpha_{ij}(\mathbf{r})$$

$$\times\Delta\alpha_{ij}(\mathbf{r}_0)f_0(v)\exp\Big\{-\frac{U(r)}{T}\Big\}d\mathbf{v}\,d\mathbf{r}, \qquad (11)$$

$$\int\Phi_1(\omega)\,d\omega=(2\pi N)^2\int\Delta\alpha_{ij}^2(\mathbf{r})\exp\Big[-\frac{U(r)}{T}\Big]d\mathbf{r}.$$

Here, $\mathbf{v}=\mathbf{v}_2-\mathbf{v}_1$ is the relative velocity of the colliding particles:

$$\Delta\alpha_{ij}(\mathbf{r})=r^{-2}(r_ir_j-{}^1/_3\delta_{ij}r^2)\Delta\alpha(r).$$

The integrand in Eq. (11) is an even function of the time t and the function itself and its derivatives have no singularities for any real value of t. These properties of the integrand are known (see, for example, Refs. 20 and 21) to be responsible for the exponential profile of the line wing. The task thus reduces to determination of the specific form of the argument of the exponential function. We shall deal with this in the approximation of rectilinear paths $[U(r) \ll T]$ of the colliding particles: $\mathbf{r}_0=\mathbf{r}-\mathbf{v}t$. It is clear from Eq. (11) that the integrand depends on three variables $\mathbf{r}$, $\mathbf{r}_0$, and the angle between the vectors $\mathbf{r}$ and $\mathbf{r}_0$ (which for fixed values of $\mathbf{r}$ and $\mathbf{r}_0$ is governed by $|\mathbf{r}-\mathbf{r}_0|$). Using the approximation of rectilinear paths, we can modify Eq. (11) so as to go over from integration with respect to $\mathbf{v}$ to integration with respect to $\mathbf{r}_0$. Then, after integration with respect to the angular variables of the vectors $\mathbf{r}$ and $\mathbf{r}_0$, we obtain

$$\Phi_1(\omega)\sim\int_0^\infty dr'F(r')\int_0^\infty d\tau\,\tau^{-3}\exp\Big[-\frac{1}{\tau^2}\Big]\cos\Big(\frac{\omega}{\bar{v}_0}r'\tau\Big), \qquad (12)$$

where

$$F(r')=\frac{1}{2r'}\int_{-r'/2^{1/2}}^{r'/2^{1/2}}dy\int_{r'/2^{1/2}}^{\infty}dx\,(x^2-y^2)$$

$$\times\Delta\alpha\Big[\Big(a^2+\frac{1}{2}(x-y)^2\Big)^{1/2}\Big]$$

$$\times\Delta\alpha\Big\{\Big[a^2+\frac{1}{2}(x+y)^2\Big]^{1/2}\Big\}\Big(\frac{3}{2}\cos^2\beta-\frac{1}{2}\Big),$$

$$\cos\beta=\frac{(r')^2-r_0^2-r}{2rr_0}.$$

Here, β is the angle between the vectors $\mathbf{r}$ and $\mathbf{r}_0$; $r'=|\mathbf{r}-\mathbf{r}_0|$;

$$\tau=\frac{t\bar{v}}{r'};\quad r=\Big[a^2+\frac{(x-y)^2}{2}\Big]^{1/2};\quad r'=\Big[a^2+\frac{(x+y)^2}{2}\Big]^{1/2},$$

where $\bar{v}=(T/m)^{1/2}$ is the thermal velocity of the gas particles. The parameter a is governed by the size (diameter) of the colliding particles. Introduction of this parameter is related to exclusion of the head-on collisions of the particles from our consideration.

The line profile given by Eq. (12) represents a set of profiles $I(\omega r'/v)$, weighted by the function $F(r')$. The function I can be reduced to a familiar special function, which if necessary can be calculated using tables.[22–24] The function $F(r')$ is finite at $r'=0$ and at this point only the fourth-order derivatives of the function are nonzero. The actual nature of the $F(r')$ dependence is governed by the nature of the function $\Delta\alpha(r)$.

The most interesting is the behavior of the function $\Phi_1(\omega)$ in the wings of the line $(\tau_{\text{coll}}\omega \gg 1)$. The separate spectral component at the fixed value of r' is governed by the known function $I(\omega r'/\bar{v})$, the asymptote of which is

$$I\Big(\frac{\omega}{\bar{v}}r'\Big)\to\exp\Big[-\frac{3}{2}\Big(\frac{\omega r'}{2\bar{v}}\Big)^{2/3}\Big]\quad\text{for}\quad \omega r'/\bar{v}\to\infty. \qquad (13)$$

The asymptote of the complete spectrum $\Phi_1(\omega)$ is governed by the analytic properties of the function $F(r')$ near $r'=0$ [see Eq. (12)]. In the subsequent equation it is convenient to alter the sequence of integration to Eq. (12) with respect to the variables r' and τ. Then, the inner integration with respect to r' reduces to a unidirectional Fourier transformation $F(r')\to\tilde{F}(\omega\tau/\bar{v})$, where $\hat{F}$ is the Fourier transform of the function F. The asymptotic high-frequency behavior of the function $\tilde{F}$ is governed, according to Fisher,[20] by the convergence radius R_F of the series representing the function $F(r')$ at $r'=0$. The general form of the asymptote $\tilde{F}(\omega\tau/\bar{v})$ is as follows:

$$\tilde{F}\left(\frac{\omega}{\bar{v}}\tau\right) \propto \exp\left[-\left(\frac{\omega\tau}{\bar{v}}\right)^{p}\right], \quad \begin{cases} p>1, & \text{if} \quad R_F=\infty, \\ p=1, & \text{if} \quad R_F \text{ is finite}, \\ p<1, & \text{if} \quad F_F=0. \end{cases}$$

Substituting the explicit form of the asymptote $\tilde{F}$ into Eq. (12) and integrating with respect to τ by the steepest descent method, we obtain the asymptote of the scattering spectrum $\Phi_1(\omega)$:

$$\Phi_1(\omega) \propto \exp\left[-\left(\frac{\omega l}{\bar{v}}\right)^{n}\right], \quad \begin{cases} n>{}^2/_3, & \text{if} \quad R_F=\infty, \\ n={}^2/_3, & \text{if} \quad R_F \text{ is finite}, \\ n<{}^2/_3, & \text{if} \quad R_F=0. \end{cases}$$

The length parameter l is governed, according to Eq. (12), either by the characteristic size of colliding particles a or by the size d of the particle interaction region where $\Delta\alpha(r)$ is induced and the size of this region obeys $d \gtrsim a$.

The former case $n > 2/3$ corresponds to an analytic function $F(r')$ with a singularity at infinity. For example, if $F(r') = \exp[-(r'/a)^2]$, we have $n = 1$ and the asymptote in the form of Φ_1 then becomes

$$\Phi_1(\omega) \propto \exp(-\omega a/\bar{v}).$$

In the second case ($n = 2/3$) we have functions characterized by a singularity in the complex plane of the variable r' (with the exception of the point $r' = 0$). This class of functions includes $F(r')$ corresponding to the dipole-induced dipole (DID) model[1-3] with a power-law fall of the polarizability $\Delta\alpha \propto r^{-k}$ at large distances. The asymptote of the spectrum is then given by Eq. (13) with $n = 2/3$, where the parameter $r' = d$ corresponds to near-zero value of the pole of the function $F(r')$. If we consider sufficiently close approaches of the particles, $r' \sim a$, when the function $\Delta\alpha$ falls more steeply with the distance (in the region of overlap of the electron shells), we find that $\Delta\alpha \propto \exp(-r/a)$ and the nature of the asymptote does not change ($n = 2/3$), but the parameter d in the exponential function is replaced with a. We shall not consider the third case ($n < 2/3$) when the function $F(r')$ has a singularity at zero, because we cannot see any physical justification for this case.

It therefore follows that the adopted approximation of rectilinear paths of the colliding particles yields a calculation equation (12) which describes the profile of the depolarized collision-induced scattering of light in a dense gas. The asymptote of the wing of the line considered in this approximation is given by Eq. (13) ($n = 2/3$) in which the parameter r' corresponds to a singularity of the function $F(r')$ closest to zero.

3.2. Fine structure of the spectrum

The fine structure of the depolarized scattering spectrum $\Phi_2(\omega) + \Phi_3(\omega)$ is given by Eq. (10) with a suitable initial condition, which is valid in the spectral range $\omega \lesssim \nu$. We can find the solution of Eq. (10) using the method of expansion of the fraction F_1 in terms of eigenfunctions of the collision operator $\hat{I}$ (Ref. 25). From the methodological point of view, the problem is similar to that of the depolarized scattering of light in a molecular gas with an intrinsic anisotropic polarizability, discussed by us earlier.[26]

In the spectrum described by Eq. (10) there is a relatively wide component $\Phi_2(\omega)$ which has a Lorentzian profile of width of the order of ν, as well as a system of narrow dips $\Phi_3(\omega)$ which depends on the polarization of light at the unshifted frequency $\omega = 0$ and at acoustic frequencies $\omega = \pm\Omega$, $\Omega = qu_s$, where $\mathbf{q}$ is the wave vector of the scattered light and u_s is the velocity of sound. We shall begin with the integrated intensity of light in the spectral region $(\omega \sim \nu)$:

$$\int\limits_{|\omega|\lesssim\nu} \Phi_2(\omega)\,d\omega = (2\pi N)^2 \int \Delta\alpha_{ij}(\mathbf{r}) f_{20} [F_1(\mathbf{v}_{10}) + F_1(\mathbf{v}_{20})]\,d\mathbf{r}\,d\mathbf{v}_1\,d\mathbf{v}_2, \tag{14}$$

where

$$F_1(\mathbf{v}_1) = -N[f_0(v_1)]^{-1} \int \frac{\partial U}{\partial \mathbf{r}} \frac{\partial}{\partial \mathbf{p}_1} \left\{ f_{20} \int_0^\infty d\tau\,\Delta\alpha_{ij}(\mathbf{r}_0) \right\} d\mathbf{v}_2\,d\mathbf{r}.$$

Comparing Eq. (14) with the integral of the function $\Phi_1(\omega)$, we obtain the following estimate:

$$\int\limits_{|\omega|\lesssim\nu} \Phi_2(\omega)\,d\omega \sim Nd^3 \int \Phi_1(\omega)\,d\omega, \quad Nd^3 \ll 1.$$

The intensity distribution in the spectrum $\Phi_2(\omega)$ is given by

$$\Phi_2(\omega) = (2\pi N)^2 \int \Delta\alpha_{ij}(\mathbf{r}) f_{20} \times \sum_{\beta>5} \frac{\nu_\beta B_\beta}{\omega^2 + \nu_\beta^2} [\chi_\beta(\mathbf{v}_{10}) + \chi_\beta(\mathbf{v}_{20})]\,d\mathbf{v}_1\,d\mathbf{v}_2\,d\mathbf{r},$$

where

$$B_\beta = -N \int \chi_\beta(\mathbf{v}_1) \frac{\partial U}{\partial \mathbf{r}} \frac{\partial}{\partial \mathbf{p}_1} \left\{ f_{20} \int_0^\infty d\tau\,\Delta\alpha_{ij}(\mathbf{r}_0) \right\} d\mathbf{v}_1\,d\mathbf{v}_2\,d\mathbf{r}. \tag{15}$$

Here, $\chi_\beta(\mathbf{v})$ represents nonhydrodynamic modes of the collision integral $\hat{I}$ and ν_β represents the corresponding positive eigenvalues.

It is clear from Eq. (15) that the intensity $\Phi_2(\omega = 0)$ is proportional to the N^2, like the intensity of the function $\Phi_1(\omega = 0)$. The width of the spectrum $\Phi_2(\omega)$ is governed by the quantities $\nu_\beta \sim \nu \sim Nv\sigma$ (m is the mass of a particle, σ is the gaskinetic cross section of the particle), which are proportional to the gas density, whereas the width of the distribution $\Phi_1(\omega)$ is of the order of τ_{coll}^{-1} and is independent of the density.

We shall now estimate $\Phi_2(\omega)$ at $\omega = 0$. We can see from Eq. (15) that the depolarized scattering spectrum contains only contributions of functions of the $\Delta\alpha_{ij}(\mathbf{r})$ type, because the scattering is governed by the second-rank tensor $\chi_\beta \propto v_i v_j$. Substituting in Eq. (15) for χ_β one function

$$\chi_{\beta 1} = \frac{m}{T} v_i v_j \quad (i \neq j),$$

we can calculate approximately $\Phi_2(\omega = 0)$:

$$\Phi_2(\omega=0) \sim 2\pi\mu B_{\beta 1}, \tag{16}$$

where

$$B_{\beta 1} = -N\frac{m}{T} \int v_{1i} v_{1j} \frac{\partial U}{\partial \mathbf{r}} \frac{\partial}{\partial \mathbf{p}_1} \left\{ f_{20} \int_0^\infty d\tau\,\Delta\alpha_{ij}(\mathbf{r}_0) \right\} d\mathbf{v}_1\,d\mathbf{v}_2\,d\mathbf{r};$$

$$\mu = 2\pi \frac{N^2}{\nu} \frac{m}{T} \int \Delta\alpha_{ij}(\mathbf{r}) f_{20} [(\mathbf{v}_{10})_i (\mathbf{v}_{10})_j + (\mathbf{v}_{20})_i (\mathbf{v}_{20})_j]\,d\mathbf{v}_1\,d\mathbf{v}_2\,d\mathbf{r}.$$

Here, μ is the Maxwell coefficient for a noble gas, and governs birefringence in a flowing viscous gas or liquid.[27] We can estimate the ratio Φ_2/Φ_1 for $\omega = 0$ by adopting the following expression for $B_{\beta 1}$ and μ:

$$B_{\beta 1} = \frac{N}{T} \int \frac{1}{r} \frac{\partial U}{\partial r} (r_i v_j + r_j v_i) f_0(v) \times \exp\left(-\frac{U}{T}\right) \left[\int_0^\infty d\tau \Delta\alpha_{ij}(\mathbf{r}_0) \right] d\mathbf{r}\, d\mathbf{v}$$

$$\sim \frac{Nd^2}{T} \int_\infty^0 r \frac{\partial U}{\partial r} e^{-U/T} \Delta\alpha(r)\, dr \sim Nd^3 \Delta\overline{\alpha} > 0.$$

The Maxwell constant is taken from Ref. 12

$$\mu \sim \theta N d^3 \overline{\Delta\alpha} (\overline{v}\sigma)^{-1} > 0,$$

where $\theta \sim U/T$ is the characteristic angle of the scattering of the colliding particles, σ is the gaskinetic cross section. Consequently, the ratio

$$\Phi_2(\omega=0)/\Phi_1(\omega=0) \sim \left(\frac{\mu}{\tau_{\text{coll}}}\right)^2 \frac{1}{(N\overline{\Delta\alpha})^2} \frac{1}{\theta},$$

i.e., the contrast of the fine structure, is independent of the gas density and is of the order of unity.

We shall now investigate the narrow structure of the spectrum $\Phi_3(\omega, \mathbf{q})$, which is due to hydrodynamic modes of a collision operator. We recall that the collision operator $\hat{I}$ has five hydrodynamic modes χ_i, where $i = 1, \ldots, 5$, corresponding to five quantities conserved in collisions: the number of particles, the three components of the velocity, and the energy.[17,18] We shall now write down the necessary hydrodynamic modes χ_i and the corresponding eigenvalues λ_i in the explicit form[19]

$$\chi_{1,2} = \left(\frac{C_v}{2C_p}\right)^{1/2} \left[\frac{1}{2C_v} (v/\overline{v})^2 \pm \left(\frac{C_p}{C_v}\right)^{1/2} \frac{\mathbf{qv}}{q\overline{v}}\right], \quad \lambda_{1,2} = \pm iqu_s + \gamma_1,$$

$$u_s = \overline{v} \left(\frac{C_p}{C_v}\right)^{1/2}, \quad \gamma_1 = \frac{q^2}{2\rho} \left[\frac{4}{3}\eta + \varkappa m \frac{1}{C_p C_v}\right].$$

The shear modes are

$$\chi_3 = \frac{[\mathbf{qv}]}{q\overline{v}}, \quad \chi_4 = \frac{[\mathbf{q}[\mathbf{qv}]]}{q^2\overline{v}}, \quad \lambda_{3,4} = \gamma_3 = \frac{q^2}{\rho}\eta.$$

Here, C_v and C_p are the specific heats of a particle at constant volume and pressure, respectively; m is the mass of the particle; ρ, κ, and η are the density, thermal conductivity, and shear viscosity of the gas.

The relationship between the hydrodynamic modes and the mode $\chi_{\beta 1}$ discussed above is given in Eq. (10) by the free motion operator $\partial \mathbf{v}/\partial \mathbf{R}$. Allowance for this relationship gives rise to dips in the depolarized scattering spectrum of a rare gas and these dips are fully analogous (including the polarization relationships) to the dips in the scattering spectrum of a molecular gas.[19,26] The main distinction of the spectrum of a rare gas is that the contrast of the dips is quite large, of the order of unity, whereas in the case of a molecular gas the contrast is small. In fact, the expression for $\Phi_3(\omega, \mathbf{q})$ can be reduced to[19,26]:

$$\Phi_3(\omega, \mathbf{q}) = -(2\pi N)^2 \int \Delta\alpha_{ij}(\mathbf{r}) f_{20} \sum_{k=1}^{4} \sum_{\alpha>5} \times \frac{\gamma_k C_{k\alpha}}{(\omega - \Omega_k)^2 + \gamma_k^2} [\chi_\alpha(\mathbf{v}_{10}) + \chi_\alpha(\mathbf{v}_{20})]\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{r},$$
$$C_{k\alpha} = \sum_{\beta>5} \langle \chi_\alpha | \hat{I}^{-1} \mathbf{qv} | \chi_k \rangle \langle \chi_k | \mathbf{qv} \hat{I}^{-1} | \chi_\beta \rangle B_\beta. \tag{17}$$

Here the angular brackets denote the matrix elements of the composite operator $\hat{\mathbf{q}}\mathbf{v}\hat{I}^{-1}$ between the hydrodynamic modes χ_k and the nonhydrodynamic modes χ_α and χ_β.

We can see from Eq. (17) that the spectrum $\Phi_3(\omega)$ consists of three narrow dips at the central frequency $\Omega_{3,4} = 0$ and of acoustic frequencies $\Omega_{1,2} = \pm qu_s$; the contrast of the dips relative to $\Phi_2(\omega = 0)$ is

$$\frac{\Phi_3(\omega=0)}{\Phi_2(\omega=0)} \sim \frac{\nu}{\gamma} \{\langle \chi_\alpha | \hat{I}^{-1} \mathbf{q}\hat{\mathbf{v}} | \chi_k \rangle\}^2 \sim \left(\frac{q\overline{v}}{\nu}\right)^2 \frac{\nu}{\gamma} \sim 1.$$

The full contrast of the narrow structure R is

$$R = \frac{\Phi_3(\omega=0)}{\Phi_1(\omega=0) + \Phi_2(\omega=0)} \sim \left(\frac{\mu}{\tau_{\text{coll}}}\right)^2 \frac{1}{(N\overline{\Delta\alpha})^2} \Big/ \left[1 + \left(\frac{\mu}{\tau_{\text{coll}}}\right)^2 \frac{1}{(N\overline{\Delta\alpha})^2 \theta}\right]. \tag{18}$$

It should be noted that Eq. (18) for the contrast R differs little from the corresponding expression in our earlier paper.[28] The difference is due to the fact that the estimate obtained in Ref. 28 applies essentially to a model of the hard sphere type ($\theta \sim 1$) and ignores the long-range part of the potential.

A qualitative description of the spectrum of the depolarized scattering of light in a rare gas is given in Fig. 1 for two polarizations corresponding to the *VH* (vertical–horizontal) and *HH* (horizontal–horizontal) scattering of light.

4. DISCUSSION

The main result of the present study seems to us the conclusion that the collision-induced depolarized light scattering spectrum of a noble gas has a complex fine structure ignored earlier [see Eqs. (17)–(20) and Fig. 1].

It is important to note that the description of this structure requires the knowledge of the Maxwell constant of the investigated gas, whereas the existing theories attempt to calculate the scattering spectrum simply by selection of the function $\Delta\alpha(r)$ (Refs. 4–10). As pointed out above, this fine structure does not alter the total integrated intensity of the scattered light, which is given by

$$\int d\omega \Phi_1(\omega) \sim N^2 \int (\Delta\alpha)^2 e^{-U/T} d\mathbf{r}, \left(\int d\omega (\Phi_2 + \Phi_3) = 0 \right),$$

but it alters significantly the spectrum. Hence, it follows that it is not possible to relate the integral intensity to the spectral profile by a single function $\Delta\alpha(r)$, as is done in many previous treatments.

The fine structure of the spectrum is thus governed by the Maxwell constant of the investigated medium. We recall that the Maxwell effect consists of the following: flow of viscous liquids or gases with anisotropic molecules gives rise to birefringence, and the effect is related to the orienting influence of the velocity gradients on anisotropic particles.

In the case of liquids this is a familiar effect and was investigated experimentally many years ago.[27] These measurements have been extended to some molecular gases.[29-31] Noble gases do not have an intrinsic polarization anisotropy of a single particle, because the Maxwell effect and the depolarized scattering of light are then related solely to the anisotropic polarizability of a pair of colliding and interacting particles. The Maxwell constant μ for noble gases (proportional to N) is compared with the corresponding value for molecular CO_2 and N_2 gases (in the case of molecular gases this constant is independent of the pressure) at noble gas pressures of the order of 100 atm (Ref. 12). This range of pressures is difficult to handle in a direct experimental determination of the constant μ because of the appearance of turbulence.[12] It seems to us that at high gas pressures the constant μ is best determined by investigating the profile of the depolarized light scattering spectrum (in the *VH* or *HH* polarizations). An experimental study of the scattering of light should include determination of the following quantities: the integrated intensity of the scattering spectrum (this can be determined independently from the pressure dependence of the Kerr constant—see Ref. 11), the half-width of the wide part of the spectrum, and the fine-structure contrast at the center of the line in the case of the *VH* polarization or at acoustic frequencies in the *HH* polarization. The magnitude of the contrast may be that of the $\Phi_3(\omega)$ contour or of the $\Phi_2(\omega)$ contour, because in both cases the contrast is proportional to μ^2 (as discussed above).

It is interesting to consider the spectrum when the gas pressure is varied and it is convenient to determine the scattering intensity in units of $\Phi(\omega)N^{-2}$. Then, the wide part of the spectrum is practically independent of the gas pressure, whereas the fine structure of $\Phi_2(\omega)$ and $\Phi_3(\omega,q)$, changes very considerably. The width of the profile Φ_2, which is equal to ν, increases proportionately to the gas density N and the width of the narrow dips γ falls proportionately to N^{-1}. The contrast of the fine structure R is independent of the gas pressure. Therefore, this approach makes it possible to separate most conveniently the fine structure of the spectrum.

The widths of the investigated spectral lines differ by many orders of magnitude (Fig. 1). For example, at a rare gas pressure of $p\sim 50$ atm the order of magnitude of the widths is $\tau_{\rm coll}^{-1}\sim 10^{12}\ {\rm s}^{-1}$, $\nu\sim 10^{11}\ {\rm s}^{-1}$, and $\gamma\sim 10^{7}\ {\rm s}^{-1}$. Hence, it is clear that in an experimental investigation of the relevant components of the spectrum $\Phi_1(\omega)$, $\Phi_2(\omega)$, $\Phi_3(\omega)$ we need apparatus with different spectral resolutions.

The wide part of the spectrum, which is governed by the function $\Phi_1(\omega)$ [Eqs. (11) and (12)], is known in the literature as the collision-induced scattering of light and it is currently being investigated quite extensively (both experimentally and theoretically), and this has been done not only for noble gases, but also for molecular gases.[1-10,32-36] In most of the investigations the spectrum is calculated simply by selecting the form of the function $\Delta\alpha(r)$ used to find numerically several first moments of the spectrum $M_k=\int\omega^k\Phi(\omega)d\omega$ where $k=0,2,4,\ldots$. The zeroth moment M_0 describes the integrated intensity of a spectrum and the higher moments represent the distribution of the intensity in the spectrum. The results of the present study show that this approach is unsatisfactory for the following reasons.

Firstly, the total spectrum should be described by the function $\Phi(\omega)=\Phi_1+\Phi_2+\Phi_3$. It is important to note that the integrated intensity of the spectrum, determined over the frequency range $\omega>\nu$ (which is usually done experimentally), contains not only a positive contribution from the function $\Phi_1(\omega)$, but also a negative contribution of the function $\Phi_2(\omega)$. The ratio of these contributions in the range $\omega>\nu$ is described by the following order-of-magnitude relationships

$$\int\limits_{\omega>\nu}\Phi_2(\omega)\,d\omega\sim\frac{\mu^2T^2}{\theta N\eta^2\overline{\Delta\alpha}^2}\int\limits_{\omega>\nu}\Phi_1(\omega)\,d\omega,\qquad\frac{\mu^2T^2}{\theta N\eta^2\overline{\Delta\alpha}^2}\sim Nd^3,$$

which shows that the contribution is of the same order as that of triple collisions in this part of the spectrum. It is also possible to determine reliably the decrease of the experimental integrated intensity in a wide part of the scattering spectrum (measured in units of N^2) when the gas density N is increased,[5-8] a decrease due entirely to the contribution of triple collisions. Using the experimental data of Ref. 6 on argon, we can obtain an upper limit (without allowance for triple collisions) of the quantity μ^2/θ in the range of gas pressures up to 100 atm. An estimate gives for an argon pressure of 100 atm a value $\mu^2/\theta\sim 10^{-30}\ {\rm s}^2$ which is not in conflict with theoretical estimates of the coefficient μ for argon obtained by us earlier.[12]

It seems to us that measurements in a wide part of the spectrum cannot be used to separate the contribution of triple collisions from the contribution of the function $\Phi_2(\omega)$ described above; the corresponding contribution of $\Phi_3(\omega)$ is much smaller [by a factor $(qv/\nu)^2\ll 1$] than that of $\Phi_2\times(\omega)$. Reliable separation of these two contributions can be made using the data on the dependence of the Kerr constant on the density of the investigated gas, which is now known for a number of molecules.[11] The Kerr constant is related directly to the integrated intensity of the depolarized scattering of light in rare gases.[1-3,6,7] Interference effects in the spectrum, which are associated with the functions $\Phi_2(\omega)$ and $\Phi_3(\omega)$, do not contribute to the Kerr constant.

Secondly, the description of the form of the spectrum by a finite number of moments M_k is correct if we expand the correlation function $\Phi(t)$ as a series in moments

$$\Phi(t)=\sum_{k=0}^{\infty}\frac{M_k}{k!}t^k$$

as a nonzero convergence radius.[20,21] This is precisely the case when the function $\Phi(\omega)$ can be restored throughout the frequency range (including distant tails) from a finite number of moments. On the other hand, the most frequently used DID approximation for the function $\Delta\alpha(r)$ [namely $\Delta\alpha(r)\propto r^{-3}$] does not satisfy this criterion and, therefore, cannot describe the wings of the lines using a finite number of moments.

The expression obtained by us for the wide spectrum $\Phi_1(\omega)$ [Eqs. (11) and (12)] makes it possible to calculate the asymptotic behavior in the wing of the line in the approximation of linear paths and this can be done irrespective of the convergence of the series in terms of the moments M_k. The approximation of rectilinear paths ignores the contribution of close approaches of the particles within the range $r\sim a$ (head-on collisions), which limits the range of validity of this approximation to the frequency interval $\omega<v/a\sim 10^{12}\ {\rm cm}^{-1}$. In this frequency interval the spectrum is governed entirely by the behavior of the polarizability

$\Delta\alpha(r)$ and is practically independent of the nature of the interaction potential.

The asymptotic expression for the wing is universal

$$\exp\left\{-\frac{3}{2}\left(\frac{\omega r'}{2\bar{v}}\right)^{2/3}\right\}$$

and it applies to the DID model and any power law describing the fall of the function $\Delta\alpha \propto (r)^{-m}$ as well as in the case of an exponential decay law $\Delta\alpha \propto \exp(-r/a)$. The value of r' is then governed by the singularity of the function $F(r')$ closest to zero. In most of the investigations known to us a study of the spectrum reduces to calculation, from the experimental data, of the first few moments of the spectrum, which are used to fit the parameters of the function $\Delta\alpha(r)$ (Refs. 1–10 and 32–36). In contrast to this traditional approach, the problem of the asymptote for the far scattering wing is discussed in detail in a thesis by Troyanovskiĭ.[21] The main conclusion reached by him is in the form of an asymptote $\exp[-(\omega\tau_{\text{coll}})^{2/3}]$ for the power-law particle interaction potential in the far wing of the line ($\omega \gg \bar{v}/a$) where an important role is played by the nature of the interaction potential. In the frequency range $\omega < \bar{v}/a$, where the approximation of rectilinear paths can be used, Troyanovskii calculated numerically the line profile using a model pair polarizability of insulating spheres. The results of this calculation give the same power exponent 2/3 and agree well with the experimental data on argon in the frequency range $\Delta\omega$ from 40 to 300 cm^{-1}.

It therefore follows that the part of the spectrum where the asymptote is $\exp[-(\omega\tau_{\text{coll}})^{2/3}]$ describes in practice the range of validity of the DID model for a given gas. It follows from the experimental data that the width of this region $\Delta\omega$ differs even for normal gases $\Delta\omega_{\text{Ar}} \lesssim 300\ \text{cm}^{-1}$ $\Delta\omega_{\text{He}} \lesssim 150\ \text{cm}^{-1}$ (Refs. 4 and 5).

At high frequencies the asymptote of the spectrum for gases becomes steeper; such a tendency is clearly demonstrated in, for example, the experiments on gaseous helium.[4,32] This range is outside the validity of our kinetic approach and, in accordance with Fisher's work,[20] can be described by the dependence $\exp(-\omega\tau^*)$. Here, τ^* is the characteristic time of reversible collisionless evolution of the system.[20]

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