Non-Lorentzian Shape of the Depolarized Rayleigh Line and the Correlation Function of the Tensor Polarization

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The correlation function of the tensor polarization relevant for the depolarized Rayleigh line of a gas of rotating linear molecules is calculated for the pressure broadening regime. Point of departure is the Waldmann-Snider equation for the distribution function of the gas. Due to the collisional coupling between the tensor polarization and other moments of the distribution function the correlation function turns out to be a sum of exponential functions. Consequently the depolarized Rayleigh line has a non-Lorentzian shape.

Recent experimental investigations [1] of light scattering from gaseous N_2 revealed that the lineshape of the pressure-broadened depolarized Rayleigh line is non-Lorentzian. More precisely, the time-correlation function obtained from the measured spectral function deviated from ane xponential function. This behaviour can be described theoretically by a slight modification of the previously developed kinetic theory for the broadening of the depolarized Rayleigh line [2, 3].

In this paper, it is indicated how the correlation function of the tensor polarization can be calculated from the Waldmann-Snider equation [4]. The importance of the collisional coupling between the tensor polarization and other moments of the distribution function of the gas is stressed. As a simple application, the consequences of a two-moments-approximation are studied in some detail.

1. General Remarks on the Calculation of the Correlation Function

For gases of linear molecules with rotational angular momentum $\hbar \boldsymbol{J}$ the time-correlation function associated with the depolarized Rayleigh line is the auto-correlation function for the (2nd rank) tensor polarization [2, 3]

$$\mathbf{a}_\mathrm{T} = \langle \boldsymbol{\Phi}_\mathrm{T} \rangle ,$$

$$\boldsymbol{\Phi}_\mathrm{T} = \sqrt{\tfrac{15}{2}} \left(\langle J^2 (J^2 - \tfrac{3}{4})^{-1} \rangle_0 \right)^{-1/2} (J^2 - \tfrac{3}{4})^{-1} \, \overline{\boldsymbol{J}\boldsymbol{J}} \, . \quad (1)$$

The brackets $\langle \dots \rangle$ and $\langle \dots \rangle_0$ refer to nonequilibrium and equilibrium averages, respectively. The symbol $\overline{\dots}$ indicates the symmetric traceless part of a tensor. The relevant correlation function is given by

$$\mathbf{a}_\mathrm{T}(t) = C(t) \, \mathbf{a}_\mathrm{T}(0) , \quad t \geqq 0 \, . \quad (2)$$

It can be calculated from transport-relaxation equations which, in turn, are derived from the Waldmann-Snider equation [4]. The linearized version of this kinetic equation can be written as

$$\partial \varphi / \partial t + \boldsymbol{c} \cdot \nabla \varphi + \omega(\varphi) = 0 , \quad (3)$$

where φ, defined by $f = f_0 (1 + \varphi)$, characterizes the deviation of the nonequilibrium distribution operator f from the equilibrium distribution f_0. In Eq. (3), $\boldsymbol{c}$ is the molecular velocity and $\omega(\dots)$ stands for the linearized Waldmann-Snider collision term. Now, a transport-relaxation equation for $\mathbf{a}_\mathrm{T}$ can be derived from Eq. (3) by application of the moment method [5]. In connection with the pressure broadening the flow term of Eq. (3) can be ignored, i.e. in essence, a spatially homogeneous system is considered. Even then, the equation for $\mathbf{a}_\mathrm{T}$ is not a closed equation due to the collision-induced coupling with other 2nd rank tensors. The collisional coupling between the tensor polarization and the friction pressure tensor is of crucial importance for the flow birefringence in gases [6, 3] and the Senftleben-Beenakker effect of the viscosity [7]. In connection with the line broadening problem other types of coupling may even be of greater importance.

For the discussion of this collisional coupling it is convenient to introduce a complete set of orthonormalized 2nd rank tensors $\boldsymbol{\Phi}_N = \boldsymbol{\Phi}_N(\boldsymbol{c}, \boldsymbol{J})$ with $\boldsymbol{\Phi}_1 \equiv \boldsymbol{\Phi}_\mathrm{T}$ and the properties

$$\langle \boldsymbol{\Phi}_N : \boldsymbol{\Phi}_{N'} \rangle_0 = 5 \, \delta_{NN'} \, . \quad (4)$$

For a spatially homogeneous system the moment equations for the $\mathbf{a}_N = \langle \boldsymbol{\Phi}_N \rangle$ are

$$\dot{\boldsymbol{a}}_N + \sum_{N'} \omega_{NN'} \, \boldsymbol{a}_{N'} = \boldsymbol{O} , \quad (5)$$

with the relaxation coefficients defined by

$$\omega_{NN'} = \tfrac{1}{5} \langle \boldsymbol{\Phi}_N : \omega(\boldsymbol{\Phi}_{N'}) \rangle_0 \, . \quad (6)$$

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Due to time reversal invariance the $\omega_{NN'}$ obey the Onsager-Casimir symmetry relation

$$\omega_{NN'} = T_N T_{N'} \, \omega_{N'N} , \tag{7}$$

where T_N is determined by

$$\mathbf{\Phi}_N(-\mathbf{c}, -\mathbf{J}) = T_N \, \mathbf{\Phi}_N(\mathbf{c}, \mathbf{J}) . \tag{8}$$

The diagonal coefficients $\omega_N \equiv \omega_{NN}$ are positive. Furthermore one has $\omega_N \, \omega_{N'} \geqq \omega_{NN'}^2$ for $T_{N'} = T_N$. These properties follow from the positive definite character of the Waldmann-Snider collision operator.

Solution of Eqs. (5) for an initial value problem yields the correlation functions $C_{NN'}(t)$ according to [8]

$$\mathbf{a}_N(t) = \sum_{N'} C_{NN'}(t) \, \mathbf{a}_{N'}(0) , \quad t \geqq 0 . \tag{9}$$

The quantity of interest for the light scattering is $C(t) \equiv C_{11}(t)$, the autocorrelation function of the tensor polarization $\mathbf{a}_1$.

In the previous theoretical treatment of the line broadening problem [2, 3] it had been assumed that the coupling coefficients ω_{1N}, $N \neq 1$ are so small that they can be ignored. Then, the correlation function $C(t)$ is equal to the exponential function $e^{-\omega_1 t}$ and the ensuing spectral function is a Lorentzian. The collisional coupling, however, leads to deviations from this simple behaviour.

2. Two-Moments-Approximation

The experimentally observed deviations of the correlation function from a function of the type $e^{-\omega_1 t}$ are small [1]. It was possible to obtain a reasonable fit of the measured correlation function by a sum of two exponential functions [9]. This indicates that the collisional coupling between the tensor polarization $\mathbf{a}_1$ and a specific 2nd rank tensor $\mathbf{a}_2 = \langle \mathbf{\Phi}_2 \rangle$ is of much higher relevance than the coupling with the other tensors $\mathbf{a}_N$, $N \neq 1, 2$. More precisely, $|\omega_{12}| \gg |\omega_{1N}|$, $|\omega_{2N}|$, $N \neq 1, 2$ can be assumed. In the two-moments-approximation to be studied now $\mathbf{a}_1$ and $\mathbf{a}_2$ only are taken into consideration. It should be stressed that it is not possible to determine $\mathbf{\Phi}_2$ from the experimental data. The guess $\mathbf{\Phi}_2 \sim \overline{\mathbf{c}\,\mathbf{c}}$ can be excluded because the collisional coupling between the tensor polarization and the friction pressure tensor is rather small [3, 6, 10]. Since the relaxation frequency of the tensor polarization depends on the rotational quantum number, $\mathbf{\Phi}_2 = S(J^2) \, \mathbf{\Phi}_{\mathrm{T}}$ seems to be a more likely guess. Here S is a scalar function of J^2. At any rate, the only property of $\mathbf{\Phi}_2$ used in the following is the assumption that it has the same time reversal behaviour as $\mathbf{\Phi}_{\mathrm{T}}$. This implies

$$\omega_{12} = \omega_{21} \tag{10}$$

and

$$\omega_{12}^2 \leqq \omega_1 \, \omega_2 . \tag{11}$$

Here $\omega_1 \equiv \omega_{11}$ and $\omega_2 \equiv \omega_{22}$ are the diagonal relaxation coefficients of $\mathbf{a}_1$ and $\mathbf{a}_2$, ω_{12} is a measure for their collisional coupling.

Next the dimensionless variables

$$K = \omega_{12} \, \omega_1^{-1} , \quad R = \omega_2 \, \omega_1^{-1} \tag{12}$$

are introduced. Notice that Eq. (11) implies $K^2 \leqq R$. With the abbreviations

$$\Omega_{1(2)} = \tfrac{1}{2} [1 + R \overset{+}{\underset{(-)}{}} W] , \quad W = [(1 - R)^2 + 4 K^2]^{1/2} , \tag{13}$$

the desired correlation function $C = C_{11}$ is given by

$$C = A_1 \, e^{-\Omega_1 \tau} + A_2 \, e^{-\Omega_2 \tau} . \tag{14}$$

Here τ stands for $t \, \omega_1$ and $A_{1(2)}$ are given by

$$A_{1(2)} = \tfrac{1}{2} [1 \overset{+}{\underset{(-)}{}} (1 - R) W^{-1}] . \tag{15}$$

For $K = 0$ one has $\Omega_1 = 1$, $\Omega_2 = R$, $A_1 = 1$, $A_2 = 0$ for $R < 1$, and $\Omega_1 = R$, $\Omega_2 = 1$, $A_1 = 0$, $A_2 = 1$ for $R > 1$, respectively. In any case, C reduces to $C_0 = e^{-\tau}$ and $\ln C$ to $-\tau$. For $K \neq 0$ deviations from this simple behaviour occur. In Fig. 1 $\ln C$ is plotted as function of τ for $R = 1.5$ and $|K| = 0$, 0.25, 0.50, 0.75, 1.0 and for the highest possible value of $|K| = \sqrt{R}$. Qualitatively, this graph is very similar to the experimental curve shown in Reference [1].

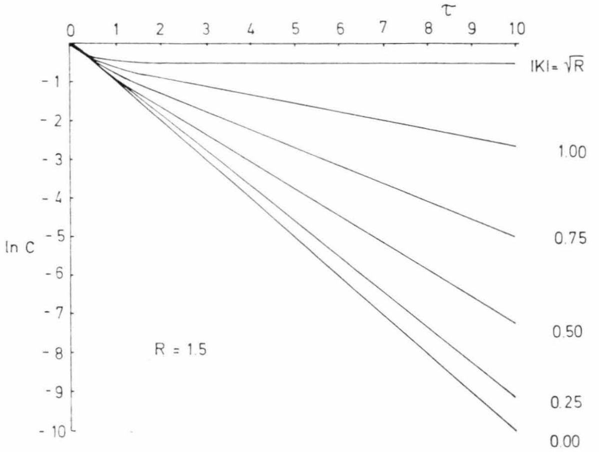

Fig. 1. $\ln C$ as a function of $\tau = t \, \omega_1$, plotted for $R = 1.5$ and six values of $|K|$ in the allowed range $0 \leqq |K| \leqq \sqrt{R}$. The case $K = 0$ corresponds to a Lorentzian spectral function.

For small times τ Eq. (14) yields

$$\ln C = -\tau + \tfrac{1}{2} K^2 \tau^2 + O(\tau^3) . \tag{16}$$

Hence the initial slope of $\ln C$ as a function of t determines the relaxation coefficient ω_1. The deviations from the correlation function $C_0 = e^{-\tau}$ corresponding to $K = 0$ are independent of R for small τ. To extract values for K and R a plott of

$$F = \tau^{-1} \ln C + 1 \tag{17}$$

versus τ seems to be useful since $F \equiv 0$ for $K = 0$. The initial slope of F for $\tau \to 0$ is determined by $\frac{1}{2} K^2$. In Fig. 2 F is shown as function of τ for the same values of R and $|K|$ used in Figure 1.

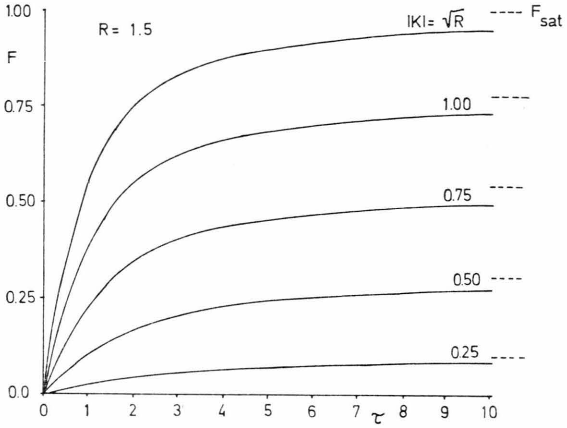

Fig. 2. $F(\tau) \equiv \tau^{-1} \ln C(\tau) + 1$ as a function of $\tau = t\,\omega_1$, plotted for $R = 1.5$ and the same values of $|K|$ used in Figure 1. For K=0 one has $F \equiv 0$.

If K is nonzero the function F approaches the "saturation value"

$$F_{\text{Sat}} = \tfrac{1}{2} [1 - R + \sqrt{(1-R)^2 + 4 K^2}] \tag{18}$$

for $\tau \to \infty$. Notice that $0 \leqq F_{\text{Sat}} \leqq 1$ for $R \geqq 1$, and $1 - R \leqq F_{\text{Sat}} \leqq 1$ for $R < 1$, respectively. The lower and upper bounds are imposed by the allowed range of $|K|$, viz. $0 \leqq |K| \leqq \sqrt{R}$. For $R < 1$ the approach to saturation takes place for

$$\tau \gg \tau_0 = W^{-1} \ln \frac{W + 1 - R}{W - (1-R)} .$$

At time τ_0 both terms in the sum (14) are of equal magnitude, for $\tau > \tau_0$ the term with the smaller relaxation frequency (Ω_2) dominates. Notice that the time constant τ_0 becomes very large for small $|K|$, viz. $\tau_0 \approx (1-R)^{-1} \ln[(1-R)/K]^2$ for $|K| \ll (1-R)/2$.

In conclusion it is stated that the experimentally observed[1] deviations of the correlation function C from $C_0 = e^{-\omega_1 t}$ can be described by a two-moments-approximation. The three parameters ω_1, $K = \omega_{12}\,\omega_1{}^{-1}$ and $R = \omega_2\,\omega_1{}^{-1}$ can in principle be obtained by

a) a plott of $\ln C$ versus t from the initial slope (ω_1),

b) a plott of $F(\tau) = \tau^{-1} \ln C(\tau) + 1$ versus $\tau = t\,\omega_1$ from the initial slope (K^2) and from the "saturation value" (R).

If the measured correlation function is fitted by a sum of two exponential functions[9] the parameters ω_1, K, R can directly be determined by comparison with Eqs. (13), (14), (15).

3. Discussion

An alternative approach for the calculation of the correlation function has been presented by McCourt, Rudensky and Moraal[11]. They made the appealing but unrealistic assumption that energetically inelastic collisions which cause transitions between the rotational levels can be disregarded (uncoupled model). Furthermore, any other type of collisional coupling was ignored. Their correlation function is given by

$$C(t) = \sum_j \gamma_j\, e^{-\Omega_j t} . \tag{19}$$

Here j is the rotational quantum number [the eigenvalues of J^2 are $j(j+1)$], γ_j is the fraction of molecules in the state "j" $(\sum_j \gamma_j = 1)$, and Ω_j is the relaxation frequency for the tensor polarization of the molecules in the rotational state "j".

The theory presented in this paper is not restricted to energetically inelastic collisions. Yet it seems to be of interest that the correlation function (19) is, for small times, formally equivalent to Equation (16). This can be seen if Ω_j is written as

$$\Omega_j = \Omega (1 + \delta_j) , \tag{20}$$

with Ω defined by

$$\Omega = \sum_j \gamma_j\, \Omega_j . \tag{21}$$

Then, of course, one has

$$\sum_j \gamma_j\, \delta_j = 0 . \tag{22}$$

Thus, with $\tau = \Omega\, t$, Eq. (19) is equivalent to

$$\ln C = -\tau + \ln (\sum_j \gamma_j\, e^{-\delta_j \tau}) . \tag{23}$$

An expansion around $\tau=0$ leads, due to (22), to an expression of the form (16) with

$$K^2=\sum_j \gamma_j\,\delta_j{}^2\,, \tag{24}$$

i. e. here K^2 is determined by the 2nd moment of the deviation of Ω_j from its average value $\Omega=\omega_1$.

In summary, it has been shown that the deviation of the experimentally observed correlation function of the tensor polarization from a simple exponential function can be understood within the frame work of the kinetic theory based on the Waldmann-Snider equation. The deviations are closely related to the collisional coupling between various moments of the distribution function of the gas. There are indications that a simple two-moments-approximation suffices to describe the experimental data. A quantitive test of the correlation function (14) and an experimental determination of the parameters $|K|$ and R are still wanting.

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