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Depolarization ratios of gas mixtures

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Collision-induced scattering is studied in a gas mixture of two kinds of optically isotropic particles. Rayleigh and vibrational Raman collisional depolarization ratios are obtained in the first-order dipole—induced-dipole (DID) approximation, in terms of two-, three-, and four-body correlation contributions. At the low-density limit, Rayleigh and vibrational Raman depolarization ratios due to the unlike-particle pairs are found to be equal and given as a function of the intermolecular pair potential. Experimental data are obtained for Rayleigh and Raman depolarization ratios of the gas mixture argon-tetrafluoromethane at 296 K. The experimental Rayleigh depolarization ratio induced by unlike-particle pair argon-tetrafluoromethane are deduced for the case of binary-collision conditions. It is in good agreement with the value calculated from the DID model using a Lennard-Jones intermolecular potential. However, a comparison between Rayleigh and Raman data shows that all collision-induced integrated intensities for the unlike-particle pair Ar-CF_4 may not be described only in terms of DID interactions.

I. INTRODUCTION

Collision-induced scattering (CIS) has been studied extensively in dense gases and fluids for several years. For an excellent review of this field up to 1974, see Ref. 1. This effect was first observed in rare gases in the spectral region of the Rayleigh band.[2,3] It has been shown that CIS appears also in the spectral region of the Raman vibrational bands of molecules.[4,5] It is quite well established now that the dipole—induced-dipole interactions (DID) generally give most of the integrated collision-induced intensities at least for rare gases at low and moderate densities. However, other interactions such as electron overlap (EO) and frame distortion (FD) for molecules may contribute also to integrated intensity and spectral shape especially at high frequencies. Up to now, studies on this subject were essentially concerned with the CIS of pure gases and fluids.

In this paper, we discuss the Rayleigh and Raman frequency integrated depolarization ratios induced by collision for a gas mixture containing two different kinds of particles (atoms or molecules). The two different particles are assumed to be optically isotropic. As in the pure gas case,[4,6] CIS appears both in the Rayleigh and the vibrational Raman bands and it is fruitful to compare the two scatterings. Furthermore, the study of CIS from unlike-particle pairs may be a new way to study intermolecular interactions. For the Raman scattering we only consider the ν_1 Raman band which corresponds to a totally symmetrical vibration. In fact, this Raman band is a favorable case to study Raman CIS since the permanent anisotropy for the corresponding Raman polarizability tensor is strictly equal to zero. Consequently, the observed Raman depolarized scattering is only due to molecular interactions. In Sec. II we give a comparative treatment of the Rayleigh and Raman depolarization ratios in the first-order DID approximation[2,6] neglecting higher multipole effects and other short-range interactions (EO and FD). In Secs. III and IV we discuss the experimental data obtained for the gas mixture argon-tetrafluoromethane at 296 K for the depolarization ratios of the Rayleigh band and the ν_1 Raman band of CF_4 ($\simeq$909 cm^{-1}). We use the comparison between Rayleigh and Raman data to test the DID model irrespective of the intermolecular potential.

II. THEORETICAL CONSIDERATIONS

We study the 90° scattering from a gas mixture illuminated by a laser beam as described in Fig. 1. The laser beam propagates along OY and is polarized along OZ. We observe the scattered intensities I_{zy} and I_{zz} propagating along OX and polarized along OY and OZ, respectively. The gas mixture contains two kinds of particles, A and B, with density ρ_A and ρ_B, respectively. All particles are optically isotropic. B is a molecule and A may be a molecule or an atom. The CIS is studied in the spectral range of the Rayleigh band and the Raman band corresponding to the totally symmetrical ν_1 vibration of the molecule B. We calculate the Rayleigh and Raman integrated depolarization ratios using the first-order DID model with the assumptions previously made for pure gases.[2]

According to this model the dipole moment $\vec{\mu}^{\,i}$ of a particle i of the gas illuminated by the laser is

$$\vec{\mu}^{\,i}=\alpha^i\vec{\mathrm{G}}^i+\delta\vec{\mu}^{\,i}\ , \tag{1}$$

where α^i is the polarizability of the particle i. $\vec{\mathrm{G}}^{\,i}$ is the average local field due to the particles lying outside a sphere D^i centered on the particle i and whose radius is much smaller than the laser wavelength. $\delta\vec{\mu}^{\,i}$ is a fluctuating dipole moment due to the particles j lying inside D^i (its average value is equal to zero[2]). For a particle i of kind A we have

$$\delta\vec{\mu}^{\,i}_A=\alpha^i_A\sum_{j\,(\neq i)}\alpha^j_A\hat{S}^{ij}\vec{\mathrm{G}}^j_A+\alpha^i_A\sum_k\alpha^k_B\hat{S}^{ik}\vec{\mathrm{G}}^k_B\ . \tag{2}$$

$\hat{S}^{ij}$ is the scattering tensor which, for small distances r^{ij} between particles i and j, is given by

$$S^{ij}_{\epsilon\mu}=\frac{1}{(r^{ij})^3}\left[\frac{3(r^i_\epsilon-r^j_\epsilon)(r^i_\mu-r^j_\mu)}{(r^{ij})^2}-\delta_{\epsilon\mu}\right]\ , \tag{3}$$

where $\epsilon,\mu=x,y,z$, and r_x,r_y,r_z are the position coordinates. δ is the Kronecker symbol. The particles contributing to $\vec{\mathrm{G}}^{\,i}$, since they are outside D^i, do not depend, for their position or their nature, on the nature of the particle i. So in Eq. (2)

$$\vec{\mathrm{G}}^j_A\simeq\vec{\mathrm{G}}^k_B=\vec{\mathrm{G}}^i\ .$$

On the other hand, we define an induced polarizability tensor

$$\delta\hat{\alpha}^i_A=\alpha^i_A\sum_{j\,(\neq i)}\alpha^j_A\hat{S}^{ij}+\alpha^i_A\sum_k\alpha^k_B\hat{S}^{ik} \tag{4}$$

so that from (2) and (4) it follows that

$$\delta\vec{\mu}^{\,i}_A=\delta\hat{\alpha}^i_A\vec{\mathrm{G}}^i\ . \tag{5}$$

The induced tensor $\delta\hat{\alpha}^i_A$ is generally anisotropic, opposite to $\hat{\alpha}^i_A$, and gives a depolarized scattering. Assuming for the laser an electric field E_z polarized along OZ,

$$E_z=E_0\cos(\omega t+\phi)\ ,$$

and neglecting the contribution of $\delta\hat{\alpha}^i_A$ to the integrated polarized intensities, the polarized E^i_{zz} and depolarized E^i_{zy} fields scattered along OX by the molecule i are, respectively,[2,6]

$$E^i_{zz}=F(\rho_A,\rho_B)(\alpha^i_A)_{zz}E_0\cos(\omega t+\phi^i)\ , \tag{6}$$

$$E^i_{zy}=F(\rho_A,\rho_B)(\delta\alpha^i_A)_{zy}E_0\cos(\omega t+\phi^i)\ . \tag{7}$$

$F(\rho_A,\rho_B)$ is a factor which includes the local field factor as well as other constant factors. From (4) and (7), and taking into account both particles A and B, the total depolarized field E_{zy} scattered along OX is

$$E_{zy}=F(\rho_A,\rho_B)E_0\left[\sum_{\substack{i,j\\i\neq j}}\alpha^i_A\alpha^j_AS^{ij}_{zy}\cos(\omega t+\phi^i)+\sum_{i,k}\alpha^i_A\alpha^k_BS^{ik}_{zy}\cos(\omega t+\phi^i)+\sum_{i,k}\alpha^i_A\alpha^k_BS^{ik}_{zy}\cos(\omega t+\phi^k)\right.$$
$$\left.+\sum_{\substack{k,l\\k\neq l}}\alpha^k_B\alpha^l_BS^{kl}_{zy}\cos(\omega t+\phi^k)\right]\ . \tag{8}$$

We use the letters i,j,p,q for particles A and k,l,r,s for particles B. The depolarized intensity I_{zy} is obtained from Eq. (8) by squaring and averaging over time and position variables. As in the case of pure fluids[2] we assume that the orientational correlations exist only for distances which are small relatively to the laser wavelength. It results[7] that the only configurations which contribute to CIS are those for which $\phi^t\simeq\phi^v$ (t and v being associated with particle A or B, respectively). So

$$\langle\cos(\phi^t-\phi^v)\rangle\simeq 1\ . \tag{9}$$

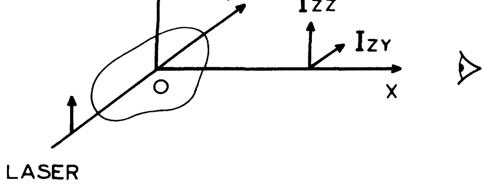

FIG. 1. Polarization of the electric field corresponding to the intensities I_{zz} and I_{zy}.

Then

$$I_{zy}=L(\rho_A,\rho_B)E_0^2(a+4b+4c+2d+4e+f)\ . \tag{10}$$

The average local field factor and other constant factors, because they are unimportant for the following discussion, are included in $L(\rho_A,\rho_B)$ and

$$a=\sum_{\substack{i,j\\i\neq j}}\sum_{\substack{p,q\\p\neq q}}\langle\alpha^i_A\alpha^j_A\alpha^p_A\alpha^q_A\rangle\langle S^{ij}_{zy}S^{pq}_{zy}\rangle\ ,$$

$$b=\sum_{\substack{i,j\\i\neq j}}\sum_{p,k}\langle\alpha^i_A\alpha^j_A\alpha^p_A\alpha^k_B\rangle\langle S^{ij}_{zy}S^{pk}_{zy}\rangle\ ,$$

$$c=\sum_{i,k}\sum_{j,l}\langle\alpha^i_A\alpha^k_B\alpha^j_A\alpha^l_B\rangle\langle S^{ik}_{zy}S^{jl}_{zy}\rangle\ ,$$

$$d=\sum_{\substack{i,j\\i\neq j}}\sum_{\substack{k,l\\k\neq l}}\langle\alpha^i_A\alpha^j_A\alpha^k_B\alpha^l_B\rangle\langle S^{ij}_{zy}S^{kl}_{zy}\rangle\ ,$$

$$e=\sum_{i,r}\sum_{\substack{k,l\\k\neq l}}\langle\alpha^i_A\alpha^r_B\alpha^k_B\alpha^l_B\rangle\langle S^{ir}_{zy}S^{kl}_{zy}\rangle\ ,$$

$$f=\sum_{\substack{k,l\\k\neq l}}\sum_{\substack{r,s\\r\neq s}}\langle\alpha^k_B\alpha^l_B\alpha^r_B\alpha^s_B\rangle\langle S^{kl}_{zy}S^{rs}_{zy}\rangle\ .$$

The intensity I_{zy} calculated in Eq. (10) includes Rayleigh and Raman scattering and we can now separately study these two different scatterings.

A. Raman scattering

As it was mentioned at the beginning of this section, we are interested, for the Raman scattering, in the ν_1 band of the isotropic molecule B. This Raman scattering is a consequence of the dependence of the polarizability α_B on the normal coordinate Q connected to the totally symmetrical mode ν_1

$$\alpha_B = \alpha_{0B} + \frac{\partial \alpha_B}{\partial Q} Q \;, \tag{11}$$

where

$$Q = Q_0 \cos(\omega' t + \psi) \;,$$

where ω' is the ν_1 Raman frequency, ψ the Raman phase and Q_0 the amplitude. The polarizability α_A is constant ($\alpha_A \simeq \alpha_{0A}$) since we do not consider any Raman spectrum for particle A. The incoherence of the Raman phase leads to

$$\langle Q^k Q^l \rangle = \langle (Q^k)^2 \rangle \delta_{kl} = \langle Q^2 \rangle \delta_{kl} \;.$$

It follows from (10) and (11) that

$$I_{zy}^{\mathrm{Ram}} = I_{zy}^{\mathrm{Ram}}(B,B) + I_{zy}^{\mathrm{Ram}}(A,B) \;, \tag{12}$$

where

$$I_{zy}^{\mathrm{Ram}}(B,B) = L(\rho_A,\rho_B) E_0^2 \alpha_{0B}^2 \left[\frac{\partial \alpha_B}{\partial Q} \right]^2 \langle Q^2 \rangle \sum_{\substack{k,l,s \\ k \neq l,\, k \neq s}} \langle S_{zy}^{kl} S_{zy}^{ks} \rangle \;, \tag{13}$$

$$I_{zy}^{\mathrm{Ram}}(A,B) = L(\rho_A,\rho_B) E_0^2 \left[\frac{\partial \alpha_B}{\partial Q} \right]^2 \langle Q^2 \rangle \left[8\alpha_{0A}\alpha_{0B} \sum_{\substack{k,l,i \\ k \neq l}} \langle S_{zy}^{kl} S_{zy}^{ki} \rangle + 4\alpha_{0A}^2 \sum_{k,i,j} \langle S_{zy}^{ki} S_{zy}^{kj} \rangle \right] . \tag{14}$$

$I_{zy}^{\mathrm{Ram}}(B,B)$ is identical to the contribution of molecules B when A-B interactions are not taken into account (except for the average local field effect). $I_{zy}^{\mathrm{Ram}}(A,B)$ specifies the new contribution to the depolarized Raman intensity involving A-B interactions only.

Following previous works[6,8] on pure gases, it is convenient to classify the various terms of the scattered intensity in doublets s^{II}, triplets s^{III}, and quadruplets s^{IV}. For a mixture of particles A and B we define[9]

$$\begin{aligned}
&s^{\mathrm{II}}(A,B) = \langle (S_{zy}^{ik})^2 \rangle \;, \\
&s^{\mathrm{III}}(A,A,B) = \langle S_{zy}^{ij} S_{zy}^{ik} \rangle \;, \quad i \neq j \\
&s^{\mathrm{III}}(A,B,A) = \langle S_{zy}^{ik} S_{zy}^{jk} \rangle \;, \quad i \neq j \\
&s^{\mathrm{IV}}(A,A,A,B) = \langle S_{zy}^{ij} S_{zy}^{pk} \rangle \;, \quad i \neq j \;, \quad i \neq p \;, \quad j \neq p \\
&s^{\mathrm{IV}}(A,A,B,B) = \langle S_{zy}^{ij} S_{zy}^{kl} \rangle \;, \quad i \neq j \;, \quad k \neq l \\
&s^{\mathrm{IV}}(A,B,A,B) = \langle S_{zy}^{ik} S_{zy}^{jl} \rangle \;, \quad i \neq j \;, \quad k \neq l \;.
\end{aligned} \tag{15}$$

Permuting A and B leads to similar definitions of $s^{\mathrm{III}}(B,B,A)$, $s^{\mathrm{III}}(B,A,B)$, and $s^{\mathrm{IV}}(B,B,B,A)$. Interactions between particles A only lead to consideration of $s^{\mathrm{II}}(A,A)$, $s^{\mathrm{III}}(A,A,A)$, and $s^{\mathrm{IV}}(A,A,A,A)$ with obvious notations. In the same way for particles B, $s^{\mathrm{II}}(B,B)$, $s^{\mathrm{III}}(B,B,B)$, and $s^{\mathrm{IV}}(B,B,B,B)$ are defined. Such terms have been calculated by molecular dynamics for several densities.[8] On the other hand, in order to eliminate the local field and other constant factors we calculate depolarized intensities relative to the polarized Raman intensity $I_{zz}^{\mathrm{Ram}}(B)$ (scattered by molecule B)

$$I_{zz}^{\mathrm{Ram}}(B) = L(\rho_A,\rho_B) E_0^2 \left[\frac{\partial \alpha_B}{\partial Q} \right]^2 \langle Q^2 \rangle N_B \tag{16}$$

so that we obtain from Eqs. (12)–(16) the Raman depolarization ratio η^{Ram}

$$\eta^{\mathrm{Ram}} = \frac{I_{zy}^{\mathrm{Ram}}}{I_{zz}^{\mathrm{Ram}}(B)} = \eta^{\mathrm{Ram}}(B,B) + \eta^{\mathrm{Ram}}(A,B) \;. \tag{17}$$

$\eta^{\mathrm{Ram}}(B,B)$ is the Raman depolarization ratio of a pure gas[6] containing N_B particles B without any particles A ($N_A = 0$):

$$\begin{aligned}
\eta^{\mathrm{Ram}}(B,B) &= \frac{I_{zy}^{\mathrm{Ram}}(B,B)}{I_{zz}^{\mathrm{Ram}}(B)} \\
&= \alpha_{0B}^2 [4N_B s^{\mathrm{II}}(B,B) + 4N_B^2 s^{\mathrm{III}}(B,B,B)] \;.
\end{aligned} \tag{18}$$

$\eta^{\mathrm{Ram}}(A,B)$ is the A-B interaction contribution to the depolarization ratio η^{Ram}:

$$\begin{aligned}
\eta^{\mathrm{Ram}}(A,B) &= \frac{I_{zy}^{\mathrm{Ram}}(A,B)}{I_{zz}^{\mathrm{Ram}}(B)} \\
&= N_A [4\alpha_{0A}^2 s^{\mathrm{II}}(A,B) + 8\alpha_{0A}\alpha_{0B} N_B s^{\mathrm{III}}(B,B,A)] \\
&\quad + 4N_A^2 \alpha_{0A}^2 s^{\mathrm{III}}(A,B,A) \;.
\end{aligned} \tag{19}$$

B. Rayleigh scattering

Rayleigh scattering is due to the constant parts α_{0A} and α_{0B} of the polarizabilities of particles A and B. It follows from Eqs. (10) and (11) that the depolarized Rayleigh scattering in the mixture may be separated into three contributions

$$I_{zy}^{\mathrm{Ray}} = I_{zy}^{\mathrm{Ray}}(A,A) + I_{zy}^{\mathrm{Ray}}(B,B) + I_{zy}^{\mathrm{Ray}}(A,B) \;, \tag{20}$$

where

$$I_{zy}^{\mathrm{Ray}}(A,A)=L(\rho_A,\rho_B)E_0^2\alpha_{0A}^4\sum_{\substack{i,j\\ i\neq j}}\sum_{\substack{p,q\\ p\neq q}}\langle S_{zy}^{ij}S_{zy}^{pq}\rangle\ , \tag{21}$$

$$I_{zy}^{\mathrm{Ray}}(B,B)=L(\rho_A,\rho_B)E_0^2\alpha_{0B}^2\sum_{\substack{k,l\\ k\neq l}}\sum_{\substack{r,s\\ r\neq s}}\langle S_{zy}^{kl}S_{zy}^{rs}\rangle\ , \tag{22}$$

$$\begin{aligned}I_{zy}^{\mathrm{Ray}}(A,B)=L(\rho_A,\rho_B)E_0^2\Bigg[&4\alpha_{0A}^3\alpha_{0B}\sum_{\substack{i,j\\ i\neq j}}\sum_{p,k}\langle S_{zy}^{ij}S_{zy}^{pk}\rangle+4\alpha_{0A}^2\alpha_{0B}^2\sum_{i,k}\sum_{j,l}\langle S_{zy}^{ik}S_{zy}^{jl}\rangle\\&+2\alpha_{0A}^2\alpha_{0B}^2\sum_{\substack{i,j\\ i\neq j}}\sum_{\substack{k,l\\ k\neq l}}\langle S_{zy}^{ij}S_{zy}^{kl}\rangle+4\alpha_{0A}\alpha_{0B}^3\sum_{i,r}\sum_{\substack{k,l\\ k\neq l}}\langle S_{zy}^{ir}S_{zy}^{kl}\rangle\Bigg]\ .\end{aligned} \tag{23}$$

The two first terms $I_{zy}^{\mathrm{Ray}}(A,A)$ and $I_{zy}^{\mathrm{Ray}}(B,B)$ come from quantities a and f, respectively, in Eq. (10). Except for the local field factor included in $L(\rho_A,\rho_B)$, $I_{zy}^{\mathrm{Ray}}(A,A)$ [or $I_{zy}^{\mathrm{Ray}}(B,B)$] is the CIS from a pure gas of particle A (or B) at density ρ_A (or ρ_B). The last term $I_{zy}^{\mathrm{Ray}}(A,B)$ gives the A-B interaction contribution to the depolarized intensity. On the other hand, we define the polarized intensity $I_{zz}^{*}(B)$ by

$$I_{zz}^{*}(B)=I_{zz}^{\mathrm{Ram}}(B)\frac{\alpha_{0B}^2}{\left[\dfrac{\partial\alpha_B}{\partial Q}\right]^2\langle Q^2\rangle}\ . \tag{24}$$

This intensity is equal to the polarized Rayleigh intensity at the low-density limit. Then, from (10), (15), and (24) we calculate the modified Rayleigh depolarization ratio[10] $\eta^{*\,\mathrm{Ray}}$:

$$\eta^{*\,\mathrm{Ray}}=\frac{I_{zy}^{\mathrm{Ray}}}{I_{zz}^{*}(B)}=\eta^{*\,\mathrm{Ray}}(A,A)+\eta^{*\,\mathrm{Ray}}(B,B)+\eta^{*\,\mathrm{Ray}}(A,B)\ . \tag{25}$$

In Eq. (25) the two first terms are deduced from pure gas results[6]

$$\begin{aligned}\eta^{*\,\mathrm{Ray}}(A,A)&=\frac{I_{zy}^{\mathrm{Ray}}(A,A)}{I_{zz}^{*}(B)}\\&=\frac{\alpha_{0A}^4}{\alpha_{0B}^2N_B}[\,2N_A^2s^{\mathrm{II}}(A,A)+4N_A^3s^{\mathrm{III}}(A,A,A)\\&\qquad+N_A^4s^{\mathrm{IV}}(A,A,A,A)]\ ,\end{aligned} \tag{26}$$

$$\begin{aligned}\eta^{*\,\mathrm{Ray}}(B,B)&=\frac{I_{zy}^{\mathrm{Ray}}(B,B)}{I_{zz}^{*}(B)}\\&=\alpha_{0B}^2[\,2N_Bs^{\mathrm{II}}(B,B)+4N_B^2s^{\mathrm{III}}(B,B,B)\\&\qquad+N^3s^{\mathrm{IV}}(B,B,B,B)]\ .\end{aligned} \tag{27}$$

The third term gives the new A-B interaction contribution to $\eta^{*\,\mathrm{Ray}}$:

$$\begin{aligned}\eta^{*\,\mathrm{Ray}}(A,B)&=\frac{I_{zy}^{\mathrm{Ray}}(A,B)}{I_{zz}^{*}(B)}\\&=N_A[4\alpha_{0A}^2s^{\mathrm{II}}(A,B)+4\alpha_{0A}^2N_Bs^{\mathrm{III}}(B,A,B)+8\alpha_{0A}\alpha_{0B}N_Bs^{\mathrm{III}}(B,B,A)+4\alpha_{0A}\alpha_{0B}N_B^2s^{\mathrm{IV}}(B,B,B,A)]\\&\quad+N_A^2\left[4\alpha_{0A}^2s^{\mathrm{III}}(A,B,A)+8\frac{\alpha_{0A}^3}{\alpha_{0B}}s^{\mathrm{III}}(B,A,A)+4\alpha_{0A}^2N_Bs^{\mathrm{IV}}(B,A,B,A)+2\alpha_{0A}^2N_Bs^{\mathrm{IV}}(B,B,A,A)\right]\\&\quad+4N_A^3\frac{\alpha_{0A}^3}{\alpha_{0B}}s^{\mathrm{IV}}(B,A,B,A)\ .\end{aligned} \tag{28}$$

C. Comparison between Raman and Rayleigh scatterings

The incoherence of Raman scattering, in contrast with the coherence of Rayleigh scattering, leads to a different density behavior for the Raman $\eta^{\mathrm{Ram}}(A,B)$ and the Rayleigh $\eta^{*\,\mathrm{Ray}}(A,B)$ depolarization ratios as shown by Eqs. (19)–(28). In particular, four-body correlations as well as $s^{\mathrm{III}}(B,A,A)$ and $s^{\mathrm{III}}(B,A,B)$ which contribute to Rayleigh intensities are absent in Raman scattering. Measurement of both Raman and Rayleigh depolarization ratios for various density conditions should give information on most of the two-, three-, and four-body correlations involved in Eqs. (17)–(28).

For low densities of particles A and B, CIS is reduced to the two-body correlation contributions and we obtain from Eqs. (17) and (25)

$$\eta^{\mathrm{Ram}}=4N_A\alpha_{0A}^2s^{\mathrm{II}}(A,B)+4N_B\alpha_{0B}^2s^{\mathrm{II}}(B,B)\ , \tag{29}$$

$$\eta^{*\,\mathrm{Ray}} = 4N_A\alpha_{0A}^2 s^{\mathrm{II}}(A,B) + 2\frac{N_A^2\alpha_{0A}^4}{N_B\alpha_{0B}^2}s^{\mathrm{II}}(A,A) + 2N_B\alpha_{0B}^2 s^{\mathrm{II}}(B,B)\ . \tag{30}$$

In these conditions the contributions to the Raman and Rayleigh depolarization ratios due to the unlike-particle pairs are the same and we deduce from Eqs. (17), (25), (29), and (30)

$$\eta^{\mathrm{Ram}}(A,B) = \eta^{*\,\mathrm{Ray}}(A,B) = 4N_A\alpha_{0A}^2 s^{\mathrm{II}}(A,B)\ . \tag{31}$$

This last result may be found partly from the double diffusion model used previously for pure gases.[4,11] Following this model the DID scattering from a pair of particles is due to the field which is scattered twice: first by one particle of the pair and then by the other particle. For a pair of unlike particles A and B there is one channel which leads to a double Rayleigh scattering corresponding to a first scattering by particle A followed by a second scattering by particle B. There is also one channel which leads to Raman scattering (at the ν_1 vibrational frequency for particle B, for example) by the similar double scattering process. It follows that, at low densities, $\eta^{\mathrm{Ram}}(A,B) = \eta^{*\,\mathrm{Ray}}(A,B)$. Under the same conditions, for pure gases (of particles B, for example), a different result has been obtained,[4,6] i.e., $\eta^{\mathrm{Ram}}(B,B) = 2\eta^{*\,\mathrm{Ray}}(B,B)$.

The two-body term $s^{\mathrm{II}}(A,B)$ depends on the intermolecular potential $V(r)$ between particles A and B (r is the intermolecular distance). From (31) and according to pure gas results,[2,11] an average over all the pairs A-B in the mixture at low densities (pair approximation) leads to

$$\eta^{\mathrm{Ram}}(A,B) = \eta^{*\,\mathrm{Ray}}(A,B) = \tfrac{48}{5}\pi\alpha_{0A}^2 n_{0A}\rho_A \int_0^\infty r^{-4}\exp\left[-\frac{V(r)}{k_BT}\right]dr\ , \tag{32}$$

where n_{0A} is the number of particles A per unit volume in standard conditions and ρ_A the density of particles A in amagat.

III. EXPERIMENTAL METHOD

The beam of an argon-ion laser (2 W at 5145 Å) was focused on a four window high-pressure cell containing the gas to be studied. The 90° scattering was analyzed with a conventional Raman double monochromator and detected with a photomultiplier associated with a photon counter. The gases purchased from Matheson Company had a purity of 99.995% for argon and 99.7% for tetrafluoromethane. The densities have been measured before mixing, for each gas, in separate high-pressure cylinders and then the two gases were mixed together.

We recorded the depolarized spectra $I_{zy}(\omega)$ and the polarized spectra $I_{zz}(\omega)$ (according to Fig. 1) with spectral slit width from 1 to 2 cm^{-1}. Then the integrated depolarization ratios were calculated from a frequency integration over the Rayleigh or the Raman band

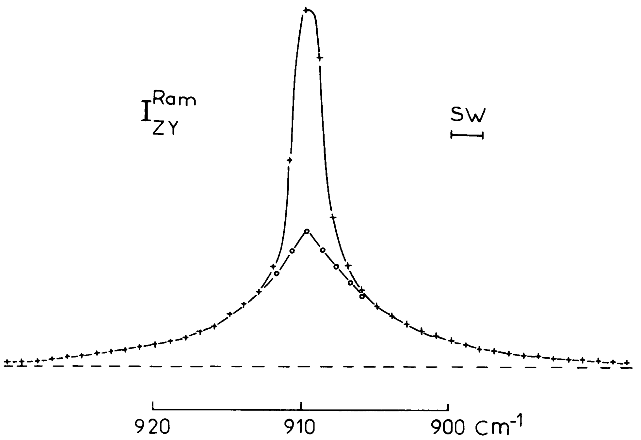

FIG. 2. Raman depolarized spectrum $I_{zy}^{\mathrm{Ram}}(\omega')$ vs the Raman frequency shift ω' for the ν_1 vibrational band of CF_4 in the gas mixture CF_4-Ar at 296 K. The CF_4 density is 55 amagat and the Ar density 30 amagat. Crosses (+) are experimental points. The circles (○) show the exponential extrapolation for the centre of the band. The spectral slit width (sw) is indicated.

$$\eta = \frac{\int I_{zy}(\omega)d\omega}{\int I_{zz}(\omega)d\omega}\ .$$

For Rayleigh depolarized spectra we observed, at low frequencies, a large stray light contribution due essentially to the laser reflections within the high-pressure cell. In order to correct the low-frequency data we have assumed in the range 0 to 6 cm^{-1} an extrapolated exponential intensity calculated from the experimental points between 6 and 12 cm^{-1}. For Raman depolarized spectrum at moderate densities ($\gtrsim 40$ amagat for CF_4 or Ar) we used a similar procedure: We assumed, for a Raman shift <3 cm^{-1} from the band center, an extrapolated exponential intensity calculated from data recorded between 3 and 9 cm^{-1} from this band center (see Fig. 2). At lower densities this method cannot be used for Raman bands because of the asymmetry of these bands. This asymmetry arises from the vibration-rotation coupling which becomes visible at these densities. So for low-density Raman spectra we put a Glan prism inside the cell in order to eliminate pressure-induced depolarization from the cell windows[12] and we deduced the integrated depolarized intensity from an integration over the whole recorded spectrum.

IV. RESULTS AND DISCUSSION

We have measured the Rayleigh depolarization ratio $\eta^{*\,\mathrm{Ray}}$ for the gas mixture Ar-CF_4 at 296 K for several densities of CF_4 from 11 to 55 amagat. For each studied density of CF_4 the density of Ar in the mixture was changed from 0 to about 50 amagat. We show in Fig. 3 the Rayleigh depolarization ratio $\eta^{*\,\mathrm{Ray}}$ for a constant density of CF_4 equal to 20.8 amagat and various densities of Ar. According to (25) $\eta^{*\,\mathrm{Ray}}$ may be represented by a polynomial of the fourth order in density ρ_A of argon:

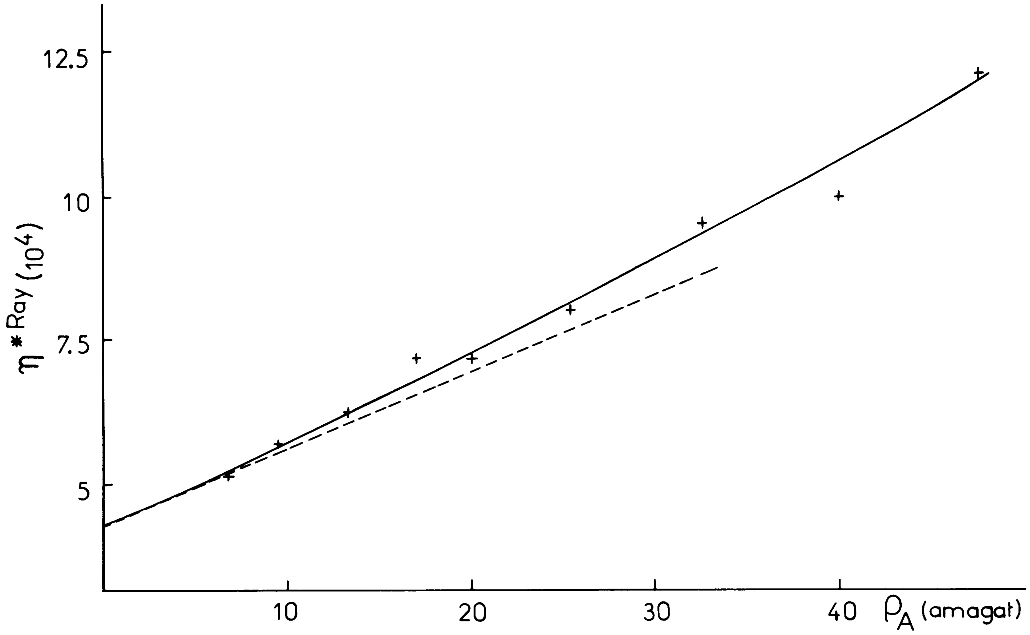

FIG. 3. Integrated Rayleigh depolarization ratio $\eta^{*\,\mathrm{Ray}}$ measured for the gas mixture CF_4-Ar (296 K) vs Ar density ρ_A. The CF_4 density is constant and equal to 20.8 amagat.

$$\eta^{*\,\mathrm{Ray}}=C_0+C_1\rho_A+C_2\rho_A^2+C_3\rho_A^3+C_4\rho_A^4\ . \tag{33}$$

Assuming this density behavior for our data, we have deduced for each density ρ_B of CF_4 the value of the coefficient C_1. Following (28), C_1 depends on the CF_4 density ρ_B and is given by

$$\begin{aligned}C_1=&\ 4\alpha_{0A}^2 n_{0A} V s^{\mathrm{II}}(A,B)+4\alpha_{0A}^2 n_{0A} n_{0B}\rho_B V^2 s^{\mathrm{III}}(B,A,B)\\&+8\alpha_{0A}\alpha_{0B} n_{0A} n_{0B}\rho_B V^2 s^{\mathrm{III}}(B,B,A)\\&+4\alpha_{0A}\alpha_{0B} n_{0A} n_{0B}^2\rho_B^2 V^3 s^{\mathrm{IV}}(B,B,B,A)\ .\end{aligned} \tag{34}$$

A and B stand for Ar and CF_4, respectively. V is the total scattering volume and n_{0B} is the number of molecules CF_4 per volume unit in standard conditions (n_{0A} is the similar number for Ar). The densities ρ_A and ρ_B are in amagat unit. In our experimental conditions the coefficient C_1, which is the slope of the function $\eta^{*\,\mathrm{Ray}}=f(\rho_A)$ when the Ar density ρ_A goes to zero, is equal to the unlike-particle pair Rayleigh depolarization ratio at 1 amagat of argon $[\eta^*(A,B)]_{\rho_A=1}$. We have plotted in Fig. 4 the experimental values of $[\eta^{*\,\mathrm{Ray}}(A,B)]_{\rho_A=1}$ versus the CF_4 density, ρ_B. According to (34) the extrapolated value of $[\eta^{*\,\mathrm{Ray}}(A,B)]_{\rho_A=1}$ for $\rho_B\to 0$ is due only to two-body correlations and is given by

$$[\eta^{*\,\mathrm{Ray}}(A,B)]^0_{\rho_A=1}=4\alpha_{0A}^2 n_{0A} V s^{\mathrm{II}}(A,B)\ . \tag{35}$$

From our data we have obtained

$$[\eta^{*\,\mathrm{Ray}}(A,B)]^0_{\rho_A=1}=(1.56\pm 0.10)\times 10^{-5}\ .$$

On the other hand, we have measured the Raman depolarization ratio η^{Ram} for the gas mixture Ar-CF_4 (296 K) for several densities of CF_4 from 25—55 amagat. As for Rayleigh scattering, in each experiment, the CF_4 density was kept constant and the Ar density changed from 0 to about 60 amagat. We have plotted in Fig. 5 the depolarization ratio η^{Ram} obtained for the ν_1 Raman band of CF_4 ($\simeq$910 cm^{-1}) vs Ar density for several mixtures with the same CF_4 density ($\rho_B=35$ amagat). Following (17), η^{Ram} may be represented by a polynomial of the second order in Ar density ρ_A:

$$\eta^{\mathrm{Ram}}=D_0+D_1\rho_A+D_2\rho_A^2\ . \tag{36}$$

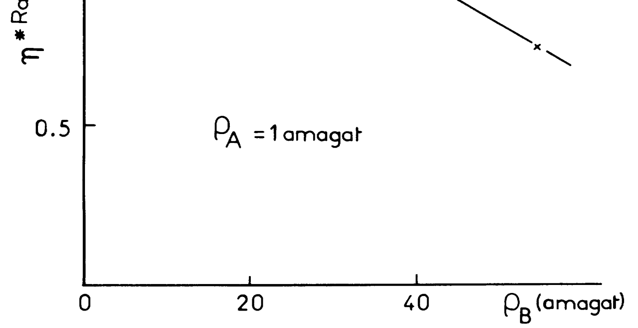

FIG. 4. Rayleigh unlike-particle pair depolarization ratio $\eta^{*\,\mathrm{Ray}}(A,B)$ for 1 amagat of Ar ($\rho_A=1$) and vs the CF_4 density ρ_B.

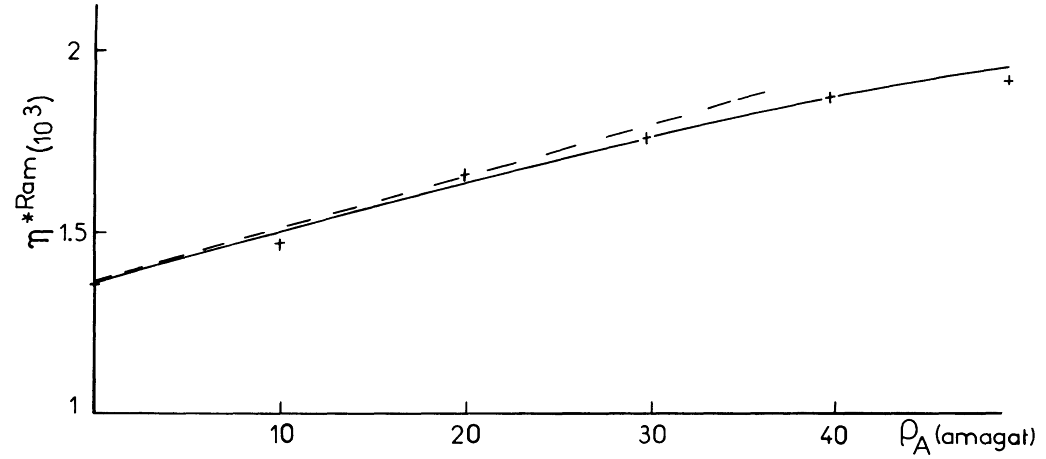

FIG. 5. Integrated Raman depolarization ratio η^{Ram} measured for the gas mixture CF$_4$-Ar (296 K) vs Ar density ρ_A. The CF$_4$ density is constant and equal to 35 amagat.

Assuming this behavior for our data, we have deduced the coefficient D_1 for each studied CF$_4$ density. Following Eqs. (19) and (36)

$$D_1 = 4\alpha_{0A}^2 n_{0A} V s^{\mathrm{II}}(A,B) + 8\alpha_{0A}\alpha_{0B} n_{0A} n_{0B} \rho_B V^2 s^{\mathrm{III}}(B,B,A) . \qquad (37)$$

In our experimental conditions D_1 is equal to the Raman depolarization ratio induced by unlike-particle pairs at 1 amagat of argon $[\eta^{\mathrm{Ram}}(A,B)]_{\rho_A=1}$. We have plotted $[\eta^{\mathrm{Ram}}(A,B)]_{\rho_A=1}$ versus the CF$_4$ density ρ_B and deduced the extrapolated value of $[\eta^{\mathrm{Ram}}(A,B)]_{\rho_A=1}$ for $\rho_B=0$

$$[\eta^{\mathrm{Ram}}(A,B)]_{\rho_A=1} = (2\pm0.3)\times10^{-5} .$$

Following (37), $[\eta^{\mathrm{Ram}}(A,B)]^0_{\rho_A=1}$ is induced by the two-body correlations only and may be compared, as well as $[\eta^{*\mathrm{Ray}}(A,B)]^0_{\rho_A=1}$ given previously, to the DID value obtained from Eq. (32). Using for the intermolecular potential of the unlike-particle pair Ar-CF$_4$ an averaged Lennard-Jones potential[13] ($\epsilon = 135.2$ K, $\sigma = 4.06$ Å) we have calculated from (32) the unlike-particle pairs depolarization ratio (Raman and Rayleigh) at 1 amagat of argon

$$[\eta^{\mathrm{Ram}}(A,B)]^{\mathrm{DID}}_{\rho_A=1} = [\eta^{*\mathrm{Ray}}(A,B)]^{\mathrm{DID}}_{\rho_A=1} = 1.57\times10^{-5} .$$

Taking into account the uncertainties for the intermolecular potential, this DID value is in quite good agreement with the experimental depolarization ratios obtained both for Rayleigh and Raman scatterings.

In order to avoid the influence of the intermolecular potential when experimental data are compared to DID results, we now look at the ratio η^{Ram} over $\eta^{*\mathrm{Ray}}$ for unlike-particle pairs Ar-CF$_4$

$$R(A,B) = \frac{\eta^{\mathrm{Ram}}(A,B)}{\eta^{*\mathrm{Ray}}(A,B)} .$$

At low densities (for Ar and CF$_4$) the experimental value of $R(A,B)$ deduced from our data is $R^{\exp}(A,B) = 1.3$ while the DID value, already discussed (see Sec. II), is $R^{\mathrm{DID}}(A,B) = 1$. Since a modification of the intermolecular potential does not change the value of $R^{\mathrm{DID}}(A,B)$ the discrepancies observed between experimental and DID values of $R(A,B)$ show that the point dipole DID model in the first-order approximation does not describe all the collision induced scattering observed from the unlike-particle pair Ar-CF$_4$. This result suggests that, if the DID interactions give most of the experimental integrated intensities, the neglected effects such as higher multipole interactions or other short-range interactions (EO and FD) contribute significantly to the CIS of the pair Ar-CF$_4$.

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and $\langle S^{tu}S^{vw}\rangle = \langle S^{tu}\rangle\langle S^{vw}\rangle = 0$. Then we may use $\langle \cos(\phi^{t}-\phi^{v})\rangle = 1$.

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[9] The three-body terms $s^{\mathrm{III}}(\alpha,\beta,\gamma)$ concerns three particles α,β,γ for which the contributions from the pairs α-β and β-γ are taken into account. Similarly, the four-body term $s^{\mathrm{IV}}(\alpha,\beta,\gamma,\delta)$ concerns the contributions of the pairs α-β and γ-δ.

[10] This ratio $\eta^{*\,\mathrm{Ray}}$ differs generally from the usual Rayleigh depolarization ratio $\eta^{\mathrm{Ray}}(\eta^{\mathrm{Ray}} = I_{zy}^{\mathrm{Ray}}/I_{zz}^{\mathrm{Ray}})$. However, the two ratios $\eta^{*\,\mathrm{Ray}}$ and η^{Ray} are equal when ρ_A and ρ_B go to zero.

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