Broadening of the Fine-Structure Raman Lines in Gaseous Oxygen

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Due to the coupling between the rotational angular momentum and the electronic spin, the depolarized Rayleigh light scattered from gaseous oxygen shows Stokes and anti-Stokes satellites shifted by about 60 GHz. The broadening of these fine-structure Raman lines is investigated theoretically for high and medium pressures where the linewidth is determined by two contributions, one proportional and the other inversely proportional to the pressure, p. The linewidth in the pressure broadening region is given by a relaxation frequency which is obtained from the Waldmann-Snider collision term. The p^{-1}contribution to the linewidth is determined by the ratio of the second moment of the fine-structure freqencies (with respect to the center of the shifted line) and another relaxation frequency. Both relaxation frequencies are sensitive to the nonspherical part of the intermolecular potential.

§ 1. Introduction

The "fine-structure" splitting of the rotational energy levels of the $^3\Sigma$ molecule O_2 is well-known from microwave absorption experiments[1]. Due to the interaction between the electronic spin $\boldsymbol{S}$ (magnitude $S=1$) and the rotational angular momentum $\boldsymbol{N}$ the rotational levels are split into 3 sublevels corresponding to the three magnitudes $(N-1,\ N,\ N+1)$ of the internal angular momentum $\boldsymbol{J}=\boldsymbol{N}+\boldsymbol{S}$. For a given $N>1$ the energy levels characterized by $J=N+1$ and $J=N-1$ lie relatively close together compared with their roughly 60 GHz ($2\ \text{cm}^{-1}$) separation from the other level. In light scattering experiments the ± 60 GHz fine-structure transitions were first seen as satellites of the rotational Raman lines[2] $(\Delta N=\pm 2)$. The pure "fine-structure Raman lines" associated with the 60 GHz transitions between the rotational sublevels ($J=N\pm 1 \rightleftarrows J=N$ with $\Delta N=0$ for $N>1$ and $J=2 \rightleftarrows J=1$ and $J=2 \rightleftarrows J=0$ for $N=1$) have recently been observed as satellites – in addition to the usual unshifted peak – in the depolarized Rayleigh spectrum of the light scattered from gaseous oxygen. The width of the fine-structure Raman lines has been investigated as a function of the pressure and these results are described in a future paper[3]. It is the purpose of this paper to present a theoretical study of the broadening of the fine-structure Raman lines for "intermediate and high" pressures where there are two contributions to the width, viz., the pressure broadening which dominates at "high" pressures and a contribution inversely proportional to the pressure p which shows up at intermediate pressures. For the central depolarized Rayleigh line[4] the "p^{-1} contribution" to the linewidth is caused by "diffusional broadening"[5–7]. For the "spin-peaks", however, the "p^{-1}-contribution" to the linewidth is much larger. In this case it is caused by the spread of the energy levels, first because the frequencies $\nu_+(N)$ and $\nu_-(N)$ for the $J=N+1 \rightleftarrows J=N$ and $J=N-1 \rightleftarrows J=N$ transitions are different and moreover because these frequecies depend on N.

The "spin-peaks" of the depolarized Rayleigh line of gaseous oxygen are also interesting from a different point of view. The spectrum of the depolarized Rayleigh light scattered from gases of linear molecules is determined by the spectral func-

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[7] S. HESS, Z. Naturforsch. **24 a**, 1852 [1969].

tion of the tensor polarization of the molecular rotational angular momenta [8–10]. Recently, it has been pointed out that for gases of molecules with a (rotational) magnetic moment the depolarized Rayleigh line should split into 5 lines (at most) upon application of a magnetic field [11, 12]. The reason for this splitting is the precessional motion of the tensor polarization due to the precession of the rotational angular momentum of a molecule about the magnetic field. Such a splitting can be caused not only by externally applied fields but also by the "internal" molecular fields that are present in paramagnetic molecules due to the coupling between the rotational angular momentum and the electronic spin. Hence the fine-structure Raman lines of O_2 are associated with the internal motion of the rotational angular momentum.

This paper proceeds as follows. First, the connection between the spectrum of the depolarized Rayleigh line and the spectral function for the tensor-polarization of the rotational angular momenta is stated, and some of the pecularities of gaseous oxygen associated with the coupling between the rotational angular momentum and the electronic spin are discussed. By application of the moment method two relaxation equations, governing the behavior of the tensor polarization, are derived from the Waldmann-Snider equation. The spectrum is then calculated from these relaxation equations. The resulting linewidths are expressed in terms of relaxation frequencies which are determined by collision integrals obtained from the linearized collision term.

§ 2. Spectral Functions of the Depolarized Rayleigh and the Fine-structure Raman Lines

The depolarized component of the scattered light is associated with orientational fluctuations. For gases of linear molecules the spectrum of the depolarized line centered at the frequency of the incident (monochromatic) light – commonly referred to as the "depolarized Rayleigh line" – is determined by the time-dependence of the fluctuations of the "tensor polarization" of the rotational angular momenta. The (2nd rank) tensor polarization is defined by [8, 10, 12]

$$\mathbf{a} = \langle \boldsymbol{\Phi} \rangle \tag{1}$$

where in Cartesian component notation $\boldsymbol{\Phi}$ is given by

$$\Phi_{\mu\nu} = \sqrt{\frac{15}{2}} \left(\left\langle \frac{N^2}{N^2 - \frac{3}{4}} \right\rangle_0 \right)^{-1/2} \cdot (N^2 - \tfrac{3}{4})^{-1} \left[\tfrac{1}{2} (N_\mu N_\nu + N_\nu N_\mu) - \tfrac{1}{3} N^2 \delta_{\mu\nu} \right]. \tag{2}$$

The bracket $\langle \dots \rangle$ refers to an average over a non-equilibrium distribution, and $\langle \dots \rangle_0$ indicates an equilibrium average. The angular momentum is treated as a quantum mechanical operator both with respect to magnetic and rotational quantum numbers. In Eq. (2), for convenience, the normalization of $\boldsymbol{\Phi}$ has been chosen such that

$$\langle \Phi_{\mu\nu} \Phi_{\mu'\nu'} \rangle_0 = \Delta_{\mu\nu,\mu'\nu'}, \tag{3}$$

where the isotropic 4-th rank tensor Δ is given by

$$\Delta_{\mu\nu,\mu'\nu'} = \tfrac{1}{2} (\delta_{\mu\mu'} \delta_{\nu\nu'} + \delta_{\mu\nu'} \delta_{\nu\mu'}) - \tfrac{1}{3} \delta_{\mu\nu} \delta_{\mu'\nu'}. \tag{4}$$

The calculation of the spectrum of the scattered light can be reduced to the solution of an initial-value problem. In particular, for the depolarized Rayleigh line, one has to consider the correlation function $A(t)$ for the tensor polarization, which is defined by [8, 12]

$$\mathbf{a}(t) = A(t)\, \mathbf{a}(0), \; t > 0. \tag{5}$$

The corresponding spectral function $S(\omega)$ is given by

$$S(\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty e^{i\omega t} A(t)\, dt. \tag{6}$$

The spectral intensity at frequency ω_1 of the depolarized Rayleigh light is given by (6) if ω is put equal to $\omega_1 - \omega_0$, where ω_0 is the frequency of the incident light. In (5) and (6) the spatial dependence of $\mathbf{a}(t)$ and the dependence of $S(\omega)$ on the wave vector have been disregarded for simplicity. This simplification is allowed as long as the pressure of the gas is high enough so that the diffusional broadening and the Doppler broadening can be neglected.

The considerations presented so far apply to linear molecules in general. The particularities of O_2 are associated with the existence of an unpaired electronic spin $\boldsymbol{S}$ and the internal coupling between the rotational angular momentum $\boldsymbol{N}$ and $\boldsymbol{S}$. If projection operators $P_k(N)$ with the properties

$$P_k(N)\, J^2 = J^2\, P_k(N) = (N+k)(N+k+1)\, P_k(N), \tag{7}$$

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are introduced for $k=0, \pm 1$ and

$$P_k(N)\, P_{k'}(N') = \delta_{NN'}\, \delta_{kk'}\, P_k(N)\,, \tag{8}$$

the internal coupling Hamiltonian, as given by TINKHAM and STRANDBERG [1], can be written as

$$H^{\text{int}} = 2\,\pi\,\hbar \sum_N \left(\nu_+(N)\, P_+(N) + \nu_-(N)\, P_-(N)\right). \tag{9}$$

The frequencies $\nu_\pm(N)$ can be obtained from microwave data [1]. It is convenient to define another set of projection operators P_k

$$P_k = \sum_N P_k(N)\,, \tag{10}$$

which have the property

$$\sum_k P_k = 1\,. \tag{10 a}$$

The operator $\boldsymbol{\Phi}$ defined by (2) can now be split into a part which commutes with H^{int} and a noncommuting part according to

$$\boldsymbol{\Phi} = \sum_k P_k\, \boldsymbol{\Phi}\, P_k + \sum_{k \neq k'} \sum P_k\, \boldsymbol{\Phi}\, P_{k'}\,. \tag{11}$$

Since (for $N>1$) $\nu_-(N) \approx \nu_+(N)$ (≈ 60 GHz) it proves convenient to rewrite (11) as

$$\boldsymbol{\Phi} = \boldsymbol{\Phi}^{\text{cent}} + \boldsymbol{\Psi} + \boldsymbol{\Psi}^\dagger\,, \tag{12}$$

where

$$\boldsymbol{\Phi}^{\text{cent}} = \sum_k P_k\, \boldsymbol{\Phi}\, P_k + P_+\, \boldsymbol{\Phi}\, P_- + P_-\, \boldsymbol{\Phi}\, P_+ \tag{13}$$

and

$$\boldsymbol{\Psi} = (P_+ + P_-)\, \boldsymbol{\Phi}\, P_0\,. \tag{14}$$

Notice that $\boldsymbol{\Phi}^{\text{cent}}$ and $\boldsymbol{\Psi}$ are orthogonal in the sense that $\langle \boldsymbol{\Psi}^\dagger \boldsymbol{\Phi}^{\text{cent}} \rangle_0 = 0$. As a consequence of (12), the tensor polarization $\mathbf{a}$ defined by (1) now becomes

$$\mathbf{a} = \mathbf{a}^{\text{cent}} + \mathbf{b} + \mathbf{b}^*\,, \tag{15}$$

with

$$\mathbf{a}^{\text{cent}} = \langle \boldsymbol{\Phi}^{\text{cent}} \rangle \tag{16}$$

and

$$\mathbf{b} = \langle \boldsymbol{\Psi} \rangle, \qquad \mathbf{b}^* = \langle \boldsymbol{\Psi}^\dagger \rangle\,. \tag{17}$$

The separation of terms in (15) is such that the time-dependence of $\mathbf{a}^{\text{cent}}$ determines the spectrum of the unshifted depolarized Rayleigh line and the time-dependence of $\mathbf{b}$ and $\mathbf{b}^*$ determines the spectrum of the "spin-peaks" or fine-structure Raman lines (provided that these lines do not overlap with the unshifted line). The spectrum of a fine-structure Raman line is given by the spectral function $S(\omega)$ pertaining to the correlation function $B(t)$ defined by

$$\mathbf{b}(t) = B(t)\, \mathbf{b}(0), \quad t>0 \tag{18}$$

[cf. Eqs. (5) and (6)]. Thus the spectrum of the fine-structure Raman lines can be calculated if relation (18) is known. The usual assumption is made that the decay of the fluctuations responsible for the light scattering is the same as that of the corresponding macroscopic deviations from the equilibrium state of the gas (Onsager). Relation (18) can then be obtained from relaxation equations which can be derived from the appropriate kinetic equation for the one-particle distribution, viz., the Waldmann-Snider equation [13].

§ 3. Relaxation Equations

The non-equilibrium state of a gas can be characterized by the distribution operator $f = f(t, \boldsymbol{x}, \boldsymbol{p}, \boldsymbol{N}, \boldsymbol{S})$. The position $\boldsymbol{x}$ and the linear momentum $\boldsymbol{p}$ of a molecule can be treated as classical variables, the internal angular momenta $\boldsymbol{N}$ and $\boldsymbol{S}$, however, are treated as quantum-mechanical observables. This point is of particular importance for a theoretical investigation of the broadening of the fine-structure Raman lines since their intensities stem mainly from molecules in the lowest rotational states (i. e. $N=1$, 3, 5). The local instantaneous average $\langle \Phi \rangle$ of an operator $\Phi = \Phi(\boldsymbol{p}, \boldsymbol{N}, \boldsymbol{S})$ is given by

$$\langle \Phi \rangle = n^{-1}\, \text{Tr} \int \mathrm{d}^3p\, \Phi\, f\,, \tag{19}$$

where "Tr" denotes the trace over the magnetic quantum numbers associated with $\boldsymbol{N}$ and $\boldsymbol{S}$ and a summation over the magnitude of the rotational angular momentum. In (19),

$$n = \text{Tr} \int \mathrm{d}^3p\, f \tag{20}$$

is the number density of the gas.

The time-dependence of mean values such as $\mathbf{b}$ can be determined from the time-dependence of the distribution operator f which obeys a kinetic equation of the type [13]

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{x}} - \frac{1}{i\,\hbar}\,[H^{\text{int}}, f] - \left(\frac{\delta f}{\delta t}\right)_{\text{coll}} = 0\,. \tag{21}$$

The 2-nd, 3-rd and 4-th terms in Eq. (21) describe the change of the distribution f caused by the free flow of molecules ($\boldsymbol{v}$ is the particle velocity), by the internal motion characterized by the Hamiltonian H^{int}, and by the (binary) collisions between molecules. For polyatomic gases, the collisional change of the distribution operator is given by the (linearized) Waldmann-Snider collision term containing

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[13] L. WALDMANN, Z. Naturforsch. **12 a**, 660 [1957]; **13 a**, 606 [1958]; R. F. SNIDER, J. Chem. Phys. **32**, 1051 [1960]; see also S. HESS, Z. Naturforsch. **22 a**, 1871 [1967].

the binary scattering amplitude and its adjoint[14]. The detailed structure of this collision term, however, is not required here.

Differential equations governing the time-dependence of mean values can be derived from the kinetic Eq. (21) by application of the moment method[15]. The moment equation for $\mathbf{b} = \langle \boldsymbol{\Psi} \rangle$ is obtained by multiplication of Eq. (21) with $\boldsymbol{\Psi}$ and application of the operations "Tr $\int \mathrm{d}^3 p$". Neglecting the spatial dependence of f and using (8), one obtains

$$\frac{\partial \mathbf{b}}{\partial t} - i\,\Omega_1\,\mathbf{b} - i\,\Omega_1\,\mathbf{c} - \left(\frac{\delta \mathbf{b}}{\delta t}\right)_{\text{coll}} = 0\,, \tag{22}$$

where the 2-nd rank tensor $\mathbf{c}$ is defined by

$$\mathbf{c} = \langle \boldsymbol{\gamma} \rangle \tag{23}$$

with

$$\boldsymbol{\gamma} = \Omega_1^{-1} \sum_N \big(\Omega_+(N)\,P_+(N)\,\boldsymbol{\Phi}\,P_0(N) + \Omega_-(N)\,P_-(N)\,\boldsymbol{\Phi}\,P_0(N)\big)\,, \tag{24}$$

$$\Omega_\pm(N) = 2\,\pi\,\nu_\pm(N) - \Omega_1\,. \tag{25}$$

Notice that $\boldsymbol{\gamma}$ is orthogonal to $\boldsymbol{\Psi}$ in the sense that $\langle \boldsymbol{\Psi}^\dagger \boldsymbol{\gamma} \rangle_0 = 0$. In Eq. (25) Ω_1 is chosen as the center of one of the fine structure spectra and is given by

$$\Omega_1 = 2\,\pi \Big\langle \sum_N \big(\nu_+(N)\,P_+(N)\,\boldsymbol{\Phi} : P_0(N)\,\boldsymbol{\Phi} + \nu_-(N)\,P_-(N)\,\boldsymbol{\Phi} : P_0(N)\,\boldsymbol{\Phi}\big) \Big\rangle_0 \cdot (\langle \boldsymbol{\Psi}^\dagger : \boldsymbol{\Psi} \rangle_0)^{-1}\,. \tag{26}$$

Although the fine-structure splitting for molecules is different in different rotational states it can be characterized by the single frequency Ω_1 because of the rapid collision-induced transitions between the rotational states at high pressures. Typically, $|\Omega_\pm(N)|/2\,\pi$ is approximately 2 GHz whereas $\Omega_1/2\,\pi \approx 60$ GHz.

Obviously, Eq. (22) is not a closed equation for $\mathbf{b}$ since the time dependence of $\mathbf{c}$ is not known and the collisional change of $\mathbf{b}$ has not been specified. Multiplying Eq. (21) by $\boldsymbol{\gamma}$, integrating over $\mathrm{d}^3 p$ and taking the trace "Tr" leads to

$$\frac{\partial \mathbf{c}}{\partial t} - i\,\Omega_1\,\mathbf{c} - i\,\Omega_1^{-1} \Big\langle \sum_N \big(\Omega_+^2(N)\,P_+\,\boldsymbol{\Phi}\,P_0 + \Omega_-^2\,P_-\,\boldsymbol{\Phi}\,P_0\big) \Big\rangle - \left(\frac{\delta \mathbf{c}}{\delta t}\right) = 0\,. \tag{27}$$

The set of Eqs. (22) and (27) is again not closed. A closed set of "relaxation equations",

$$\frac{\partial \mathbf{b}}{\partial t} - i\,\Omega_1\,\mathbf{b} - i\,\Omega_1\,\mathbf{c} + \omega_b\,\mathbf{b} = 0\,, \tag{28}$$

$$\frac{\partial \mathbf{c}}{\partial t} - i\,\Omega_1\,\mathbf{c} - i\,\Omega_2{}^2\,\Omega_1{}^{-1}\,\mathbf{b} + \omega_c\,\mathbf{c} = 0\,, \tag{29}$$

is obtatined upon approximating the third term in Eq. (27) by $-i(\Omega_2{}^2/\Omega_1)\,\mathbf{b}$ with the frequency Ω_2 defined through[16]

$$\Omega_2{}^2 = \Big\langle \sum_N \big(\Omega_+^2(N)\,P_-(N)\,\boldsymbol{\Phi} : P_0(N)\,\boldsymbol{\Phi} + \Omega_-^2(N)\,P_-(N)\,\boldsymbol{\Phi} : P_0(N)\,\boldsymbol{\Phi}\big) \Big\rangle_0 \cdot (\langle \boldsymbol{\Psi}^\dagger : \boldsymbol{\Psi} \rangle_0)^{-1}\,. \tag{30}$$

This means that higher moments of the fine-structure spectrum of a free molecule are disregarded.

In Eqs. (28), (29) the "relaxation coefficients" ω_b, ω_c have been introduced. Ignoring the (small) collisional frequency shift (i. e., the imaginary parts of ω_b and ω_c), these relaxation coefficients are related to the linearized positive definite Waldmann-Snider collision operator ω by[12, 14]:

$$\begin{aligned} \omega_b &= \tfrac{1}{2}\big(\langle \boldsymbol{\Psi} : \omega(\boldsymbol{\Psi}^\dagger) \rangle_0 + \langle \boldsymbol{\Psi}^\dagger : \omega(\boldsymbol{\Psi}) \rangle_0\big) \cdot (\langle \boldsymbol{\Psi}^\dagger : \boldsymbol{\Psi} \rangle_0)^{-1} \\ \omega_c &= \tfrac{1}{2}\big(\langle \boldsymbol{\gamma} : \omega(\boldsymbol{\gamma}^\dagger) \rangle_0 + \langle \boldsymbol{\gamma}^\dagger : \omega(\boldsymbol{\gamma}) \rangle_0\big) \cdot (\langle \boldsymbol{\gamma}^\dagger : \boldsymbol{\gamma} \rangle_0)^{-1} \end{aligned} \tag{31}$$

Effective cross-sections σ_b and σ_c pertaining to the collisional change of $\mathbf{b}$ and $\mathbf{c}$ can be defined by

$$\omega_b = n\,v_{\text{therm}}\,\sigma_b\,, \qquad \omega_c = n\,v_{\text{therm}}\,\sigma_c \tag{32}$$

where

$$v_{\text{therm}} = (8\,k\,T/\pi\,m_{\text{red}})^{\frac{1}{2}} \tag{33}$$

is a thermal velocity and n is the number density. Thus, for constant temperatures, ω_b and ω_c are proportional to the pressure $p = n\,k\,T$. Both ω_b and ω_c are sensitive to the nonspherical part of the interaction potential.

§ 4. Broadening of the Fine-structure Raman Lines

From Eqs. (28), (29) the function $B(t)$ defined by (18) can be calculated and then the spectrum can be obtained according to (6) with $A(t)$ replaced by $B(t)$. The full Eqs. (28), (29) lead to a

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[14] 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].

[15] S. HESS and L. WALDMANN, Z. Naturforsch. **21 a**, 1529 [1966]. — H. RAUM and W. E. KÖHLER, Z. Naturforsch. **25 a**, 1178 [1970].

[16] Since $\langle P_+(N)\,\boldsymbol{\Phi} : P_0(N)\boldsymbol{\Phi}\,\cdot \rangle_0$ is proportional to the relative intensity of he fine-strucure line which stems from the molecules in the N-th rotational state, Ω_1 determines the "center of gravity" of the line and $\Omega_2{}^2$ is he 2nd moment with respect to Ω_1.

non-Lorentzian line shape. A "Lorentzian approximation" to the spectral function is obtained if it is assumed that

$$(\partial \mathbf{c}/\partial t) - i\,\Omega_1\,\mathbf{c} \approx 0\,, \tag{34}$$

so that Eq. (29) has a solution

$$\mathbf{c}\,(t) \approx i(\Omega_2{}^2/\omega_c\,\Omega_1)\;\mathbf{b}\,(t)\,. \tag{35}$$

Approximation (34) is physically analogous to the assumption of stationarity in the rotating frame which is commonly employed in the theory of magnetic relaxation[17]. Eq. (34) and consequently Eq. (35) are valid only, when the condition

$$\Omega_1 \gg \omega_b \tag{36}$$

is satisfied. Furthermore, the coupling between **b** and **c** which is caused by the frequency spread should not be too strong, i. e.,

$$\Omega_2 \lesssim \sqrt{\omega_b\,\omega_c}\,. \tag{37}$$

For gaseous oxygen, both conditions (36) and (37) confine the applicability of the spectral function to be calculated to the pressure range of roughly 2.5 to 20 atm.

If approximation (35) for $\mathbf{c}\,(t)$ is inserted into (29) the following first order differential equation is obtained for $\mathbf{b}\,(t)$:

$$\partial \mathbf{b}/\partial t - i\,\Omega_1\,\mathbf{b} + (\omega_b + \Omega_2{}^2/\omega_c)\;\mathbf{b} = 0\,. \tag{38}$$

Eq. (38) immediately yields the correlation function

$$B(t) = \exp\left\{\left(i\,\Omega_1 - \omega_b - \frac{\Omega_2{}^2}{\omega_c}\right)t\right\}. \tag{39}$$

Hence the relevant spectral function of the fine-structure Raman line is

$$S(\omega) = \frac{1}{\pi}\,\frac{(\varDelta\omega)_{1/2}}{(\omega+\Omega_1)^2 + (\varDelta\omega)_{1/2}} \tag{40}$$

where the Lorentzian half-width is given by

$$(\varDelta\omega)_{1/2} = \omega_b + \Omega_2{}^2/\omega_c\,. \tag{41}$$

Eq. (40) is the spectrum for the Stokes-line. The spectrum for the anti-Stokes line, associated with the time-dependence of $\mathbf{b}^*$, is given by Eq. (40) with Ω_1 replaced by $-\Omega_1$.

Finally, a few remarks on the pressure-dependence of the line width (41) are in order. For this purpose it is recalled that both relaxation coefficients ω_b and ω_c are proportional to the number density n [cf. Eq. (32)] and hence proportional to the pressure for constant temperature. Thus for high pressures the 2-nd term in (41) can be disregarded and the width of the fine-structure Raman-lines is caused by "collisional broadening" (pressure broadening) which is characterized by $\omega_b \propto n$. At intermediate pressures the second term in (41) which is proportional to n^{-1} shows up in the line-width. This second contribution determined by the ratio of the 2-nd moment of the frequency spread [cf. Eqs. (26), (30)] divided by a relaxation frequency is very similar in nature to the diffusional broadening[5–7] where the frequency spread is caused by the Doppler shift. Of course, the relaxation frequencies involved are different for both cases. As a broadening influence the Doppler width has been disregarded here, since its contribution to the line-width is much smaller than that of the second term in Eq. (41). The fine-structure Raman lines have been observed as satellites of the depolarized Rayleigh line. As will be shown in a future paper[3] the linewidth can be described by Eq. (41) over a considerable pressure range.

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