POSSIBLE RESONANCE PHENOMENA IN THE KINETICS OF MOLECULAR GASES

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We consider the viscosity and thermal conductivity and also sound propagation in molecular gases in mutually perpendicular constant and variable magnetic (or electric) fields. We show that for well-defined relations between the magnitude of the constant field and the amplitude and frequency of the variable field the change in the transfer and sound absorption coefficients shows a resonance character. The effect depends essentially on the form of the angular dependence of the non-spherical part of the interaction potential of the molecules.

1. INTRODUCTION

IT has been shown in a number of experimental and theoretical papers[1-11] that the transfer coefficients of molecular gases are changed in magnetic and electric fields. Such an effect is explained by the existence of a non-spherical dependence of the molecular collision cross section on the angle between the relative velocity of the colliding molecules and their angular momenta. The precession of the molecules caused by the interaction of the magnetic moment of the molecule and the magnetic field (or the dipole moment and the electric field) leads to an increase of the collision cross-section. The transfer coefficients in an external field have a tensor character and the tensors contain both components which are even in the field and components which are odd.

A qualitative discussion given by us together with L. L. Gorelik and V. V. Sinitsyn of the problem of the influence of crossed constant and variable fields on the transfer phenomena in gases enabled us to assume that in such fields a resonance decrease of the transfer coefficients must take place. This assumption was experimentally corroborated for the example of the thermal conductivity of oxygen.[12]

It is well known[13] that the motion of particles with a magnetic moment in "crossed" magnetic fields has a resonance character when the frequency of the rotating field is equal to the precession frequency in the constant field. In contradistinction to the usual precession in a constant field, in the case considered there occurs a complicated precessional motion (the end of the angular momentum vector M describes a spiral line) leading to an additional increase in the scattering cross-section of non-spherical molecules. This fact, in turn, leads to the occurrence of effects connected with a resonance increase in the scattering cross-section of the molecules for a well-defined relation between the amplitudes of the constant field B_0 and the variable field B_1 and the frequency ω of the variable field.

In the present paper we give a theoretical consideration of the viscosity, thermal conductivity, and the propagation of sound in molecular gases in crossed (magnetic and electric) fields. In the following we show that for a well-defined relation between B_0, B_1, and ω the change in the transfer coefficients has a resonance character and depend on the form of the non-spherical part of the molecular collision operator. The change in the transfer coefficients of a molecular gas in external constant and variable fields[9,10] is not critically dependent on the model for the non-spherical part of the scattering cross section. It is thus rather complicated to deduce the angular dependence of the collisional cross section of the molecules from experiments in constant and variable fields. This becomes possible if we consider the change in the transfer coefficients of molecular gases in crossed fields.

2. SOLUTION OF THE KINETIC EQUATION

We consider a gas with rotating molecules in a crossed (magnetic or electric) field **B**

$$\mathbf{B} = -\mathbf{i}B_1 \sin \omega t + \mathbf{j}B_1 \cos \omega t + \mathbf{k}B_0, \tag{2.1}$$

where B_0 is the intensity of the constant field, B_1 and ω the amplitude and frequency of the rotating field. The linearized kinetic equation written down in a spherical system of coordinates in which the z axis is taken along the direction of the constant field B_0, has the form[6]

$$\frac{\partial\chi}{\partial t} + N + \gamma[\mathbf{MB}]\frac{\partial\chi}{\partial\mathbf{M}} = -\hat{I}\chi, \qquad (2.2)^*$$

where $f = f_0(1 + \chi)$, f_0 is the equilibrium distribution function,

$$N = \sum_{l,m} a_{lm}{}^* A_{lm}, \quad A_{1m} = Y_{1m}(\mathbf{u})\,(u^2 + H_{\text{rot}}{}^2 - c_p),$$
$$A_{2m} = Y_{2m}(\mathbf{u}), \quad A_{00} = \frac{2}{3}u^2 - \frac{1}{c_v}(u^2 + H_{\text{rot}}); \tag{2.3}$$

$$\hat{I}\chi = \int f_{01}[(\chi + \chi_1)W - (\chi' + \chi_1')W']\,d\Gamma_1\,d\Gamma'\,d\Gamma_1', \tag{2.4}$$

$d\Gamma$ a phase volume, $Y_{lm}(u) = u^l Y_{lm}(\varphi_u, \vartheta_u)$; u and H_{rot} are the dimensionless velocity and rotational energy. The quantities a_{lm} are given in[6].

Equation (2.2) is obtained by averaging over the fast rotation of the molecules around their axis and describes the behavior of a gas with linear molecules and with "symmetric top" kind of molecules in an external field. The quantity γ is defined by the following relations:

$$\gamma = d\sigma / M, \quad \sigma = \cos(\widehat{\mathbf{dM}}) \tag{2.5a}$$

for polar symmetric top kind of molecules with a dipole moment d in an electric field;

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*$[\mathbf{MB}] \equiv \mathbf{M} \times \mathbf{B}$.

$$\gamma = \frac{2\mu_0\sigma}{M} + \frac{2\mu_0\hbar}{M^2}\delta_{\sigma 0}, \quad \sigma = 0, \pm 1 \tag{2.5b}$$

for paramagnetic molecules (O_2) in a magnetic field[11] (μ_0—Bohr magneton);

$$\gamma = \mu_{\text{rot}}\hbar \tag{2.5c}$$

for non-paramagnetic molecules with a magnetic moment μ_{rot}.

In a crossed field the operator which takes the interaction of the rotating molecules with the field into account has in the chosen system of coordinates the form

$$\gamma[\mathbf{MB}]\frac{\partial}{\partial \mathbf{M}} = i(\gamma_0 \hat{l}_z + \gamma_1 \hat{l}_+ e^{-i\omega t} + \gamma_1 \hat{l}_- e^{i\omega t}), \tag{2.6}$$

where $\gamma_0 = \gamma B_0$, $\gamma_1 = \frac{1}{2}\gamma B_1$; $\hat{1}$ is the operator of the angular momentum of the particles.[14]

We shall look for a solution of Eq. (2.2) in the form

$$\chi = -\sum_{l,m} a_{lm}{}^{*}\chi_{lm}. \tag{2.7}$$

The functions χ_{lm} must satisfy the equation

$$\partial\chi_{lm}/\partial t + i(\gamma_0\hat{l}_z + \gamma_1\hat{l}_+ e^{-i\omega t} + \gamma_1\hat{l}_- e^{i\omega t})\chi_{lm} = A_{lm} - \hat{I}\chi_{lm}. \tag{2.8}$$

Following[6] we split the collision operator (2.4) into two parts:

$$\hat{I} = \hat{I}^{(0)} + \varepsilon\hat{I}^{(1)}, \tag{2.9}$$

where $\hat{I}^{(0)}$ describes the collisions without taking into account the rotational degrees of freedom of the molecules, $\epsilon\hat{I}^{(1)}$ is a small operator which takes into account the dependence of the collision cross-section on the rotating moments (ϵ is a small parameter).

We shall assume that $\hat{I}^{(0)}$ is the Maxwellian collision integral,[6] i.e., its eigenfunctions from a complete set of orthonormalized functions and are determined by the following expressions:

$$\hat{I}^{(0)}\psi_n = \lambda_n\psi_n, \tag{2.10}$$

$$\psi_n = \psi_{lml_1l_2r_1r_2s} = \sum_{m_1+m_2=m} C^{lm}_{l_1m_1l_2m_2} Y_{l_1m_1}(\mathbf{u})$$
$$\times Y_{l_2m_2}(\mathbf{M})\, L_{r_1}{}^{l_1}(u^2)\, L_{r_2}^{l_2+\alpha}(H_{\text{rot}})\,\varphi_s(\sigma),$$
$$\lambda_n = \alpha_{l_1r_1}\delta_{r_20}\delta_{l_20}\delta_{s0} + \beta_{l_1r_1}(1 - \delta_{r_20}\delta_{l_20}\delta_{s0}), \tag{2.11}$$

where $C^{lm}_{l_1m_1l_2m_2}$ are Clebsch-Gordan coefficients, $L^{l}_{r}(x)$ Laguerre polynomials; for linear molecules $\alpha = 0$ and for symmetrical top kind molecules $\alpha = \frac{1}{2}$. The eigenvalues (2.11) differ from those introduced in[6] by a factor n (n—the density) and have the dimensions of frequency.

Using (2.9) we write Eq. (2.8) for χ_{lm} in the form

$$\hat{K}^{-1}\chi_{lm} = A_{lm} - \varepsilon\hat{I}^{(1)}\chi_{lm}, \tag{2.12}$$

where

$$\hat{K}^{-1} = \frac{\partial}{\partial t} + \hat{I}^{(0)} + i(\gamma_0\hat{l}_z + \gamma_1\hat{l}_+ e^{-i\omega t} + \gamma_1\hat{l}_- e^{i\omega t}). \tag{2.13}$$

We shall look for the solution of Eq. (2.12) in the form of an expansion in the small parameter ϵ:

$$\chi_{lm} = \chi^{(0)}_{lm} + \varepsilon\chi^{(1)}_{lm} + \varepsilon^2\chi^{(2)}_{lm} + \ldots \tag{2.14}$$

We substitute (2.14) into Eq. (2.13). Separating the equation for $\chi^{(0)}_{lm}$ and using the explicit form (2.3) for A_{lm}, we get

$$\chi^{(0)}_{lm} = \sum_n \lambda_{n_0}{}^{-1}\langle\psi_{n_0}, A_{lm}\rangle\,\psi_{n_0}, \quad n_0 = (l, m, l_1, 0, r_1, r_2, 0), \tag{2.15}$$

where $\langle F_1, F_2\rangle = \int f_0 F_1^{*} F_2\, d\Gamma\, d\sigma$ in the case of an electric field. In the case of a magnetic field the integration over σ is replaced by a summation.

The equation for the function $\chi^{(1)}_{lm}$ has the form

$$\hat{K}^{-1}\chi^{(1)}_{lm} = -\sum_n B_n{}^{lm}\psi_n. \tag{2.16}$$

Here

$$B_n{}^{lm} = \sum_{n_0} \lambda_{n_0}{}^{-1}\langle\psi_{n_0}, A_{lm}\rangle\, I^{(1)}_{n_0n}. \tag{2.17}$$

We shall look for its solution in the form

$$\chi^{(1)}_{lm} = -\sum_n B_n{}^{lm} C^{lm}_{l_1m_1l_2m_2} Y_{l_1m_1}(\mathbf{u})\, L_{r_1}{}^{l_1}(u^2)\, L_{r_2}{}^{l_2}(H_{\text{rot}})\,\varphi_s(\sigma)\,\chi^{(1)}_{l_2m_2}, \tag{2.18}$$

where the unknown functions $\chi^{(1)}_{l_2m_2}$ satisfy the equation

$$\hat{K}^{-1}\chi^{(1)}_{l_2m_2} = Y_{l_2m_2}(\mathbf{M}). \tag{2.19}$$

We write $\chi^{(1)}_{l_2m_2}$ as a sum

$$\chi^{(1)}_{l_2m_2} = \sum_k a_{qm_2k} Y_{l_2k}(\mathbf{M})\, e^{i\omega t(m_2-k)}, \quad q = (l_1r_1l_2r_2). \tag{2.20}$$

Substituting (2.20) into Eq. (2.19) we get

$$\sum_k e^{i\omega t(m_2-k)}\big[(ik\tilde{\gamma}_0 + \tilde{\lambda}_n)a_{qm_2k} + \gamma_1 \bar{l}_{k,k+1} a_{qm_2k+1}$$
$$+ \gamma_1 l_{k,k-1} a_{qm_2k-1}\big] Y_{l_2k}(\mathbf{M}) = Y_{l_2m_2}(\mathbf{M}), \tag{2.21}$$

where

$$\tilde{\gamma}_0 = \gamma_0 - \omega, \quad \lambda_n = \lambda_n + im_2\omega.$$

It is clear from (2.21) that the problem of determining the unknown coefficients a_{qm_2k} reduces to solving the equation

$$[\hat{\tilde{I}} + i(\tilde{\gamma}_0\hat{l}_z + \gamma_1\hat{l}_+ + \gamma_1\hat{l}_-)]\tilde{\chi}(\mathbf{M}) = Y_{l_2m_2}(\mathbf{M}), \tag{2.22}$$

where $\hat{\tilde{I}} = \hat{I}^{(0)} + im_2\omega$,

$$\tilde{\chi}(\mathbf{M}) = \sum_k a_{qm_2k} Y_{l_2k}(\mathbf{M}). \tag{2.23}$$

We rotate the system of coordinates in angular momentum space over an angle ϑ_1 defined by

$$\cos\vartheta_1 = \tilde{\gamma}/\sqrt{\tilde{\gamma}^2 + \gamma_1^2}. \tag{2.24}$$

The new z′ axis is then directed along the effective field

$$\gamma^2_{\text{eff}} = \tilde{\gamma}^2 + \gamma_1^2. \tag{2.25}$$

This transformation of the system of coordinates corresponds to a linear transformation in the space of the functions $Y_{l_2k}(\mathbf{M})$:

$$Y_{l_2k}(\mathbf{M}) = \sum_p T_{kp}{}^{l_2} Y_{l_2p}(\mathbf{M}'), \tag{2.26}$$

where $T^{l_2}_{kp} = i^{k-p} P^{l_2}_{kp}(\cos\vartheta_1)$. The functions $P^{l_2}_{kp}(\cos\vartheta)$ are defined in[15].

In the rotated system of coordinates Eq. (2.22) has the form

$$(\tilde{I} + i\gamma_{\text{eff}}\hat{l}_{z'})\tilde{\chi} = \sum_p T^{l_2}_{m_2p} Y_{l_2p}(\mathbf{M}'). \tag{2.27}$$

Performing the inverse transformation to the old system of coordinates in the solution of Eq. (2.27) we get an expression for the coefficients a_{qm_2k}:

$$a_{qm_2k} = \sum_p (\lambda_n + im_2\omega + ip\gamma_{\text{eff}})^{-1} T_{m_2p}(T^{-1})_{pk}{}^{l_2}. \tag{2.28}$$

Substituting (2.28) into (2.20) and (2.18) we can find $\chi^{(1)}_{lm}$. Formally we can write the expression for $\chi^{(2)}_{lm}$ as follows

$$\chi^{(2)}_{lm} = -\varepsilon\hat{K}\hat{I}^{(1)}\chi^{(1)}_{lm_1} \tag{2.29}$$

where $\hat{K}$ is the operator which is the inverse of $\hat{K}^{-1}$.

3. THERMAL CONDUCTIVITY, VISCOSITY

We shall consider the viscosity and thermal conductivity of molecular gases in a crossed field. It has been shown earlier[6] that the viscosity and thermal conductivity coefficients in a constant field are determined by the expression

$$c_{l'm',\,lm} = \langle A_{l'm'}, \chi_{lm}\rangle. \tag{3.1}$$

In the case considered the coefficients (3.1) which are off-diagonal in m differ from zero. From the form of the operators $\hat{K}^{-1}$ and $\hat{I}(1)$ the following properties of the coefficients $c_{lm,l'm'}$ are determined:

$$\begin{gathered} c_{lm,\,l'm'}(t) = e^{i\omega t(m-m')}c_{lm,\,l'm'},\\ c_{lm,\,l'm'}(B_0, B_1) = c^{*}_{l'm',\,lm}(-B_0, -B_1),\\ c_{lm,\,l'm'}(t) = (-1)^{m-m'}c^{*}_{l-m,\,l'-m'}(t). \end{gathered} \tag{3.2}$$

Bearing these properties of the coefficients $c_{lm,l'm'}$ in mind we can write down the thermal conductivity and viscosity tensors. The thermal conductivity tensor has the form

$$\begin{aligned} \varkappa_{ik} = \frac{2T}{3m}\Big\{ & \delta_{ik}\operatorname{Re}c_{11,11} + b_i^0 b_k^0(c_{10,10} - \operatorname{Re}c_{11,11}) + b_{ik}^0 \operatorname{Im}c_{11,11} \\ & + \frac{1}{\sqrt{2}}(b_i^0\dot{b}_k^1 + b_k^0\dot{b}_i^1)\operatorname{Re}c_{10,11} + \frac{1}{\sqrt{2}}(b_k^0 b_i^1 - b_k^1 b_i^0)\operatorname{Im}c_{10,11} \\ & + (b_i^1 b_k^1 - \dot{b}_i^1\dot{b}_k^1)\operatorname{Re}c_{11,\,1-1} + (b_k^1\dot{b}_i^1 - b_i^1\dot{b}_k^1)\operatorname{Im}c_{11,\,1-1}\Big\}. \end{aligned} \tag{3.3}$$

Here

$$b_i^0 = \frac{B_{0i}}{B_0}, \quad b_i^1 = \frac{B_{1i}}{B_1}, \quad b_{ik}^0 = \varepsilon_{ikl}b_l^0, \quad \dot{b}_i^1 = \frac{1}{\omega B_1} - \frac{dB_{1i}}{dt}.$$

The viscosity tensor is very complicated; part of it is completely analogous to the viscosity tensor in a constant field. The remaining terms describe the time-dependent components of the tensor.

Both Eq. (3.3) and the viscosity tensor satisfy the Onsager symmetry principle for kinetic coefficients in a magnetic field

$$\varkappa_{ik}(\mathbf{H}) = \varkappa_{ki}(-\mathbf{H}), \qquad \eta_{iklm}(\mathbf{H}) = \eta_{lmik}(-\mathbf{H}), \tag{3.4}$$

and in an electric field

$$\varkappa_{ik}(\mathbf{E}) = \varkappa_{ki}(\mathbf{E}), \qquad \eta_{iklm}(\mathbf{E}) = \eta_{lmik}(\mathbf{E}). \tag{3.5}$$

The relation (3.5) for an electric field follows from the fact that the terms χ_{lm} which are odd in the field are also odd in σ and the averaging over σ therefore makes them vanish. We must emphasize that it is possible that there occur terms which are odd in the field in the expression for the $c_{lm,l'm'}$, if $l - l'$ is an odd integer. However, such terms do not occur in the viscosity and thermal conductivity tensors. The latter describe the mutual influence of viscosity and thermal conductivity phenomena[7] (cross effect). Therefore, in a crossed magnetic field the thermal conductivity of a molecular gas is determined by seven coefficients, and in an electric field by four. The viscosity in crossed magnetic or crossed electric fields is determined, respectively, by nineteen and twelve coefficients. The coefficients which are additional as compared to the case of static fields describe time-dependent components of the viscosity and thermal conductivity tensors. It is clear from (3.3) that the thermal conductivity tensor contains first and second harmonics of ω. In the viscosity tensor harmonics up to the fourth occur. We note that all coefficients $c_{lm,l'm'}$ which describe the time dependence of the viscosity and thermal conductivity tensors are of order ϵ^2. The other coefficients are of the same order as in a constant field.[6]

Let us consider the dependence of the coefficients $c_{l'm',\,lm}$ on the magnitude of the constant and the variable fields and the frequency. We can in accordance with the expansion (2.14) write the coefficients (3.1) also as power series in ϵ:

$$c_{l'm',\,lm} = c^{(0)}_{l'm',\,lm} + \varepsilon c^{(1)}_{l'm',\,lm} + \varepsilon^2 c^{(2)}_{l'm',\,lm} + \ldots \tag{3.6}$$

It is clear from Eqs. (2.3), (2.15), (2.17), and (2.29) that the field-dependence occurs only in $c^{(2)}_{l'm,l'm}$

$$c^{(2)}_{l'm',\,lm} = \langle A_{l'm'}, \hat{K}\hat{I}^{(1)}\chi^{(1)}_{lm}\rangle. \tag{3.7}$$

Using the explicit form of A_{lm} and $\chi^{(1)}_{lm}$ and the symmetry properties of the operators $\hat{K}$ and $\hat{I}^{(1)}$ we can write Eq. (2.37) as follows

$$c^{(2)}_{l'm',\,lm} = \langle\chi^{(1)}_{lm}, \hat{I}^{(1)}\hat{K}A_{l'm'}\rangle. \tag{3.8}$$

Using Eqs. (2.17), (2.19), and (2.28) we find that the coefficients $c^{(2)}_{l'm',lm}$ are equal to

$$c^{(2)}_{l'm',\,lm} = e^{i\omega t(m-m')}\sum_{n,n'} B_n^{lm}B_{n'}^{l'm'}G_{nn'}, \tag{3.9}$$

$$\begin{aligned} G_{nn'} = \sum_{\substack{m_1+m_2=m\\ m_1+m_2'=m'}} & C^{lm}_{l_1m_1l_2m_2}C^{l'm'}_{l_1m_1l_2m_2'}\delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{m_1m_1'}\delta_{r_1r_1'} \\ & \times\langle L_{r_2}^{l_2}(H_{\text{rot}})M^{2l_2}\varphi_s(\sigma), a_{qm_2m_2'}L_{r_2'}^{l_2}(H_{\text{rot}})\varphi_{s'}(\sigma)\rangle. \end{aligned} \tag{3.10}$$

The quantities B_n^{lm} were defined in (2.17).

We consider the change in the time-averaged transfer coefficients in a crossed field. Such changes in the transfer coefficients are described by the coefficients $c^{(2)}_{l'm',lm}$ for which m′ = m. Using the relation

$$\sum_p |P_{mp}^l(\cos\vartheta)|^2 = 1, \tag{3.11}$$

which follows from the unitarity of the representation of the rotation group[15] we can write Eq. (3.10) in the form

$$G_{nn'} = \lambda_n^{-1}\delta_{nn'} + \Delta G_{nn'}, \tag{3.12}$$

$$\begin{aligned} \Delta G_{nn'} = -\lambda_n^{-1}\sum_{m_1+m_2=m} & C^{lm}_{l_1m_1l_2m_2}C^{l'm}_{l_1m_1l_2m_2}\delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{m_1m_1'} \\ & \times\delta_{m_2m_2'}\delta_{r_1r_1'}\langle L_{r_2}^{l_2}(H_{\text{rot}})M^{2l_2}\varphi_s(\sigma), \Delta a_{qm_2m_2}L_{r_2'}(H_{\text{rot}})\varphi_{s'}(\sigma)\rangle, \end{aligned} \tag{3.13}$$

$$\Delta a_{qm_2m_2} = \sum_p |P^{l_2}_{m_2p}(\cos\vartheta_1)|^2\frac{(m_2\omega + p\gamma_{\text{eff}})^2 + i\lambda_n(m_2\omega + p\gamma_{\text{eff}})}{\lambda_n^2 + (m_2\omega + p\gamma_{\text{eff}})^2}. \tag{3.14}$$

From this it follows that the change in the coefficients $c^{(2)}_{l'm',lm}$ in a crossed field is equal to

$$\Delta c^{(2)}_{l'm,\,lm} = \sum_{n,n'} B_n^{lm}B_{n'}^{l'm}\,\Delta G_{nn'}. \tag{3.15}$$

Equations (3.12) to (3.15) completely describe the dependence of the time-averaged changes in the transfer coefficients of polar, para- and non-para magnetic gases on the magnitude of the constant field, the amplitude and frequency of the variable field, and the pressure (P) since as we indicated above in (2.5), (2.11), and (2.25) $\gamma_0 \sim B_0$, $\gamma_1 \sim B_1$, $\lambda_n \sim P$. For nonparamagnetic gases Eqs. (3.12), (3.14), and (3.15) remain as before, but (3.13) simplifies as γ_0 and γ_1 are independent of M:

$$\Delta G_{nn'} = -\lambda_n{}^{-1} \sum_{m_1+m_2=m} C^{lm}_{l_1m_1l_2m_2} C^{l'm}_{l_1m_1l_2m_2} \delta_{l_1l_1'} \delta_{l_2l_2'} \delta_{m_1m_1'} \times \delta_{m_2m_2'} \delta_{r_1r_1'} \delta_{r_2r_2'} \Delta a_{qm_2m_2}. \tag{3.16}$$

Even and odd effects are described, respectively, by the real and imaginary parts of expressions (3.13) and (3.16). From Eqs. (3.12) to (3.16) it follows that the effect is, generally speaking, larger in a crossed field than in a constant field since all terms with different m_2 give non-vanishing contributions in the sum over m_1 and m_2. In the case of a constant field in the analogous expressions terms with $m_2 = 0$ did not contribute to the effect.[6] For arbitrary values of γ_0, γ_1, ω, and λ_n the behavior of the changes in the transfer coefficients in a crossed field is rather complicated.

Let us consider the case of large magnitudes of the fields. We require that the inequalities

$$|\gamma_{\text{eff}} - \omega| \gg \lambda_n, \qquad \gamma_0, \omega \gg \lambda_n. \tag{3.17}$$

are satisfied. The real part of Eq. (3.16) then takes in the case of a non-paramagnetic gas, and taking (3.11) into account, the form

$$\operatorname{Re} \Delta G_{nn'} = -\lambda_n{}^{-1} \delta_{l_1l_1'} \delta_{l_2l_2'} \delta_{m_1m_1'} \delta_{m_2m_2'} \delta_{r_1r_1'} \delta_{r_2r_2'} G_{l_1l_2}^{lm,\,l'm},$$
$$G_{l_1l_2}^{lm,l'm} = \sum_{\substack{m_1+m_2=m \\ m_2\neq 0}} C^{lm}_{l_1m_1l_2m_2} C^{l'm}_{l_1m_1l_2m_2} + C^{lm}_{l_1m_1l_20} C^{l'm}_{l_1m_1l_20} [1 - P_{l_2}{}^2(\cos\vartheta_1)] = \delta_{ll'} - C^{lm}_{l_1m_1l_20} C^{l'm}_{l_1m_1l_20} P_{l_2}{}^2(\cos\vartheta_1), \tag{3.18}$$

where P_{l_2} is a Legendre polynomial of rank l_2 ($P^{l_2}_{00}(\cos\vartheta) = P_{l_2}(\cos\vartheta)$). The sum in Eq. (3.18) corresponds to a saturation of the even effect in a constant field when $\gamma_0 \gg \lambda_n$. The second term describes an additional change in the transfer coefficients in a crossed field. When the angle ϑ_1 is changed the magnitude of the second term goes through a maximum when it reaches the value $C^{lm}_{l_1m_1l_20} C^{l'm}_{l_1m_1l_20}$. The relative increase in the time-averaged coefficients $C^{(2)}_{l'm,lm}$ with $l = l'$ in a crossed field as compared with their value in saturation in a constant field is thus determined by the expression

$$(C^{lm}_{l_1m_1l_20})^2/[1 - (C^{lm}_{l_1m_1l_20})^2]. \tag{3.19}$$

For instance, for the coefficient $c_{10,10}$ which determines the change in the thermal conductivity coefficient in the direction of $\mathbf{B}_0$ this quantity is $2/3$.

It is clear from (3.10) that the dependence of the effect on the parameters ω, γ_0, and γ_1 in a crossed field shows several maxima. The collection of maxima and the relations between ω, γ_0, and γ_1 in the point of maximum are determined by the model of the collision integral operator $\hat{I}^{(1)}$ which takes into account the mixing of the rotational and translational degrees of freedom. We consider a model of $\hat{I}^{(1)}$ for which the magnetic elements $I^{(1)}_{n_0n}$ occurring in Eqs. (2.17) and (3.15) are non-vanishing only for "transitions into a state" with $n = (lml_12000)$. Then the second term in (3.18) has the form

$$C^{lm}_{l_1m_120} C^{l'm}_{l_1m_120} (1 - P_2{}^2(\cos\vartheta_1)) \tag{3.20}$$

and reaches its maximum value for $\cos^2\vartheta = 1/3$, or

$$\omega = \gamma_0 \pm \frac{1}{\sqrt{2}} \gamma_1. \tag{3.21}$$

Equations (3.18) to (3.20) are approximately true for polar and paramagnetic gases if we substitute into them the values of γ_0 and γ_1 containing the average values of the angular momentum M.

The exact expression for the $C^{lm,l'm}_{l_1l_2}$ for a paramagnetic gas in the case, of the collision operator considered above, has the form

$$G_{l_12}^{lm,l'm} = \sum_{\substack{m_1+m_2=m \\ m_2\neq 0}} C^{lm}_{l_1m_12m_2} C^{l'm}_{l_1m_12m_2} + C^{lm}_{l_1m_120} C^{l'm}_{l_1m_120} \frac{1}{2s+1} \sum_{\sigma} \frac{3}{4} \int_0^\infty e^{-M^2} M^5 \frac{4(\xi - \eta/\gamma)^2 + 1}{[(\xi - \eta/\gamma)^2 + 1]^2} dM, \tag{3.22}$$

where $\xi = 2B_0/B_1$; $\eta = 2\omega/B_1$; γ defined in (2.5b). From (3.22) and (2.5b) it follows that for oxygen the resonance curves must have two paired maxima for the states $\sigma = \pm 1$ and $\sigma = 0$ when we use the chosen model for $\hat{I}(1)$.

In the case of an arbitrary model for the collision of the molecules and when the inequalities (3.17) are satisfied, there will be in Eq. (3.15) be a sum of squares of Legendre polynomials $P^2_{l_2}(\cos\vartheta_1)$. From this it follows that an experimental study of the dependence of the effect on $\cos\vartheta_1$ enables us in principle to establish the angular dependence of the non-spherical scattering of the molecules.

It is necessary to note that in a paramagnetic gas such as oxygen another kind of resonance behavior of the transfer coefficients in a crossed field is possible. This is connected with the fact that a rotating field of frequency ω will cause transitions of molecules changing the quantum number σ from +1 to −1 and vice versa, if $\hbar\omega = \alpha$, where α is the energy gap between the states with $\sigma = +1$ and $\sigma = -1$. For oxygen $\alpha = 1.98\ \text{cm}^{-1}$ and $\omega = 7.5 \times 10^{11}$ Hz.[16] It is clear that then the precession of a paramagnetic molecule and with it the change in the transfer coefficients caused by a constant field disappears. A similar situation may occur apparently also in the case of polar gases with long linear molecules or asymmetric top kind molecules with a small asymmetry parameter. For such molecules the presence of a pair of close-lying states differing in the direction of the dipole moments (for linear molecules the splitting of rotational states is connected with transverse oscillations) is characteristic. The energy difference between these states is appreciably less (in frequency 10^4 to 10^6 Hz) than for oxygen and depends on the rotational moment of the molecule.

4. SOUND PROPAGATION

Let there be a sound wave excited with a frequency ω_0. Its propagation in a constant field is described by the distribution function

$$f = f_0(1 + \chi e^{i\mathbf{kr} - i\omega_0 t}). \tag{4.1}$$

In the presence of a rotating field of frequency ω this wave excited additional harmonics of frequencies $\Omega = \omega_0 + n\omega$ (n is an integer) the amplitudes of which are small, if $|\Omega| \neq \omega_0$. In the opposite case resonance occurs.

Far from the resonance the nature of the change in sound propagation in crossed fields is the same as in the case of a constant field and is described by formulae containing the quantities $c_{l'm', lm}$.[17] The role of the rotating field in this case reduces basically to an additional decrease in the sound absorption.

We consider the resonance phenomenon. For the sake of simplicity we restrict ourselves to resonance at the lowest possible sound frequency (we assume that the frequency of the rotating field is given), i.e.,

$$\omega_0 = {}^1\!/_2\omega + \Delta\Omega, \qquad \Delta\Omega / \omega \ll 1. \tag{4.2}$$

We shall look for the distribution function in the form

$$\begin{aligned} f = f_0\Big[1 + \chi_+ \exp\Big\{i\mathbf{kr} - i\Big(\frac{\omega}{2} + \Delta\Omega\Big)t\Big\} \\ + \chi_- \exp\Big\{i\mathbf{kr} + i\Big(\frac{\omega}{2} - \Delta\Omega\Big)t\Big\} + \Delta\chi\Big]. \end{aligned} \tag{4.3}$$

The other harmonics whose amplitudes are small occur in $\Delta\chi$ and we shall not take them into account.

The functions χ_+ and χ_- satisfy the equations ($c_0 = \sqrt{(2T/m)}$):

$$\begin{aligned} \Big(-i\frac{\omega}{2} - i\Delta\Omega + ic_0\mathbf{ku}\Big)\chi_+ + \gamma_0\hat{l}_z\chi_+ + \gamma_1\hat{l}_+\chi_- = -\hat{I}\chi_+, \\ \Big(i\frac{\omega}{2} - i\Delta\Omega + ic_0\mathbf{ku}\Big)\chi_- + \gamma_0\hat{l}_z\chi_- + \gamma_1\hat{l}_-\chi_+ = -\hat{I}\chi_-. \end{aligned} \tag{4.4}$$

To solve (4.4) it is convenient to write χ_+ and χ_- in the form

$$\chi_\pm = \chi_\pm{}^u + \chi_\pm{}^M, \tag{4.5}$$

where the $\chi_\pm^u$ are independent of the direction of **M**. The functions $\chi_\pm^u$ and $\chi_\pm^M$ are determined from the equations

$$\begin{aligned} i\Big(-\frac{\omega}{2} - \Delta\Omega + c_0\mathbf{ku}\Big)\chi_+{}^u = -\hat{I}^{(0)}\chi_+{}^u - \varepsilon\hat{I}^{(1)}\chi_+{}^M, \\ \gamma_0\hat{l}_z\chi_+{}^M + \gamma_1\hat{l}_+\chi_-{}^M = -\hat{I}^{(0)}\chi_+{}^M - \varepsilon\hat{I}^{(1)}\chi_+{}^u, \\ i\Big(\frac{\omega}{2} - \Delta\Omega + c_0\mathbf{ku}\Big)\chi_-{}^u = -\hat{I}^{(0)}\chi_-{}^u - \varepsilon\hat{I}^{(1)}\chi_-{}^M, \\ \gamma_0\hat{l}_z\chi_-{}^M + \gamma_1\hat{l}_-\chi_+{}^M = -\hat{I}^{(0)}\chi_-{}^M - \varepsilon\hat{I}^{(1)}\chi_-{}^u. \end{aligned} \tag{4.6}$$

We have used in (4.6) the fact that the ultrasound frequency (and kc_0) is small compared with the collision frequency, i.e., with the non-zero matrix elements of the collision operator.

From the second and fourth of Eqs. (4.6) we can express $\chi_\pm^M$ in terms of $\chi_\pm^u$ and substitute the expressions obtained into the first and third Eqs. (4.6). We have

$$i\Big(\mp\frac{\omega}{2} - \Delta\Omega + c_0\mathbf{ku}\Big)\chi_\pm{}^u = -\hat{I}^{(0)}\chi_\pm{}^u + \varepsilon^2\hat{A}_\pm\chi_\pm{}^u + \varepsilon^2\hat{B}_\pm\chi_\mp{}^u, \tag{4.7}$$

$$\begin{aligned} \hat{A}_\pm = \hat{I}^{(1)}[\hat{l}_z + \hat{I}^{(0)} - \hat{l}_\pm(\hat{l}_z + \hat{I}^{(0)})^{-1}\hat{l}_\mp]^{-1}\hat{I}^{(1)}, \\ \hat{B}_\pm = -\hat{I}^{(1)}[\hat{l}_z + \hat{I}^{(0)} - \hat{l}_\pm(\hat{l}_z + \hat{I}^{(0)})^{-1}\hat{l}_\mp]^{-1}\hat{l}_\pm(\hat{l}_z + \hat{I}^{(0)})^{-1}\hat{I}^{(1)}. \end{aligned} \tag{4.8}$$

As the operators $\hat{A}_\pm$ and $\hat{B}_\pm$ are bounded we can solve Eq. (4.7) by perturbation theory methods with respect to the parameter ϵ. The corrections to the sound velocity and absorption coefficient are expressed by the equations

$$v^{(2)} = \varepsilon^2\frac{v}{\omega}\operatorname{Re}\Omega^{(2)}, \quad \gamma^{(2)} = -\frac{\varepsilon^2}{v}\operatorname{Im}\Omega^{(2)}, \tag{4.9}$$

in which $\Omega^{(2)}$ is determined from the equation

$$\begin{aligned} (i\Omega^{(2)} - \langle\chi_+{}^{(0)*}\hat{A}_+\chi_+{}^{(0)}\rangle)(-2i\Delta\Omega + i\Omega^{(2)} + \varepsilon^2\langle\chi_-{}^{(0)*}\hat{A}_-\chi_-{}^{(0)}\rangle) \\ + \varepsilon^2\langle\chi_+{}^{(0)*}\hat{B}_+\chi_-{}^{(0)}\rangle\langle\chi_-{}^{(0)*}\hat{B}_-\chi_+{}^{(0)}\rangle = 0. \end{aligned} \tag{4.10}$$

Here $\chi_\pm^{(0)}$ is the solution of equations whose explicit form was given in[17]

$$(\mp i\omega \mp i\Delta\Omega + ic_0\mathbf{ku})\chi_\pm{}^{(0)} = -\hat{I}^{(0)}\chi_\pm{}^{(0)}, \qquad \langle\chi_\pm{}^{(0)*}, \chi_\pm{}^{(0)}\rangle = 1. \tag{4.11}$$

Solving (4.9) we have

$$\begin{aligned} 2i\Omega^{(2)} = 2i\Delta\Omega\varepsilon^{-2} + \langle\chi_+{}^{(0)*}\hat{A}_+\chi_+{}^{(0)}\rangle + \langle\chi_-{}^{(0)*}\hat{A}_-\chi_-{}^{(0)}\rangle \\ - [(2i\Delta\Omega\varepsilon^{-2} + \langle\chi_+{}^{(0)*}\hat{A}_+\chi_+{}^{(0)}\rangle - \langle\chi_-{}^{(0)*}\hat{A}_-\chi_-{}^{(0)}\rangle)^2 \\ - 4\langle\chi_+{}^{(0)*}\hat{B}_+\chi_-{}^{(0)}\rangle\langle\chi_-{}^{(0)*}\hat{B}_-\chi_+{}^{(0)}\rangle]^{1/2}. \end{aligned} \tag{4.12}$$

Assuming $\operatorname{Im}\Omega^{(2)}$ and $\operatorname{Re}\Omega^{(2)}$ to be quantities of the same order we get for the order of magnitude of the ratio of the relative magnitudes of the changes in the sound velocity and absorption the expression

$$\frac{\omega_0}{\omega_{\text{tr}}} + \frac{\omega_0\omega_{\text{rot}}}{\omega_0^2 + \omega^2_{\text{rot}}}$$

(ω_{rot} and ω_{tr} are the frequencies of the rotational and translational relaxation). We need therefore take into account the change in the sound velocity only if $\omega_0 \sim \omega_{\text{rot}}$. In the opposite case it changes appreciably less than the absorption.

The matrix elements $\langle \chi_\pm^{(0)*}\hat{A}_\pm\chi_\pm^{(0)} \rangle$ and $\chi_\pm^{(0)*}\hat{B}_\pm\chi_\pm^{(0)} \rangle$ are for small sound frequencies ($\omega_0 \ll \epsilon\lambda_0$) of order ϵ^{-2} and for high frequencies of order unity. Therefore, at high frequencies the resonance is narrower (resonance width $\sim\epsilon^2$) than at low ones (width of order unity).

It follows from (4.12) that a resonance change takes place if the matrix elements $\langle \chi_\pm^{(0)*}\hat{B}_\pm\chi_\pm^{(0)} \rangle$ are non-vanishing. However, the operators $\hat{B}_\pm$ tend to zero as $B \to \infty$. For high fields, therefore, there will be no resonance sound absorption. The effect will be appreciable only for such fields that $\gamma_1 \sim \gamma_0 \sim \omega_{\text{tr}}$.

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[1] H. Senftleben, Phys. Z. 31, 961 (1930); Ann. Physik 7, 273 (1965).

[2] J. J. M. Beenakker, G. Scoles, H. F. P. Knapp, and R. M. Jonkman, Phys. Lett. 2, 5 (1962).

[3] L. L. Gorelik and V. V. Sinitsyn, Zh. Eksp. Teor. Fiz. 46, 401 (1964); ZhETF Pis. Red. 3, 145 (1966) [Sov. Phys.-JETP 19, 272 (1964); JETP Lett. 3, 91 (1966)].

[4] L. L. Gorelik, Yu. N. Redkoboronyĭ, and V. V. Sinitsyn, Zh. Eksp. Teor. Fiz. 48, 761 (1965) [Sov. Phys.-JETP 21, 503 (1965)].

[5] J. Korving, The influence of a magnetic field on the transport properties of gases of polyatomic molecules, Thesis, Leiden, 1967.

[6] Yu. M. Kagan and L. A. Maksimov, Zh. Eksp. Teor. Fiz. **41**, 842 (1961); **51**, 1893 (1966) [Sov. Phys.-JETP 14, 604 (1962); **24**, 1272 (1967)].

[7] Yu. V. Mikhaĭlova and L. A. Maksimov, Zh. Eksp. Teor. Fiz. **51**, 1880 (1966) [Sov. Phys.-JETP 24, 1265 (1967)].

[8] V. D. Borman, B. I. Nikolaev, and N. I. Nikolaev, Zh. Eksp. Teor. Fiz. **50**, 821 (1966); **51**, 579 (1966) [Sov. Phys.-JETP **23**, 544 (1966); **24**, 387 (1967)].

[9] V. D. Borman, L. L. Gorelik, B. I. Nikolaev, and V. V. Sinitsyn, ZhETF Pis. Red. 5, 105 (1967) [JETP Lett. **5**, 85 (1967)].

[10] V. D. Borman, L. A. Maksimov, and B. I. Nikolaev, Zh. Eksp. Teor. Fiz. **52**, 1305 (1967) [Sov. Phys.-JETP **25**, 868 (1967)].

[11] H. F. P. Knaap and J. J. M. Beenakker, Physica **33**, 643 (1967).

[12] V. D. Borman, L. L. Gorelik, B. I. Nikolaev, and V. V. Sinitsyn, ZhETF Pis. Red. **6**, 945 (1967) [JETP Lett. **6**, 362 (1968)].

[13] I. I. Rabi, N. F. Ramsey, and J. Schwinger, Rev. Mod. Phys. 26, 167 (1954).

[14] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics) Fizmatgiz, 1963 [English translation published by Pergamon Press, 1965].

[15] I. M. Gel'fand, R. A. Minlos, and Z. Ya. Shapiro, Predstavleniya gruppy vrashcheniĭ i gruppy Lorentsa, ikh primeneniya (Representations of the Rotational and Lorentz Groups and Their Applications) Fizmatgiz, 1958 [English translation published by Pergamon Press 1963].

[16] R. Schlapp, Phys. Rev. 51, 342 (1937).

[17] L. A. Maksimov and Yu. V. Mikhaĭlova, Zh. Eksp. Teor. Fiz. **53**, 228 (1967) [Sov. Phys.-JETP 26, 153 (1968)].

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