3) For $l \leqq 2$ the following trace formulas for triple products of T-tensors hold:

$$\operatorname{tr}\{T^{jj'}_{\mu}\, T^{j'j}_{\nu}\, T^{jj}_{\varkappa\lambda}\} = 3\, W(j\,j\,1\,1;2\,j')\, \Delta_{\mu\nu,\,\varkappa\lambda}\,, \tag{A7}$$

and

$$\operatorname{tr}\{T^{jj'}_{\mu\nu}\, T^{j'j}_{\varkappa\lambda}\, T^{jj}_{\sigma\tau}\} = -10\sqrt{\tfrac{3}{7}}\, W(j\,j\,2\,2;2\,j')\, \Delta_{\mu\nu,\,\mu'\nu'}\, \Delta_{\varkappa\lambda,\,\mu'\lambda'}\, \Delta_{\sigma\tau,\,\nu'\lambda'}\,, \tag{A8}$$

where $W(j\,j\,1\,1;2\,j')$ and $W(j\,j\,2\,2;2\,j')$ are Racah coefficients. Formula (A8) together with the explicit expression for $W(j\,j\,2\,2;2\,j+2)$ has been used for deriving Eq. (4.19b).

Spectrum of the Depolarized Rayleigh Light Scattered by Gases of Linear Molecules

SIEGFRIED HESS

Institut für Theoretische Physik der Universität Erlangen-Nürnberg, Erlangen

(Z. Naturforsch. **25 a**, 350—362 [1970]; received 24 October 1969)

The spectrum of the depolarized Rayleigh light scattered by a gas of linear molecules is calculated by a kinetic theory approach based on the Waldman-Snider equation. Collisional and diffusional broadening are studied. The line width is related to relaxation coefficients which are collision brackets obtained from the linearized Waldmann-Snider collision term involving the binary molecular scattering amplitude and its adjoint. It is shown under which conditions the relaxation coefficients characterizing the line width can be compared with data obtained from Sentfleben-Beenakker effect and nuclear magnetic relaxation measurements.

The "depolarized Rayleigh" component[1] of the light scattered by a gas of linear molecules is associated with fluctuations of the (2nd rank) tensor polarization of the rotational angular momentum of the molecules and, in particular, its spectrum is determined by the spectral function of the tensor polarization[2, 3]. The spectrum of the depolarized Rayleigh light has resently been measured[4] for some gases of linear molecules (H_2, N_2, CO_2) in the pressure region where the width of the line is primarily caused by collisional broadening (pressure broadening). In this paper, the spectrum of the depolarized Rayleigh ligth is calculated by a kinetic theory approach based on the Waldmann-Snider equation[5]. Both collisional and diffusional broadening are studied.

Collisional broadening of the depolarized Rayleigh scattering has been treated theoretically by GORDON[6] who developed a classical theory which is akin to Anderson's impact theory[7] for the pressure broadening of absorption and emission spectra.

By the kinetic equation approach used in this paper the calculation of the spectrum of the light scattered by a gas is based on the same generalized Boltzmann equation (Waldmann-Snider equation) as the calculation of transport properties of polyatomic gases. The line width is expressed in terms of collision brackets obtained from the linearized Waldmann-Snider collision term which involves the binary scattering amplitude operator and its adjoint. Thus a rigorous connection between the line width and the molecular (binary) collision processes is established. Furthermore it is possible to obtain relations between line widths and transport properties since transport coefficients can also be expressed in terms of collision brackets.

This paper proceeds as follows: Firstly, after some preliminary remarks on the one-particle distribution function operator for a gas of linear molecules and the definition of the second rank tensor polarization, the connection between the spectrum of the depolarized Rayleigh light and the spectral

---

[1] "Depolarized" refers to the component of the scattered light whose electric field vector is perpendicular to the electric field of the linearly polarized incident light. "Rayleigh" refers to the line of the spectrum of the scattered light which is centered at the frequency of the incident (monochromatic) light. Some of the results derived in this paper have been reported earlier, cf. S. HESS, Z. Naturforsch. **24 a**, 1852 [1969].

[2] S. HESS, Phys. Letters **29 A**, 108 [1969].

[3] S. HESS, Z. Naturforsch. **24 a**, 1675 [1969].

[4] V. G. COOPER, A. D. MAY, E. H. HARA, and H. F. P. KNAPP, Phys. Letters **27 A**, 52 [1968].

[5] L. WALDMANN, Z. Naturforsch. **12 a**, 660 [1957]; **13 a**, 609 [1958]; R. F. SNIDER, J. Chem. Phys. **32**, 1051 [1960], see also S. HESS, Z. Naturforsch. **22 a**, 1871 [1967].

[6] R. G. GORDON, J. Chem. Phys. **44**, 3083 [1966].

[7] P. W. ANDERSON, Phys. Rev. **76**, 647 [1949].

function of the spatial Fourier transform of the tensor polarization is stated (§ 1). Then, by using the moment method, transport-relaxation equations for the (time- and space-dependent) tensor polarization and "tensor polarization flow" are derived from the linearized Waldmann-Snider equation. The relaxation coefficients involved are collision brackets which are proportional to the number density of the gas (§ 2). Next, the spectral function of the spatial Fourier transform of the tensor polarization is calculated from the transport-relaxation equations (§ 3.) For high pressures where the mean free path l of a molecule is very short compared with the wave length λ of the light ($l \ll \lambda$) the resulting spectrum of the depolarized Rayleigh light has a Lorentzian line shape with a half-width determined by the relaxation coefficient for the tensor polarization. At lower pressures where $l \lesssim \lambda$ the line shape is no longer Lorentzian. Diffusional broadening characterized by a diffusion coefficient which is different from the self-diffusion coefficient contributes to the half-width. Furthermore it is indicated that propagating tensor polarizaton waves may exist (under suitable conditions) which cause a splitting of the line into two components or lead to an effective broadening when the splitting cannot be resolved. Then the relaxation coefficients are studied in more detail (§ 4). The relaxation coefficient for the tensor polarization is expressed by a collision bracket where only the nonspherical part of the scattering amplitude gives a nonvanishing contribution. Finally the interrelation between the half-width of the depolarized Rayleigh line and certain other transport and relaxation phenomena is considered (§ 5). It is discussed under which conditions the relaxation coefficient for the tensor polarization can also be extracted from measurements of the (magnetic) Senftleben-Beenakker effect [8, 9] on the viscosity and of nuclear spin relaxation times and when the diffusion coefficient for the "tensor polarization" can be compared with data obtained from the Senftleben-Beenaker effect on the heat conductivity.

§ 1. General Remarks

In this section the relation between the spectrum of the depolarized Rayleigh light and the spectral function of the tensor polarization is stated. Firstly, however, a number of preliminary remarks are necessary.

For a gas at room temperature the translational motion of the molecules can be treated classically, i. e. position and linear momentum of a molecule are specified by the classical variables $\boldsymbol{x}$ and $\boldsymbol{p}$. The rotational motion of a molecule, treated quantum mechanically, is characterized by the rotational angular momentum operator $\boldsymbol{J}$ (in units of $\hbar$). The Cartesian components of $\boldsymbol{J}$ obey the commutation relations [10]

$$J_\mu J_\nu - J_\nu J_\mu = i\, \varepsilon_{\mu\nu\lambda} J_\lambda \tag{1.1}$$

where $\varepsilon_{\mu\nu\lambda}$ is the 3rd rank isotropic tensor with $\varepsilon_{123} = 1$. It is convenient to define the projection operator

$$P_j = \sum_m | j\, m \rangle \langle j\, m | , \tag{1.2}$$

where $| j\, m \rangle$ is a normalized internal wave function for a linear molecule in the j-th rotational state and m is the magnetic quantum number with respect to an arbitrary axis of quantization. Then the magnitude of the rotational angular momentum (in units of $\hbar$) is given by

$$P_j J^2 = J^2 P_j = j(j+1)\, P_j\,, \quad j = 0, 1, 2, \dots . \tag{1.3}$$

Obviously $\boldsymbol{J}$ is treated as an operator with respect to both magnetic and rotational quantum numbers; it is diagonal with respect to the latter.

Now a brief discussion of the one-particle distribution function operator of a gas of linear molecules can be given. The part of the distribution function which is diagonal with respect to the rotational quantum numbers is written as

$$f(t, \boldsymbol{x}, \boldsymbol{p}, \boldsymbol{J}) . \tag{1.4}$$

The local instantaneous mean value of an operator $\Phi = \Phi(\boldsymbol{p}, \boldsymbol{J})$ is given by

$$\langle \Phi \rangle = n^{-1}\, \mathrm{Tr} \int \mathrm{d}^3 p\, \Phi f\,, \tag{1.5}$$

where "Tr" denotes the trace over magnetic and rotational quantum numbers and

$$n(t, \boldsymbol{x}) = \mathrm{Tr} \int \mathrm{d}^3 p\, f(t, \boldsymbol{x}, \boldsymbol{p}, \boldsymbol{J}) \tag{1.6}$$

---

[8] H. SENFTLEBEN, Phys. Z. **31**, 822, 961 [1930]. — J. J. M. BEENAKKER, G. SCOLES, H. F. P. KNAPP, and R. M. JONKMAN, Phys. Letters **2**, 5 [1962].

[9] J. J. M. BEENAKKER, The Influence of Electric and Magnetic Fields on the Transport Properties of Polyatomic Dilute Gases, in ed. O. MADELUNG, Festkörperprobleme VIII, Vieweg, Braunschweig 1968. — J. J. M. BEENAKKER and F. R. MCCOURT, Ann. Rev. Phys. Chem. 1970.

[10] Cartesian components of vectors and tensors are denoted be Greek subscripts. The summation convention is used.

is the local number density. Averages over an equilibrium distribution f_0 specified by the equilibrium density n_0 and temperature T_0 will also be needed and are denoted by $\langle \ldots \rangle_0$.

The 2nd rank tensor polarization (which in the following will always be referred to as the "tensor polarization") is defined by

$$a_{\mu\nu}(t, \boldsymbol{x}) = \langle \Phi_{\mu\nu} \rangle, \tag{1.7}$$

where

$$\Phi_{\mu\nu} = \sqrt{\frac{15}{2}}\, [J^2(J^2 - \tfrac{3}{4})]^{-1/2}\, \overline{J_\mu J_\nu}\,. \tag{1.8}$$

The sign $\overline{\ldots}$ denotes the irreducible (symmetric traceless) part of a tensor, e. g.

$$\overline{J_\mu J_\nu} = \tfrac{1}{2}\,(J_\mu J_\nu + J_\nu J_\mu) - \tfrac{1}{3}\, J^2\, \delta_{\mu\nu}\,. \tag{1.9}$$

For convenience the constant occurring in (1.8) has been chosen such that

$$\langle \Phi_{\mu\nu}\, \Phi_{\mu'\nu'} \rangle_0 = \Delta_{\mu\nu,\, \mu'\nu'}\,, \tag{1.10}$$

where

$$\Delta_{\mu\nu,\, \mu'\nu'} = \tfrac{1}{2}\,(\delta_{\mu\mu'}\, \delta_{\nu\nu'} + \delta_{\mu\nu'}\, \delta_{\nu\mu'}) - \tfrac{1}{3}\, \delta_{\mu\nu}\, \delta_{\mu'\nu'} \tag{1.11}$$

is an isotropic 4th rank tensor.

The spatial Fourier transform $\hat{a}_{\mu\nu}(t, \boldsymbol{k})$ of the tensor polarization $a_{\mu\nu}(t, \boldsymbol{x})$ is given by

$$\hat{a}_{\mu\nu}(t, \boldsymbol{k}) = \int \exp\{-i\, \boldsymbol{k} \cdot \boldsymbol{x}\}\, a_{\mu\nu}(t, \boldsymbol{x})\, \mathrm{d}^3x\,. \tag{1.12}$$

The spectral function of the tensor polarization is[3]

$$S(\omega \,|\, \boldsymbol{k}) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty e^{i\omega t}\, A(t \,|\, \boldsymbol{k})\, \mathrm{d}t \tag{1.13}$$

where the function $A(t \,|\, \boldsymbol{k})$ characterizes the time dependence of the spatial Fourier transform (1.12), i. e.,

$$\hat{a}_{\mu\nu}(t, \boldsymbol{k}) = A(t \,|\, \boldsymbol{k})\, \hat{a}_{\mu\nu}(0, \boldsymbol{k})\,; \quad t \geqq 0\,. \tag{1.14}$$

No external fields are considered here; otherwise $A(t \,|\, \boldsymbol{k})$ in Eq. (1.14) should be replaced by a 4th rank tensor[3].

The spectrum of the depolarized Rayleigh light is given by the spectral function (1.13) if ω and $\boldsymbol{k}$ are put equal to the differences between the frequencies $\omega_1 - \omega_0$ and wave vectors $\boldsymbol{k}_1 - \boldsymbol{k}_0$, respectively, of the incident and the detected scattered light. Hence in order to calculate the spectrum of the depolarized Rayleigh line one has to know the relation (1.14) for the fluctuating tensor polarization. By using Onsager's assumption that the regression of spontaneous fluctuations is the same as that of small macroscopic deviations from the equilibrium state of the gas the function $A(t \,|\, \boldsymbol{k})$ can be obtained from "transport-relaxation" equations which are derived in the next section.

§ 2. Transport-Relaxation Equations

In this section the transport-relaxation equations which are relevant for the calculation of the spectral function (1.13) are derived from the linearized Waldmann-Snider equation by application of the moment method[11, 12].

Firstly, the nonequilibrium distribution f is written as

$$f(t, \boldsymbol{x}, \boldsymbol{p}, \boldsymbol{J}) = f_0(\boldsymbol{p}, \boldsymbol{J})\, [1 + \Phi(t, \boldsymbol{x}, \boldsymbol{p}, \boldsymbol{J})]\,, \tag{2.1}$$

where

$$f_0(\boldsymbol{p}, \boldsymbol{J}) = n_0 (2\, \pi\, m\, k_{\mathrm{B}}\, T_0)^{-3/2}\, Q_0^{-1} \cdot \exp\left\{-\left(\frac{p^2}{2\, m\, k_{\mathrm{B}}\, T_0} + \frac{E(J^2)}{k_{\mathrm{B}}\, T_0}\right)\right\} \tag{2.2}$$

is an equilibrium distribution and $\Phi(t, \boldsymbol{x}, \boldsymbol{p}, \boldsymbol{J})$ measures the deviation of f from f_0. In Eq. (2.2) n_0 and T_0 are the equilibrium number density and temperature, respectively; k_{B} is Boltzmann's constant,

$$E(J^2) = \frac{\hbar^2\, J^2}{2\, \Theta} \tag{2.3}$$

is the rotational energy of a linear molecule with the moment of inertia Θ, and

$$Q_0 = \operatorname{Tr} \exp\left\{-\frac{E(J^2)}{k_{\mathrm{B}}\, T_0}\right\} \tag{2.4}$$

is the internal partition function.

The quantity Φ defined by (2.1) obeys the linearized Waldmann-Snider equation:

$$\frac{\partial \Phi}{\partial t} + \boldsymbol{v} \cdot \frac{\partial \Phi}{\partial \boldsymbol{x}} + \omega(\Phi) = 0 \tag{2.5}$$

if the deviation from the equilibrium state is small. This condition is certainly fulfilled if the deviation is produced by spontaneous fluctuations. In Eq. (2.5) $\boldsymbol{v} = m^{-1}\, \boldsymbol{p}$ is the particle velocity and $\omega(\ldots)$ is the linearized Waldmann-Snider collision term involving the binary scattering amplitude operator and its adjoint. The explicit definition of $\omega(\Phi)$ is stated in § 4. In this section only some general properties of $\omega(\Phi)$ and their implications for the collision brackets are needed.

For two operators $\Psi = \Psi(\boldsymbol{p}, \boldsymbol{J})$ and $\Phi = \Phi(\boldsymbol{p}, \boldsymbol{J})$ the collision bracket pertaining to the linearized collision term $\omega(\ldots)$ is defined by

$$\langle \Psi\, \omega(\Phi) \rangle_0 . \tag{2.6}$$

If Ψ and Φ are dimensionless quantities the collision bracket (2.6) has the dimension of an inverse time (effective "collision time"). It is of importance to notice that the collision term $\omega(\ldots)$ and consequently the collision brackets are proportional to the equilibrium number density n_0. Furthermore $\omega(\ldots)$ is positive semi-definite, i. e.

$$\langle \Psi\, \omega(\Psi) \rangle_0 \geqq 0 . \tag{2.7}$$

In (2.7) the equality sign occurs only if Ψ is a "conserved quantity". The "isotropy" of the collision operator implies that the collision bracket vanishes for two irreducible tensors of different rank. For further (symmetry) properties of the Waldmann-Snider collision brackets which, however, are not needed in this paper, see Ref. [11, 12].

By expanding the quantity Φ occurring in Eq. (2.5) with respect to a (complete) set of orthogonal "expansion tensors" depending on $\boldsymbol{p}$ and $\boldsymbol{J}$ and taking moments of the Waldmann-Snider equation (2.5) the (infinite) set of transport-relaxation equations for the time- and space-dependent "expansion coefficients" can be derived [11, 12]. To obtain the transport-relaxation equations that are required for the calculation of the spectral function of the tensor polarization at "high and medium" pressures the following ansatz is made for Φ:

$$\Phi = a_{\mu\nu}\, \Phi_{\mu\nu} + a_{\lambda,\,\mu\nu}\, \Phi_{\lambda,\,\mu\nu} \tag{2.8}$$

with

$$\Phi_{\lambda,\,\mu\nu} = \sqrt{\frac{k_{\mathrm{B}} T_0}{m}}\; v_\lambda\, \Phi_{\mu\nu} . \tag{2.9}$$

The 3rd rank tensor

$$a_{\lambda,\,\mu\nu} = \langle \Phi_{\lambda,\,\mu\nu} \rangle \tag{2.10}$$

is the "tensor polarization flux". The normalization occurring in (2.9) has been chosen such that

$$\langle \Phi_{\lambda,\,\mu\nu}\, \Phi_{\lambda,\,\mu'\nu'} \rangle_0 = \delta_{\lambda\lambda'}\, \Delta_{\mu\nu,\,\mu'\nu'} . \tag{2.11}$$

Due to the isotropy of the collision operator $\omega(\ldots)$ the collision bracket pertaining to the expansion tensor $\Phi_{\mu\nu}$ can be written as

$$\langle \Phi_{\mu\nu}\, \omega(\Phi_{\mu'\nu'}) \rangle_0 = \omega_{\mathrm{T}}\, \Delta_{\mu\nu,\,\mu'\nu'} , \tag{2.12}$$

where the relaxation coefficient (inverse relaxation time) ω_{T} for the tensor polarization is given by

$$\omega_{\mathrm{T}} = \tfrac{1}{5} \langle \Phi_{\mu\nu}\, \omega(\Phi_{\mu\nu}) \rangle_0 . \tag{2.13}$$

Assuming that the relaxation coefficients for the 3 irreducible parts of the tensor $a_{\lambda,\,\mu\nu}$ are approximately equal to each other ("spherical approximation" [13]) one has

$$\langle \Phi_{\lambda,\,\mu\nu}\, \omega(\Phi_{\lambda',\,\mu'\nu'}) \rangle_0 = \omega_{\mathrm{TF}}\, \delta_{\lambda\lambda'}\, \Delta_{\mu\nu,\,\mu'\nu'} \tag{2.14}$$

where

$$\omega_{\mathrm{TF}} = \frac{1}{15} \langle \Phi_{\lambda,\,\mu\nu}\, \omega(\Phi_{\lambda,\,\mu\nu}) \rangle_0 \tag{2.15}$$

is the relaxation coefficient of the tensor polarization flux.

Using the ansatz (2.8), the Eqs. (1.7), (1.10), (2.10) to (2.15), and

$$\langle v_\lambda\, \Phi_{\mu\nu}\, \Phi_{\lambda',\,\mu'\nu'} \rangle_0 = \sqrt{\frac{k_{\mathrm{B}} T_0}{m}}\; \delta_{\lambda\lambda'}\, \Delta_{\mu\nu,\,\mu'\nu'} \tag{2.16}$$

the following transport-relaxation equations are obtained from the Waldmann-Snider equation (2.5):

$$\frac{\partial a_{\mu\nu}}{\partial t} + \sqrt{\frac{k_{\mathrm{B}} T_0}{m}}\; \frac{\partial}{\partial x_\lambda}\, a_{\lambda,\,\mu\nu} + \omega_{\mathrm{T}}\, a_{\mu\nu} = 0, \tag{2.17}$$

$$\frac{\partial a_{\lambda,\,\mu\nu}}{\partial t} + \sqrt{\frac{k_{\mathrm{B}} T_0}{m}}\; \frac{\partial}{\partial x_\lambda}\, a_{\mu\nu} + \omega_{\mathrm{TF}}\, a_{\lambda,\,\mu\nu} = 0. \tag{2.18}$$

The spectrum of the depolarized Rayleigh line will be calculated from Eqs. (2.17) and (2.18) in the next section.

§ 3. Spectrum, Line Width

To calculate the spectrum of the depolarized Rayleigh light it is firstly assumed that the time derivative in Eq. (2.18) can be neglected compared with the relaxation term. This approximation leads to a Lorentzian line shape and is refered to as the "Lorentzian approximation" (part a). Secondly, in part b of this section, the spectral function is calculated from the full Eqs. (2.17) and (2.18). Then (part c) the posible existence of tensor polarization waves leading to a splitting of the depolarized Rayleigh line into two components is discussed.

---

[11] L. Waldmann, Z. Naturforsch. **15 a**, 19 [1960]; **18 a**, 1033 [1963].

[12] S. Hess and L. Waldmann, Z. Naturforsch. **21 a**, 1529 [1966].

[13] A. C. Levi and F. R. McCourt, Physica **38**, 415 [1968]. — F. R. McCourt, H. F. P. Knaap, and H. Moraal, Physica **43**, 485 [1969].

a) Lorentzian Approximation

Firstly, Eq. (2.18) is approximated by

$$a_{\lambda,\,\mu\nu} = -\sqrt{\frac{k_{\mathrm{B}}\,T_0}{m}}\;\omega_{\mathrm{TF}}^{-1}\,\frac{\partial a_{\mu\nu}}{\partial x_\lambda}\,, \tag{3.1}$$

so that, using (3.1), Eqs. (2.17) reduces to the following closed equation for the tensor polarization:

$$\frac{\partial a_{\mu\nu}}{\partial t} - D_{\mathrm{T}}\,\Delta a_{\mu\nu} + \omega_{\mathrm{T}}\,a_{\mu\nu} = 0. \tag{3.2}$$

Here the "tensor polarization diffusion coefficient"

$$D_{\mathrm{T}} = \frac{k_{\mathrm{B}}\,T_0}{m\,\omega_{\mathrm{TF}}} \tag{3.3}$$

has been introduced and $\Delta = \partial^2/\partial x_\varrho\,\partial x_\varrho$ is the Laplacian. A spatial Fourier transformation of Eq. (3.2) leads to [cf. Eq. (1.12)]

$$\frac{\partial}{\partial t}\,\hat{a}_{\mu\nu}(t,\boldsymbol{k}) + (k^2\,D_{\mathrm{T}} + \omega_{\mathrm{T}})\;\hat{a}_{\mu\nu}(t,\boldsymbol{k}) = 0, \tag{3.4}$$

and hence

$$\hat{a}_{\mu\nu}(t,\boldsymbol{k}) = A(t\,|\,\boldsymbol{k})\;\hat{a}_{\mu\nu}(0,\boldsymbol{k})$$

with

$$A(t\,|\,\boldsymbol{k}) = \exp\{-(\omega_{\mathrm{T}} + k^2\,D_{\mathrm{T}})\;t\} \tag{3.5}$$

for $t \geqq 0$.

From this result, the following Lorentzian line is obtained for the spectrum of the depolarized Rayleigh line [cf. Eq. (1.13)]

$$S_{\mathrm{L}}(\omega\,|\,\boldsymbol{k}) = \frac{1}{\pi}\,\frac{\omega_{\mathrm{T}} + k^2\,D_{\mathrm{T}}}{\omega^2 + (\omega_{\mathrm{T}} + k^2\,D_{\mathrm{T}})^2}\,. \tag{3.6}$$

The half of the width at half height is

$$(\Delta\omega)_{1/2} = \omega_{\mathrm{T}} + k^2\,D_{\mathrm{T}}\,. \tag{3.7}$$

Clearly the line width is determined by two additive contributions: "collisional" or "pressure" broadening characterized by the relaxation coefficient $\omega_{\mathrm{T}} \propto n_0$ for the tensor polarization and diffusional broadening determined by $k^2\,D_{\mathrm{T}} \propto {n_0}^{-1}$. The latter contribution depends on the scattering angle χ between the wave vectors $\boldsymbol{k}_0$, $\boldsymbol{k}_1$ of the incident and the scattered light, for ${k_1}^2 \approx {k_0}^2$ one has

$$k^2 \approx {k_0}^2\,2\,(1-\cos\chi)\,. \tag{3.8}$$

The relative importance of diffusional and collisional broadening is characterized by the ratio

$$\xi = \omega_{\mathrm{T}}^{-1}\,k^2\,D_{\mathrm{T}} = \varepsilon^{-1}\,k^2\,l^2 \tag{3.9}$$

where

$$l = \sqrt{k_{\mathrm{B}}\,T_0/m}\;\omega_{\mathrm{TF}}^{-1} \tag{3.10}$$

is the mean free path of the tensor polarization flux and

$$\varepsilon = \omega_{\mathrm{T}}/\omega_{\mathrm{TF}} \tag{3.11}$$

is the ratio of the relaxation coefficients for the tensor polarization and the tensor polarization flux. For most gases of linear molecules – except for the hydrogen isotopes where $\varepsilon \approx 10^{-1}$ – ε is of the order of 1. Since the wave number k is of the order of λ^{-1} for scattering under 90°, collisional broadening dominates if

$$(l/\lambda)^2 \ll \varepsilon\,, \tag{3.12}$$

i. e., if the pressure is high enough that the mean free path of a molecule is very short compared with the wave length λ of the light.

A Lorentzian line shape of the form (3.6) where the diffusional broadening is characterized by the self-diffusion coefficient has first been discussed by DICKE [14] for emision spectra and more recently by COOPER [15] for the spectra of the rotational Raman lines. It seems appropriate to discuss some of the approximations involved in the use of the ansatz (2.8) and of the transport-relaxation Eqs. (2.17) and (2.18). Firstly, the collisional coupling between the tensor polarization and other 2nd rank tensors, e. g., the friction pressure tensor which is of importance for the Senftleben-Beenakker effect on the viscosity, has been disregarded. The relative error of the line width in the pressure broadening region caused by this approximation is of the order of the maximal relative change of the viscosity in a magnetic field, i. e. of the order of 1%. Secondly, higher rank tensors, e. g. terms of the type $a_{\lambda\varkappa,\,\mu\nu}\langle v_\lambda\,v_\varkappa\,\Phi_{\mu\nu}\rangle$ have been neglected in (2.8). Inclusion of (3.12) leads to a set of three coupled transport-relaxation equations instead of (2.17), (2.18), and these yield a line width of the form

$$(\Delta\omega)_{1/2} = \omega_{\mathrm{TF}}[\varepsilon + (l/\lambda)^2 + \ldots (l/\lambda)^4]$$

[cf. (3.9)] instead of (3.7). Thus Eq. (3.7) is only valid for small values of $(l/\lambda)^2$ such that terms of order $(l/\lambda)^4$ can be disregarded. Furthermore, the fact that Eq. (3.7) yields an infinite line width for $n_0 \to 0$ (i. e. $l/\lambda \to \infty$) whereas the line width for small pressures is finite and determined by the

---

[14] R. N. DICKE, Phys. Rev. **89**, 472 [1953].

[15] V. G. COOPER, Thesis, Toronto 1968. — V. G. COOPER, A. D. MAY, E. H. HARA, and H. F. P. KNAAP, Can. J. Phys. **46**, 2019 [1968].

Doppler broadening clearly indicates that Eq. (3.7) is not valid if the mean free path l is larger than the wave length λ of the light. So far, the spectrum of the depolarized Rayleigh light has been investigated experimentally only in the pressure broadening region[4] ($l/\lambda \ll 1$). The validity of the approximation (3.1) is discussed in the followig two parts of this section.

b) Non-Lorentzian Line Shape

Now the spectral function $S(\omega \mid \boldsymbol{k})$ is calculated from Eqs. (2.17), (2.18) without the approximation (3.1). Elimination of $a_{\lambda,\mu\nu}$ from Eqs. (2.17), (2.18) yields the 2nd order differential equation

$$\omega_{\mathrm{TF}}^{-1}\, \ddot{a}_{\mu\nu}(t,\boldsymbol{x}) + (1+\varepsilon)\, \dot{a}_{\mu\nu}(t,\boldsymbol{x}) - D_{\mathrm{T}}\, \Delta a_{\mu\nu}(t,\boldsymbol{x}) + \omega_{\mathrm{T}}\, a_{\mu\nu}(t,\boldsymbol{x}) = 0, \qquad (3.13)$$

where the dot denotes differentiation with respect to time. As far as the calculation of the spectral function is concerned, the initial conditions imposed on the tensor polarization and the tensor polarization flux are

$$a_{\mu\nu}(0,\boldsymbol{x}) \propto \delta(\boldsymbol{x}), \quad a_{\lambda,\mu\nu}(0,\boldsymbol{x}) = 0. \qquad (3.14)$$

Thus Eq. (2.17) implies

$$\dot{a}_{\mu\nu}(0,\boldsymbol{x}) = -\omega_{\mathrm{T}}\, a_{\mu\nu}(0,\boldsymbol{x}). \qquad (3.15)$$

By taking the spatial Fourier transform of Eq. (3.13) and using the definition (1.14) for the function $A(t \mid \boldsymbol{k})$ the following differential equations for A is obtained:

$$\omega_{\mathrm{TF}}^{-1}\, \ddot{A} + \left(1 + \frac{\omega_{\mathrm{T}}}{\omega_{\mathrm{TF}}}\right) \dot{A} + (k^2 D_{\mathrm{T}} + \omega_{\mathrm{T}})\, A = 0. \qquad (3.16)$$

The initial conditions for $A(t \mid \boldsymbol{k})$ are

$$A(0 \mid \boldsymbol{k}) = 1; \quad \dot{A}(0 \mid \boldsymbol{k}) = -\omega_{\mathrm{T}}. \qquad (3.17)$$

With the abbreviations

$$\omega_{\mathrm{Dop}}^2 = k^2 \cdot k_{\mathrm{B}}\, T_0/m, \qquad (3.18)$$

$$\omega' = \tfrac{1}{2}(1+\varepsilon)\, \omega_{\mathrm{TF}}, \qquad (3.19)$$

$$\omega'' = \tfrac{1}{2}\, \omega_{\mathrm{TF}} [(1-\varepsilon)^2 - 4\, \omega_{\mathrm{Dop}}^2/\omega_{\mathrm{TF}}^2]^{1/2}, \qquad (3.20)$$

the solution of Eq. (3.16) subject to the initial conditions (3.17) is given by

$$A(t \mid \boldsymbol{k}) = e^{-\omega' t} \left[\cosh \omega'' t + \frac{\omega' - \omega_{\mathrm{T}}}{\omega''} \sinh \omega'' t\right]. \qquad (3.21)$$

Clearly the function $A(t \mid \boldsymbol{k})$ as given by (3.21) is different from (3.5). For $\varepsilon \neq 1$ and high pressures where

$$4\, \frac{\omega_{\mathrm{Dop}}^2}{\omega_{\mathrm{TF}}^2} \ll (1-\varepsilon)^2$$

one has

$$\omega'' \approx \tfrac{1}{2}(1-\varepsilon)\, \omega_{\mathrm{TF}}$$

and (3.21) reduces to the exponential function $e^{-\omega_{\mathrm{T}} t}$ much as (3.5) does for high pressures.

Next the spectral function $S(\omega \mid \boldsymbol{k})$ is obtained from (3.21) according to (1.13). Using the dimensionless frequency variable

$$\Omega = \omega/\omega_{\mathrm{Dop}} \qquad (3.22)$$

and introducing the spectral function $S(\Omega \mid \boldsymbol{k})$ by

$$S(\Omega \mid \boldsymbol{k})\, \mathrm{d}\Omega = S(\omega \mid \boldsymbol{k})\, \mathrm{d}\omega, \qquad (3.23)$$

one finds

$$\pi S(\Omega \mid \boldsymbol{k}) = \frac{\varepsilon y + y^{-1} + \varepsilon y^{-1} \Omega^2}{\Omega^2[(1+\varepsilon^2) - 2y^{-2} + \Omega^2 y^{-2}] + (\varepsilon y + y^{-1})^2} \qquad (3.24)$$

where

$$y = \omega_{\mathrm{TF}}/\omega_{\mathrm{D}} = (k\, l)^{-1} \propto \lambda/l \qquad (3.24\mathrm{a})$$

is a dimensionless collision frequency which is proportional to the number density of the gas. The theory presented here can be considered to be applicable for $y \geqq 2$ only.

The Lorentzian function (3.6) is equivalent to

$$\pi S_{\mathrm{L}}(\Omega \mid \boldsymbol{k}) = \frac{\varepsilon y + y^{-1}}{\Omega^2 + (\varepsilon y + y^{-1})^2}. \qquad (3.25)$$

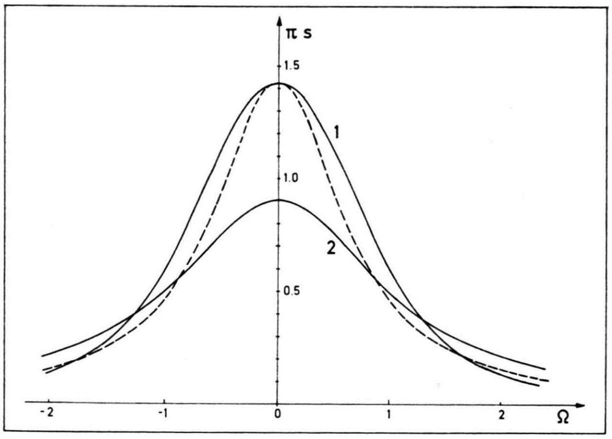

Fig. 1. The spectrum of the depolarized Rayleigh light for $\varepsilon \equiv \omega_{\mathrm{T}}/\omega_{\mathrm{TF}} = 0.1$. Curves 1 and 2 are the graphical representation of the functions $\pi S(\Omega)$ as given by Eq. (3.24) for $y=2$ and $y=10$. For the definition of Ω and y see Eqs. (3.22) and (3.24a). The dashed curve is the Lorentzian approximation $\pi S_{\mathrm{L}}(\Omega)$ [as given by Eq. (3.25] to curve 1. The Lorentzian curve for $y=10$ cannot be distinguished from curve 2 on the scale of the figure.

In Fig. 1, $\pi S(\Omega)$ and $\pi S_{\rm L}(\Omega)$ are plotted for $\varepsilon = 0.1$, $y = 2$ and $\varepsilon = 0.1$, $y = 10$. In the latter case both spectral functions cannot be distinguished on the scale of the figure. For $y = 2$, the spectral function (3.24) is broader than the Lorentzian function (3.25) for small Ω and falls off faster for large values of Ω.

For practical purposes, the quantity

$$\delta = [S(\Omega) - S_{\rm L}(\Omega])/S(0) \qquad (3.26)$$

rather than $[S(\Omega) - S_{\rm L}(\Omega)]/S(\Omega)$ should be used for a comparison of (3.24) with (3.25). A numerical analysis for $\varepsilon = 0.1$, 0.5, 1.0, 1.5 showes that $\delta \leqq 14\%$, $\leqq 6\%$ and $\delta \leqq 2\%$ for $y = 2$, 3 and $y \geqq 5$, respectively. Hence the deviation of (3.24) from (3.25) can be disregarded for $y \geqq 5$.

The width at half height $(\Delta\Omega)_{1/2}$ of the spectral function (3.24) is larger than the Lorentzian width $\varepsilon y + y^{-1}$. Since the collisional broadening that dominates for $y \gg 1$ is the same in both cases, the difference of the walf widths is associated with diffusional broadening. Hence if the width of the spectral function (3.24) is analyzed according to the formula for the Lorentzian half width, one finds an effective diffusion coefficient $D_{\rm eff}$ that is larger than $D_{\rm T}$ by the factor $y[(\Delta\Omega)_{1/2} - \varepsilon y]$ which, for $y \gg 1$, approaches the value $1 + \varepsilon/(1+\varepsilon^2)$. In Table 1, the ratio $D_{\rm eff}/D_{\rm T}$ is given for several values of ε and y.

ε \ y	2.0	3.0	4.0	5.0	10.0	∞
0.1	1.36	1.24	1.18	1.15	1.11	1.10
0.5	1.46	1.45	1.43	1.42	1.41	1.40
1.0	1.42	1.47	1.49	1.50	1.50	1.50

Table 1. $D_{\rm eff}/D_{\rm T}$ for several values of ε and y.

Considerations similar to those given here for the depolarized Rayleigh scattering should also hold for the rotational Raman scattering[15].

c) Tensor Polarization Waves

The frequency ω'' as given by (3.20) is imaginary if

$$4\,\omega_{\rm Dop}^2/\omega_{\rm TF}^2 = (2/y)^2 > (1-\varepsilon)^2 \qquad (3.27)$$

and this has the consequence that $A(t\,|\,\boldsymbol{k})$ becomes a periodic function. The occurrence of propagating modes is associated with damped "tensor polarization waves" which are analogous to the spin (vector polarization waves.

For $\varepsilon \neq 1$ these tensor polarization waves do not show up unless the pressure of the gas is sufficiently low such that the inequality (3.27) is fulfilled. For $\varepsilon = 1$, i. e., $\omega_{\rm T} = \omega_{\rm TF}$, however, (3.27) always holds and (3.21) takes the simple form

$$A(t\,|\,\boldsymbol{k}) = e^{-\omega_{\rm TF}t} \cos \omega_{\rm Dop}\, t\,, \quad (\varepsilon = 1). \qquad (3.28)$$

The propagating modes will cause a splitting of the depolarized Rayleigh line into two components shifted by $\pm\omega_{\rm sh}$ where $\omega_{\rm sh}$ is determined by

$$\omega_{\rm sh}^2 = \omega_{\rm Dop}^2 - \tfrac{1}{4}(1-\varepsilon)^2\,\omega_{\rm TF}^2\,, \qquad (3.29)$$

or by

$$\Omega_{\rm sh}^2 = 1 - \tfrac{1}{4}(1-\varepsilon)^2 y^2. \qquad (3.30)$$

For $\varepsilon = 1$ this splitting occurs for all pressures and Eq. (3.24) can be written as the sum of the spectral functions for two Lorentzian lines shifted by ± 1:

$$\pi S(\Omega\,|\,\boldsymbol{k}) = \frac{1}{2}\left[\frac{y}{(\Omega-1)^2+y^2} + \frac{y}{(\Omega+1)^2+y^2}\right], \quad (\varepsilon = 1). \qquad (3.31)$$

In Fig. 2 these shifted Lorentzian lines and their sum (3.31) are plotted together with the Lorentzian function (3.25) for $y = 2$. For pressures where $\omega_{\rm sh} \lesssim \omega'$ or equivalently

$$y^2 \gtrsim 2(1+\varepsilon^2)^{-1} \qquad (3.32)$$

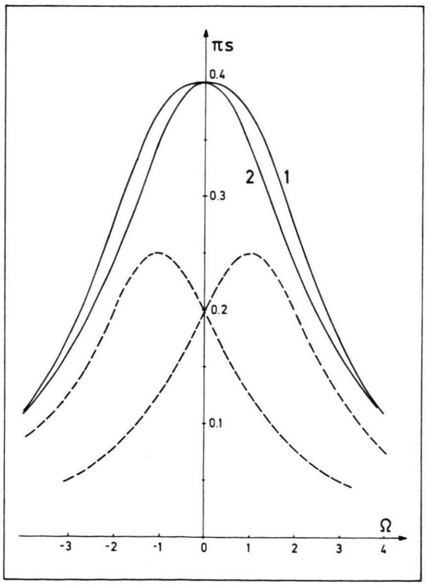

Fig. 2. The spectrum of the depolarized Rayleigh light for $\varepsilon = 1.0$ and $y = 2$. Curve 1 represents the non-Lorentzian spectral function $\pi S(\Omega)$ which is the sum of the two dashed Lorentzian curves shifted by $\Omega_{\rm sh} = \pm 1$ [cf. Eq. (3.31)]. Curve 2 is the Lorentzian spectral function $\pi S_{\rm L}(\Omega)$ [cf. Eq. (3.25)].

the splitting caused by the tensor polarization waves cannot be resolved and consequently it will lead to an effective broadening of the depolarized Rayleigh line.

A splitting of the depolarized Rayleigh line into two peaks has been observed for liquids of nonspherical molecules[16]. In the liquid, however, the splitting is caused by shear waves[17] (transverse sound waves) rather than by tensor polarization waves. For ligth scattering by gases these shear waves can be expected to play a minor role since the coupling between the anisotropic electric permeability tensor, i. e. the tensor polarization and the friction pressure tensor is rather small (as is known from the Senftleben-Beenakker effect on the shear viscosity).

§ 4. Relaxation Coefficients

In this section the linearized Waldmann-Snider collision term and the pertaining collision brackets are stated explicitly. Then the relaxation coefficients ω_{T} and ω_{TF} are studied in more detail.

For a "dilute" gas the collision term of the kinetic equation is related to binary scattering events. The two colliding particles are labelled by 1 and 2. Decomposing their momenta $\boldsymbol{p}_1', \boldsymbol{p}_2'$ and $\boldsymbol{p}_1, \boldsymbol{p}_2$ before and after a collision, respectively, into a center of mass momentum $\boldsymbol{P}$ and the relative momenta $\boldsymbol{p}_{12}', \boldsymbol{p}_{12}$ by

$$\begin{aligned} \boldsymbol{p}_1 &= \tfrac{1}{2}\boldsymbol{P} + \boldsymbol{p}_{12}\,; & \boldsymbol{p}_2 &= \tfrac{1}{2}\boldsymbol{P} - \boldsymbol{p}_{12}\,, \\ \boldsymbol{p}_1' &= \tfrac{1}{2}\boldsymbol{P} + \boldsymbol{p}_{12}'\,; & \boldsymbol{p}_2' &= \tfrac{1}{2}\boldsymbol{P} - \boldsymbol{p}_{12}'\,, \end{aligned} \tag{4.1}$$

denoting the reduced mass by m_{12}, and using the abbreviations

$$\Phi_i = \Phi(\boldsymbol{p}_i\,\boldsymbol{J}_i)\,; \quad \Phi_i' = \Phi(\boldsymbol{p}_i', \boldsymbol{J}_i)\,; \; i = 1, 2\,, \tag{4.2}$$

the Waldmann-Snider collision term can be written as

$$\begin{aligned} \omega_1(\Phi) = -\mathrm{Tr}_2 \int \mathrm{d}^3 p_2\, f_{02} \Bigg\{ &\int \frac{\mathrm{d}^3 p_{12}'}{m_{12}^{\,2}}\, \bar{a}(\boldsymbol{p}_{12}, \boldsymbol{p}_{12}')\,(\Phi_1' + \Phi_2')\; a^{\dagger}(\boldsymbol{p}_{12}', \boldsymbol{p}_{12}) \\ &- \frac{h}{i\,m_{12}}\,[a(\boldsymbol{p}_{12}, \boldsymbol{p}_{12})\,(\Phi_1 + \Phi_2) - (\Phi_1 + \Phi_2)\; a^{\dagger}(\boldsymbol{p}_{12}, \boldsymbol{p}_{12})] \Bigg\}. \end{aligned} \tag{4.3}$$

In Eq. (4.3) an operator notation with respect to magnetic and rotational quantum numbers is used. The binary scattering amplitude operator is denoted by $a(\boldsymbol{p}_{12}, \boldsymbol{p}_{12}')$; due to Galilean invariance it does not depend on the center of mass momentum $\boldsymbol{P}$. The operator $\bar{a}$ is in essence the scattering amplitude a multiplied by a δ-function with respect to energy:

$$\begin{aligned} &\bar{a}(\boldsymbol{p}_{12}, \boldsymbol{p}_{12}') \\ &= \frac{1}{2\pi} \int \frac{\mathrm{d}\tau}{\hbar} \exp\left\{ \frac{i\tau}{\hbar} \left(\frac{p_{12}^2}{2\,m_{12}} + E(J_1^{\,2}) + E(J_2^{\,2}) \right) \right\} a(\boldsymbol{p}_{12}, \boldsymbol{p}_{12}') \cdot \exp\left\{ -\frac{i\tau}{\hbar} \left(\frac{p_{12}'^2}{2\,m_{12}} + E(J_1^{\,2}) + E(J_2^{\,2}) \right) \right\}. \end{aligned} \tag{4.4}$$

The explicit form of the collision bracket for two operators can now be obtained from (4.3) with the help of the definition (2.6). Notice that both ω_{T} and ω_{TF} are "diagonal" collision brackets of the form $\langle \Phi\, \omega(\Phi) \rangle_0$. Application of the optical theorem

$$\begin{aligned} \frac{h}{i}\,[a(\boldsymbol{p}_{12}, \boldsymbol{p}_{12}) \; - a^{\dagger}(\boldsymbol{p}_{12}, \boldsymbol{p}_{12})] &= m_{12}^{-1} \int \mathrm{d}^3 p_{12}'\, \bar{a}(\boldsymbol{p}_{12}, \boldsymbol{p}_{12}')\; a^{\dagger}(\boldsymbol{p}_{12}', \boldsymbol{p}_{12}) \\ &= m_{12}^{-1} \int \mathrm{d}^3 p_{12}'\; a^{\dagger}(\boldsymbol{p}_{12}, \boldsymbol{p}_{12}')\; \bar{a}(\boldsymbol{p}_{12}', \boldsymbol{p}_{12}) \end{aligned} \tag{4.5}$$

leads to the following expression for a diagonal collision bracket:

$$\begin{aligned} \langle \Phi\, \omega(\Phi) \rangle_0 = n_0^{-1}\, \mathrm{Tr}_1\, \mathrm{Tr}_2 \iiint \mathrm{d}^3 p_1\, \mathrm{d}^3 p_2 \frac{\mathrm{d}^3 p_{12}'}{m_{12}^{\,2}}\, f_{01}\, f_{02}\, \Phi_1\, \bar{a}(\boldsymbol{p}_{12}, \boldsymbol{p}_{12}') \\ \times [a^{\dagger}(\boldsymbol{p}_{12}', \boldsymbol{p}_{12})\,(\Phi_1 + \Phi_2) - (\Phi_1' + \Phi_2')\; a^{\dagger}(\boldsymbol{p}_{12}', \boldsymbol{p}_{12})]. \end{aligned} \tag{4.6}$$

---

[16] V. S. STARUNOV, E. V. TIGANOV, and I. L. FABELINSKII, JETP Letters **4**, 176 [1966]. — A. SZÖKE, E. COURTENS, and A. BEN REUVEN, Chem. Phys. Letters **1**, 87 [1967]. — G. I. A. STEGEMAN and B. P. STOICHEFF, Phys. Rev. Lett. **21**, 202 [1968].

[17] V. VOLTERRA, Phys. Rev. **180**, 156 [1969].

In Eq. (4.6) the identity

$$d^3p_1\, d^3p_2 = d^3P\, d^3p_{12} \tag{4.7}$$

can be used and the integration over the center of mass momentum $\boldsymbol{P}$ can be performed for any given Φ since a and $a^\dagger$ do not depend on $\boldsymbol{P}$.

For convenience, Eq. (4.6) is rewritten in a slightly different way. Firstly the dimensionless momentum variables $\boldsymbol{V}$, $\gamma\, \boldsymbol{e}$, $\gamma'\, \boldsymbol{e}'$ defined by

$$\boldsymbol{P} = 2\sqrt{m\, k_B\, T_0}\, \boldsymbol{V}\,, \tag{4.8}$$

$$\boldsymbol{p}_{12} = \sqrt{m\, k_B\, T_0}\, \gamma\, \boldsymbol{e}\,, \qquad \boldsymbol{p}_{12}' = \sqrt{m\, k_B\, T_0}\, \gamma'\, \boldsymbol{e}', \tag{4.9}$$

where $\boldsymbol{e}$ and $\boldsymbol{e}'$ are unit vectors are used. Then one has

$$n_0^{-1}\, f_{01}\, f_{02}\, d^3p_1\, d^3p_2 = n_0\, \pi^{-3}\, e^{-V^2}\, d^3V\, e^{-\gamma^2}\, \gamma^2\, d\gamma\, d^2e\, Q_0^{-2} \exp\{-[E(J_1) + E(J_2)/k_B\, T_0\} \tag{4.10}$$

and

$$m_{12}^{-2}\, d^3p_{12}' = 2\sqrt{\pi}\, c_0\, k_B\, T_0\, \gamma'\, d\gamma'^2\, d^2e' \tag{4.11}$$

where

$$c_0 = \sqrt{k_B\, T_0/2\, \pi\, m_{12}}\,. \tag{4.12}$$

Secondly the single channel scattering operator

$$a_{j_1j_2,j_1'j_2'}\, (\boldsymbol{p}_{12}, \boldsymbol{p}_{12}') = P_{j_1}\, P_{j_2}\, a(\boldsymbol{p}_{12}, \boldsymbol{p}_{12}')\, P_{j_1'}\, P_{j_2'} \tag{4.13}$$

is introduced; for the definition of the projection operator P_j see Eq. (1.2). Using

$$\bar{a}_{j_1j_2,j_1'j_2'}\, (\boldsymbol{p}_{12}, \boldsymbol{p}_{12}') = a_{j_1j_2,j_1'j_2'}\, (\boldsymbol{p}_{12}, \boldsymbol{p}_{12}')\, \delta(\gamma^2 + \varepsilon_{j_1} + \varepsilon_{j_2} - \gamma'^2 - \varepsilon_{j_1'} - \varepsilon_{j_2'})\, (k_B\, T_0)^{-1} \tag{4.14}$$

where

$$\varepsilon_j = E_j/k_B\, T_0\,, \tag{4.15}$$

one can immediately perform the integration over $d\gamma'^2$ in Eq. (4.6).

Thus (4.6) is rewritten as

$$\langle \Phi\, \omega(\Phi) \rangle_0 = n_0\, c_0\, \frac{8}{\pi^{3/2}} \int d^3V\, e^{-V^2}\, \{\Phi_1\, a(a^\dagger(\Phi_1 + \Phi_2) - (\Phi_1' + \Phi_2')\, a^\dagger)\}\,, \tag{4.16}$$

where

$$\{\ldots\} = \int_0^\infty d\gamma\, e^{-\gamma^2}\, \gamma^3\, \frac{1}{4\pi} \iint d^2e\, d^2e' \sum_{\substack{j_1j_2\\ j_1'j_2'}} \frac{(2\,j_1+1)\,(2\,j_2+1)}{Q_0^2} \exp\{-\varepsilon_{j_1} - \varepsilon_{j^2}\}\, [[\ldots]]_{j_1j_2,j_1'j_2'}\,, \tag{4.17}$$

and

$$\begin{aligned} &[[\Phi_1\, a(a^\dagger(\Phi_1 + \Phi_2) - (\Phi_1' + \Phi_2')a^\dagger)]]_{j_1j_2,j_1'j_2'} \\ &\quad = \frac{\gamma'}{\gamma}\, \frac{\mathrm{tr}_1\, \mathrm{tr}_2}{(2\,j_1+1)\,(2\,j_2+1)}\, \Phi_1\, a_{j_1j_2,j_1'j_2'}\, (a^\dagger_{j_1'j_2',j_1j_2}\, (\Phi_1 + \Phi_2) - (\Phi_1' + \Phi_2')\, a^\dagger_{j_1'j_2',j_1j_2})\,. \end{aligned} \tag{4.18}$$

In Eq. (4.18), γ' which also occurs in Φ_1', Φ_2', a and $a^\dagger$ is no longer an independent variable but given by

$$\gamma'^2 = \gamma^2 + \varepsilon_{j_1} + \varepsilon_{j_2} - \varepsilon_{j_1'} - \varepsilon_{j_2'}\,. \tag{4.19}$$

In (4.17) the scattering amplitude has to be put equal to zero for those γ which, according to (4.19), would lead to a negative value for γ'^2. The trace over the magnetic quantum numbers is denoted by "tr".

For a Φ which is diagonal with respect to the magnetic quantum numbers (4.18) reduces to

$$\Phi_1(\Phi_1 + \Phi_2 - \Phi_1' - \Phi_2')\, \sigma(\boldsymbol{e}', \boldsymbol{e}\,|\, j_1'\, j_2', j_1\, j_2) \tag{4.20}$$

where $$\sigma(\boldsymbol{e}', \boldsymbol{e}\,|\, j_1'\, j_2', j_1\, j_2) = \frac{\gamma'}{\gamma}\, \frac{\mathrm{tr}_1\, \mathrm{tr}_2}{(2\,j_1+1)\,(2\,j_2+1)}\, a_{j_1j_2,j_1'j_2'}(\boldsymbol{p}_{12}, \boldsymbol{p}_{12}')\, a^\dagger_{j_1'j_2',j_1j_2}\, (\boldsymbol{p}_{12}', \boldsymbol{p}_{12}) \tag{4.21}$$

is a cross section averaged over the magnetic substates.

Now it is relevant to discuss the relaxation coefficients ω_{T} and ω_{TF} [cf. (2.13), (2.15)]. Integration over $\mathrm{d}^3 V$ leads to

$$\omega_{\mathrm{T}} = n_0\, c_0\, \tfrac{8}{5} \left\{ \Phi_{1\mu\nu}\, a [a^\dagger, (\Phi_{1\mu\nu} + \Phi_{2\mu\nu})] \right\}, \tag{4.22}$$

where the bracket $[\ldots,\ldots]$ denotes the commutator. For the definition of $\Phi_{\mu\nu}$ see (1.8). Clearly, ω_{T} vanishes if $(\Phi_{1\mu\nu} + \Phi_{2\mu\nu})$ commutes with $a^\dagger$. Hence ω_{T} is particularly sensitive to the nonspherical part of the scattering amplitude, i. e. if the scattering amplitude operator a is split into a spherical part a_{sph} which is diagonal with respect to magnetic quantum numbers and into a nonspherical part a_{nsph}, then a and $a^\dagger$ occurring in Eq. (4.22) can be replaced by a_{nsph} and $a^\dagger_{\mathrm{nsph}}$.

According to (2.9), (2.15), (4.1), (4.9), (4.10) the relaxation coefficient for the tensor polarization flux is given by

$$\begin{aligned} \omega_{\mathrm{TF}} = n_0\, c_0 \frac{8}{15\, \pi^{3/2}} \int \mathrm{d}^3 V\, e^{-V^2} \{ \Phi_{1\mu\nu}(V_\lambda + \gamma\, e_\lambda)\, a \\ \cdot [a^\dagger (\Phi_{1\mu\nu}(V_\lambda + \gamma\, e_\lambda) + \Phi_{2\mu\nu}(V_\lambda - \gamma\, e_\lambda)) - (\Phi_{1\mu\nu}(V_\lambda + \gamma'\, e_\lambda') + \Phi_{2\mu\nu}(V_\lambda - \gamma'\, e_\lambda'))\, a^\dagger] \} . \end{aligned} \tag{4.23}$$

Integration over $\mathrm{d}^3 V$ leads to

$$\omega_{\mathrm{TF}} = \tfrac{1}{2}\, \omega_{\mathrm{T}} + n_0\, c_0\, \tfrac{8}{15} \{ \Phi_{1\mu\nu}\, a [a^\dagger (\Phi_{1\mu\nu} - \Phi_{2\mu\nu})\, \gamma^2 - (\Phi_{1\mu\nu} - \Phi_{2\mu\nu})\, a^\dagger\, \gamma\, \gamma'\, \boldsymbol{e} \cdot \boldsymbol{e}'] \} . \tag{4.24}$$

Using $\quad a^\dagger\, \Phi_{1\mu\nu} = \Phi_{1\mu\nu}\, a^\dagger + [a^\dagger, \Phi_{1\mu\nu}] \quad$ and $\quad \Phi_{\mu\nu}\, \Phi_{\mu\nu} = 5$,

one can rewrite Eq. (4.24) as

$$\omega_{\mathrm{TF}} = \tfrac{1}{2}\, \omega_{\mathrm{T}} + \omega_{\mathrm{D}} + \tilde{\omega}_{\mathrm{TF}}, \tag{4.25}$$

with

$$\omega_{\mathrm{D}} = n_0\, c_0\, \tfrac{8}{8} \{ (\gamma^2 - \gamma\, \gamma'\, \boldsymbol{e} \cdot \boldsymbol{e}')\, a\, a^\dagger \}, \tag{4.26}$$

and

$$\tilde{\omega}_{\mathrm{TF}} = - n_0\, c_0\, \tfrac{8}{15} \{ \Phi_{1\mu\nu}\, a [a^\dagger\, \Phi_{2\mu\nu}\, \gamma^2 - \Phi_{2\mu\nu}\, a^\dagger\, \gamma\, \gamma'\, \boldsymbol{e} \cdot \boldsymbol{e}'] + \Phi_{1\mu\nu}\, a [a^\dagger, \Phi_{1\mu\nu}]\, \gamma\, \gamma'\, \boldsymbol{e} \cdot \boldsymbol{e}' \}, \tag{4.27}$$

if the number of molecules in the rotational state $j = 0$ is very small compared with the number of molecules in the states $j \geqq 1$.

The relaxation coefficient ω_{D} is related to the self-diffusion coefficient D_{self} by

$$D_{\mathrm{self}} = k_{\mathrm{B}}\, T_0 / m\, \omega_{\mathrm{D}} . \tag{4.28}$$

Notice that $\omega_{\mathrm{TF}} \neq \omega_{\mathrm{D}}$ unless the nonspherical part of the scattering amplitude is small compared with spherical part. Hence, in general, D_{T} differs from the diffusion coefficient (4.28).

Effective cross sections σ_{T} and σ_{TF} pertaining to ω_{T} and ω_{TF} can be defined by

$$\omega_{\mathrm{T}} = n_0\, \bar{v}_0\, \sigma_{\mathrm{T}}, \quad \omega_{\mathrm{TF}} = n_0\, \bar{v}_0\, \sigma_{\mathrm{TF}} \tag{4.29}$$

with

$$\bar{v}_0 = \sqrt{8\, k_{\mathrm{B}}\, T_0 / \pi\, m_{12}} = 4\, c_0 . \tag{4.30}$$

Hence, according to (4.22), the "reorientation cross section" σ_{T} is given by

$$\sigma_{\mathrm{T}} = \tfrac{2}{5} \{ \Phi_{1\mu\nu}\, a [a^\dagger, (\Phi_{1\mu\nu} + \Phi_{2\mu\nu})] \} . \tag{4.31}$$

The analogous relation for σ_{TF} can be obtained from Eq. (4.24).

To proceed further in the calculation of the relaxation coefficient or of the effective cross sections a knowledge of the scattering amplitude is required. For a discussion of the nonspherical scattering amplitude operator see Ref. [18].

§ 5. On the Comparison of the Line Width with Senftleben-Beenakker Effect and NMR Data

In § 3, it has been shown how the width of the depolarized Rayleigh line is related to the relaxation coefficients ω_{T} and ω_{TF}. It has been conjectured earlier [4, 9], that ω_{T} characterizing the width of the depolarized Rayleigh line in the pressure broadening region can be compared with data obtained from measurements of the Senftleben-Beenakker effect on the viscosity and of the nuclear spin relaxation time (if the relaxation of the nuclear magnetization is mainly associated with intramolecular quadrupole coupling). It is the purpose of this section to point out under which conditions this comparison actually can be made and furthermore to indicate that it should be possible to compare the relaxation coefficient ω_{TF} with data obtained from the Senftleben-Beenakker effect on heat conductivity.

---

[18] S. HESS and W. E. KÖHLER, Z. Naturforsch. **23 a**, 1903 [1968]. — W. E. KÖHLER, S. HESS, and L. WALDMANN, Z. Naturforsch. **25 a**, 336 [1970].

a) Comparison with Senftleben-Beenakker Effect Measurements

Transport process in polyatomic gases lead to a correlation between the linear and rotational angular momenta of the molecules; i. e., to a partial alignment of the angular momenta. The alignment, in turn, influences the values of the transport coefficients. Hence if the alignment is (partially) destroyed by the precessional motion of the rotational angular momentum about an applied magnetic field the transport coefficients are altered (Senftleben-Beenakker effect). The differences between the transport coefficients measured with and without an applied magnetic field of strength H depend on the ratio $\omega_{\mathrm{H}}/\omega_{\mathrm{coll}}$ where $\omega_{\mathrm{H}} = \gamma H$ (γ is the rotational gyromagnetic ratio) is the precession frequency of the rotational angular momentum and ω_{coll} is a specific) "collision" frequency. Since ω_{coll} is proportional to the number density n_0, the magnetic-field-induced change of a transport coefficient is a function of H/p_0 where $p_0 = n_0 k_{\mathrm{B}} T_0$ is the (equilibrium) pressure of the gas.

Assuming that the dominant types of alignment that are responsible for the influence of a magnetic field on the viscosity and the heat conductivity are given by

$$\tilde{a}_{\mu\nu} = \langle R\, \Phi_{\mu\nu} \rangle \tag{5.1}$$

and

$$\tilde{a}_{\lambda,\,\mu\nu} = \langle Q\, V_\lambda\, \Phi_{\mu\nu} \rangle , \tag{5.2}$$

respectively, where R and Q are (scalar) functions depending on V^2 and J^2 [for $\Phi_{\mu\nu}$ see (1.8)] one obtains theoretical curves for $\Delta\eta = \eta(H) - \eta(0)$ and $\Delta\lambda = \lambda(H) - \lambda(0)$ which are in good agreement with the H/p-dependence of these quantities measured for gases of linear molecules. The collision frequencies involved are the relaxation frequencies

$$\tilde{\omega}_{\mathrm{T}} = \langle R\, \Phi_{\mu\nu}\, \omega(R\, \Phi_{\mu\nu}) \rangle_0 / \langle R^2\, \Phi_{\mu\nu}\, \Phi_{\mu\nu} \rangle_0 \tag{5.3}$$

and

$$\tilde{\omega}_{\mathrm{TF}} = \langle Q\, V_\lambda\, \Phi_{\mu\nu}\, \omega(Q\, V_\lambda\, \Phi_{\mu\nu}) \rangle_0 / \langle Q^2\, V^2\, \Phi_{\mu\nu}\, \Phi_{\mu\nu} \rangle_0 \tag{5.4}$$

pertaining to the quantities (5.1) and (5.2). They can be obtained experimentally, either from the values $(H/p)_{1/2}$ for which $\Delta\eta$ or $\Delta\lambda$ attain half their saturation values (obtained for $H/p \rightarrow \infty$) or from the values $(H/\mathrm{p})_{\max}$ for which the transverse effects reach their maximal values.

In particular $\tilde{\omega}_{\mathrm{T}}$ can be obtained from shear viscosity measurements as

$$\tilde{\omega}_{\mathrm{T}} = p_0\, \gamma\, (H/p)^{(3)}_{1/2} \tag{5.5}$$

where $(H/p)^{(3)}_{1/2}$ is the position of the "half-value" for $\Delta\eta_3$. The notation of DE GROOT and MAZUR[19] is used for the viscosity coefficients, i. e., "3" refers to the case where the magnetic field lies in the plane determined by the direction of the velocity and its gradient. Likewise, $\tilde{\omega}_{\mathrm{TF}}$ can be obtained from heat conductivity measurements (in spherical approximation)

$$\tilde{\omega}_{\mathrm{TF}} = p_0\, \gamma\, (H/p)^{\|}_{1/2} \tag{5.6}$$

where (H/p) is the position of the half-value for $\lambda_{\|}$ (magnetic field parallel to the temperature gradient).

Notice that it is not possible to infer from the Senftleben-Beenakker measurements alone which function R and Q should be chosen for (5.1) and (5.2). In fact, in the investigations published so far[20]

$$R = Q = \left[\frac{J^2 (J^2 - \frac{3}{4})}{\langle J^2 (J^2 - \frac{3}{4}) \rangle_0} \right]^{1/2} \tag{5.7}$$

has been used: Classically speaking, $\Phi_{\mu\nu} \propto J^{-2}\, \overline{J_\mu J_\nu}$ is proportional to the 2nd rank tensor constructed from the unit vector parallel to the rotational angular momentum vector $\boldsymbol{J}$, $R\, \Phi_{\mu\nu} \propto \overline{J_\mu J_\nu}$, on the other hand, is proportional to the 2nd rank tensor constructed from $\boldsymbol{J}$ itself.

Now, if (5.7) would be the appropriate expression for R, $\tilde{\omega}_{\mathrm{T}}$ as obtained from the Senftleben-Beenakker effect on the viscosity would be different from ω_{T} as obtained from the width of the depolarized Rayleigh line in the pressure broadening region (unless the magnitude of $\boldsymbol{J}$ would not be affected by collisions). The close agreement between the relaxation coefficients or effective (reorientation) cross sections obtained from Senftleben-Beenakker effect and from line width measurements for N_2, as found in Ref. [4], however, suggests that $R = 1$ in (5.1) would be a better "choice" for a "single term description" of the Senftleben-Beenakker effect on the viscosity.

---

[19] S. R. DE GROOT and P. MAZUR, Non-Equilibrium Thermodynamics, North-Holland Publ. Co., Amsterdam 1962.

[20] F. R. MCCOURT and R. F. SNIDER, J. Chem. Phys. **46**, 2387 [1967]; J. Chem. Phys. **47**, 4117 [1967]. — A. C. LEVI and F. R. MCCOURT, Physica **38**, 415 [1968]. — A. C. LEVI, F. R. MCCOURT, and A. TIP, Physica **39**, 165 [1968]. — S. HESS and F. R. MCCOURT, Physica **44**, 19 [1969].

In analogy, one may expect that one may use $Q=1$ instead of (5.7) in (5.2) for the theory of the Senftleben-Beenakker effect on heat conductivity. Unfortunately, however, no measurements of the width of the depolarized Rayleigh line are presently available in the "diffusional broadening region" and consequently no values of ω_{TF} have been determined from light scattering experiments; thus the comparison with the Senftleben-Beenakker effect cannot yet be made.

b) Comparison with NMR Data

The relaxation of the nuclear magnetization of polyatomic gases is predominantly connected with the coupling of the nucear spin with the rotational motion of the molecule (intramolecular coupling). For a comparison of data obtained from nuclear spin relaxation times with the relaxation coefficient ω_{T} two cases may be distinguised, (i) the relaxation of a nuclear spin $\geqq 1$ (e. g. deuterium in HD, ^{14}N in NO or N_2), and (ii) of two spins 1/2 (eq. ortho-H_2). In both cases the Hamiltonian $\mathcal{H}$ associated with the coupling of the spin with the rotational motion can be written in the form [21, 22]

$$\frac{1}{\hbar}\,\mathcal{H}=c_1\,I_\mu\,J_\mu\;+c_2\,\overline{I_\mu\,I_\nu}\,\overline{u_\mu\,u_\nu}$$

where $\boldsymbol{u}$ is a unit vector parallel to the molecular axis and c_1 is the scalar spin-rotation coupling constant. For case (i) $\boldsymbol{I}$ is the nuclear spin vector operator and c_2 is the quadrupolar coupling constant; for case (ii) $\boldsymbol{I}$ is the sum of the two spin vectors in the triplet state and $2\,c_2$ is the dipolar coupling constant. In a dilute gas a molecule undergoes many rotations between two successive collisions. This implies that only the part of the tensor $\overline{\boldsymbol{u}\,\boldsymbol{u}}$ that is diagonal with respect to the rotational quantum numbers has to be considered for spin-relaxation. This part is proportional to $\Phi_{\mu\nu}$ [cf. (1.8)]. It is due to this fact that collision brackets similar to ω_{T} occur for NMR.

Recently, CHEN and SNIDER [23] treated nuclear spin relaxation in dilute gases of linear molecules by a kinetic theory approach based on the Waldmann-Snider equation. Compared with the traditional correlation function treatment [24] this approach has the advantage that a precise connection between the Bloch-relaxation times and certain collision brackets obtained from the linearized Waldmann-Snider collision term can be established.

In particular, in the "extreme narrowing limit" (collision frequency $\gg$ precession frequencies of the nuclear spin and the rotational angular momentum about the applied magnetic field) both Bloch-relaxation times become equal and one has

$$T_1^{-1}=T_\lambda^{-1}=\tfrac{2}{3}\,\langle J^2\rangle_0\,\frac{{c_1}^2}{\omega_{\mathrm{V}}{}'}+\frac{2}{15}\,[I(I+1)-\tfrac{3}{4}]\,\frac{{c_2}^2}{\omega_{\mathrm{T}}{}'}\,. \tag{5.9}$$

In Eq. (5.9), $\omega_{\mathrm{V}}{}'$ and $\omega_{\mathrm{T}}{}'$ are relaxation coefficients. The latter is of particular interest for the comparison with the width of the depolarized Rayleigh line. Before discussing the explicit meaning of $\omega_{\mathrm{T}}{}'$, it seems worthwhile to make a few remarks on the possibilities of obtaiing values of this relaxation coefficient from NMR experiments.

If the relaxation time T of a nuclear spin $\geqq 1$ is measured the relaxation coefficient $\omega_{\mathrm{T}}{}'$ can be obtained from (5.9) since in this case $c_1 \ll c_2$. For molecules with nuclear spins 1/2 (eq. ortho-H_2) the coupling constants c_1 and c_2 are of equal order of magnitude. Hence in that case it is not possible to determine $\omega_{\mathrm{T}}{}'$ from a measurement of the nuclear relaxation time in the extreme narrowing region alone. However, as has been demonstrated by HARDY [25], it is posible to determine $\omega_{\mathrm{T}}{}'$ (and $\omega_{\mathrm{V}}{}'$) from measurements at lower values of H/p where the Bloch-relaxation times depend on the strength of the applied magnetic field.

Next, the relaxation coefficient is discussed in more detail. Upon the assumption that the nuclear spins are not affected by collisions $\omega_{\mathrm{T}}{}'$ can be reduced to

$$\omega_{\mathrm{T}}{}'=n_0\,c_0\,\tfrac{8}{5}\,\{\Phi_{1\mu\nu}\,a[a^\dagger,\Phi_{1\mu\nu}]\}=n_0\,4\,c_0\,\sigma_{\mathrm{T}}{}'. \tag{5.10}$$

In Eq. (5.10) the notations of § 4 have been used. A comparison of (5.10) with (4.22) shows that in general $\omega_{\mathrm{T}}{}' \neq \omega_{\mathrm{T}}$ (or $\sigma_{\mathrm{T}}{}' \neq \sigma_{\mathrm{T}}$).

However, one has $\omega_{\mathrm{T}}{}'=\omega_{\mathrm{T}}$ for collisions where only one of the colliding particles changes its inter-

---

[21] A. ABRAGAM, The Principles of Nuclear Magnetism, Oxford University Press, Oxford 1961.

[22] P. KUSCH and V. W. HUGHES, in Handbuch der Physik, Vol. **37/1**, 1 (ed. S. FLÜGGE, Springer, Berlin 1959).

[23] F. M. CHEN and R. F. SNIDER, J. Chem. Phys. **48**, 3185 [1968].

[24] M. BLOOM and I. OPPENHEIM, Adv. Chem. Phys. **12**, 459 [1967].

[25] W. N. HARDY, Can. J. Phys. **44**, 265 [1966].

nal state. This may be approximately true for H_2-H_2 collisions. It is certainly the case for collisions of linear molecules with monatomics. Hence, for the infinite dilution limit of linear molecules in mixtures with monatomic gases, the ω_T obtained from the light scattering experiment is equal to the ω_T' obtained from NMR data.

Recently, SPEIGHT and ARMSTRONG[26] compared the effective cross section σ_T' obtained from their NMR measurements in gaseous N_2 with reorientation cross sections extracted from the Senftleben-Beenakker effect on the viscosity and the width of the depolarized Rayleigh line.

Final Remarks

The main results of this paper are the spectrum of the depolarized Rayleigh line as given by (3.24) and Eqs. (4.22), (4.24) which establish a rigorous connection between the relaxation coefficients ω_T and ω_{TF} characterizing the width of the depolarized Rayleigh line and the scattering amplitude operator characterizing the (binary) molecular collision process. Furthermore, the possible comparison of these relaxation coefficients with experimental data obtained from measurements of the Senftleben-Beenakker effect and NMR has been discussed.

So far, experimental results have been published on collisional broadening of the depolarized Rayleigh line of the light scattered from gases of H_2, N_2 and CO_2 at room temperature[4]. It would be desirable to extend further experiments in a number of directions.

(i) Measurements of the spectrum at lower pressures, i. e. in the "diffusional broadening regime" would be of interest, firstly in order to find deviations from the Lorentzian line shape and possibly evidence for the existence of tensor polarization waves, and secondly, in order to obtain experimental values of the relaxation coefficient ω_{TF} or the diffusion coefficient D_T.

(ii) In view of the fact that the relaxation coefficient ω_T is particularly sensitive to the nonspherical part of the scattering amplitude operator a systematic study of the collisional broadening of the depolarized Rayleigh line of a great number of gases of linear molecules (also for different temperatures) would be desirable. Of particular interest are the hydrogen isotopes since their nonspherical interaction potential is relatively well-known and only a few rotational levels are excited at room temperature. A comparison of gases like CO_2, OCS, and CS_2 or H_2, HCl, and Cl_2 would yield information on the influence of the electric dipole-dipole interaction (present for OCS and HCl) on the relaxation of the tensor polarization.

(iii) Measurements of the collisional broadening of the depolarized Rayleigh lines (as well as of the Senftleben-Beenakker effect on viscosity and of NMR) for gas mixtures of linear molecules with monatomics are desirable in order to obtain the effective reorientation cross sections for collisions of molecules with noble gas atoms which could be compared with NMR-data.

Further theoretical studies of the spectrum of the depolarized Rayleigh light should be concerned with the removal of the spherical approximation (2.14) employed in Eq. (2.18), with the "transition regime" between the pressure regions for which collisional and diffusional broadening on the one side and Doppler broadening on the other side determine the spectral width. Also, an extension of the theory developed here for linear molecules to the case of symmetric top molecules would be desirable. It seems feasible to treat rotational Raman scattering by a similar "kinetic equation approach" where, however, a kinetic equation for a distribution operator which is nondiagonal with respect to the rotational quantum numbers has to be used.

Acknowledgements

Part of this research has been performed at the Kamerlingh Onnes Laboratorium (University of Leiden, Netherlands). I thank Prof. Dr. J. J. M. BEENAKKER and Dr. H. F. P. KNAAP for the hospitality extended to me and for stimulating discussions. Also, helpful discussions with Prof. Dr. L. WALDMANN, Dr. F. R. MC COURT, Dr. V. G. COOPER, and Dipl.-Phys. W. E. KÖHLER are gratefully acknowledged. I tank Dipl.-Phys. W. E. KÖHLER and Dipl.-Phys. H. VESTNER for the preparation of the data for Table 1 and Figs. 1, 2.

---

[26] P. A. SPEIGHT and R. L. ARMSTRONG, Can. J. Phys. **47**, 1475 [1969].