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Collision-induced scattering at a vibrational Raman frequency

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Experimental data on collision-induced scattering in the frequency range of the vibrational Raman band ν_1 of CF_4 up to 280 amagat at 296°K are discussed within the framework of dipole-induced dipole (DID) approximation using computer calculations and previous Rayleigh results for the same molecule. Satisfactory agreement between theoretical and experimental results is obtained for the low-frequency line shape at low densities and for the density dependence of the integrated intensity. However, the point-dipole DID approximation in its present form is unable to describe exactly either the whole detailed line shape or the absolute value of the integrated depolarization factor. The different influences of the three- and four-body interactions are discussed for Rayleigh and Raman scattering.

I. INTRODUCTION

Several experiments,[1] particularly during the last ten years, have shown that for a fluid of isotropic molecules illuminated by a polarized laser beam, the 90° scattered light includes a depolarized component at frequencies close to the laser frequency (Rayleigh scattering). From a theoretical point of view, this depolarized scattering is related to the anisotropic polarizability induced by molecular interactions in the fluid.[1(b),2] In this work we have studied a similar scattering which appears in the spectral range of the vibrational Raman bands. For instance, for the totally symmetric vibration ν_1 of an optically isotropic molecule, the Raman polarizability tensor for this vibration is completely isotropic and the corresponding depolarization factor is strictly zero when this molecule is isolated. However, when the molecule is perturbed by neighboring molecules in a compressed gas, the Raman tensor becomes slightly anisotropic. In the low-density limit, where only the two body interactions are important, the depolarized Raman-scattered intensity at the ν_1 vibration frequency by a pair of interacting molecules A and B is caused by, in the first order of the dipole-induced dipole approximation (DID), a Raman anisotropic polarizability for this pair[3]

$$\beta' = 6\alpha^B \frac{\partial \alpha^A}{\partial Q_1^A} Q_1^A r^{-3} + 6\alpha^A \frac{\partial \alpha^B}{\partial Q_1^B} Q_1^B r^{-3}. \tag{1}$$

Here α is the polarizability of the unperturbed molecule, Q_1 is the normal coordinate for the vibration ν_1, and r the distance between the two molecules A and B. The two terms in relation (1) describe the two independent channels of Raman-A-Rayleigh-B or Rayleigh-A-Raman-B scattering which lead to a collisional-induced intensity at the frequency of the ν_1 Raman vibration. The Raman depolarization factor calculated from (1) is

$$\eta_s^{\text{Ram}} = \frac{48\pi}{5} \alpha_0^2 n \int_0^\infty r^{-4} g(r)\, dr , \tag{2}$$

where $g(r)$ is the radial pair distribution function and n the number density. This Raman factor is exactly twice the corresponding Rayleigh factor.[1(b)]

For low-density gases (< 30 amagat) this Raman scattering has been shown experimentally for optically isotropic molecules.[3] In this paper we study the scattering induced in the frequency region of the ν_1 Raman vibration ($\simeq$909 cm^{-1}) of the molecule CF_4 for densities up to 280 amagat at room temperature. In particular we pay special attention to the multiple-collision effects. Because of the incoherence of the Raman scattering in contrast to the coherence of the Rayleigh scattering, the effects of the high-order collisions are expected to be relatively less important for Raman than for Rayleigh scattering. The main experimental difficulty in this work is the very low intensity of the Raman collision-induced scattering (CIS) which is smaller than the Rayleigh CIS by a factor of 10^3 to 10^4.

II. EXPERIMENTAL METHOD

The apparatus used here is typical of laser Raman studies. The beam of an Ar^+ laser (1 W at 5145 Å) is focused on a four-window high-pressure cell containing the gas to be studied. The 90° scattered light is analyzed with a double monochromator Coderg PH 1 and detected by a photomultiplier associated with a photon counter. The gas CF_4, purchased from the Matheson company, has a purity greater than 99.7%.

In order to measure the integrated depolarization factor η_s, we record the spectra I_v and I_h cor-

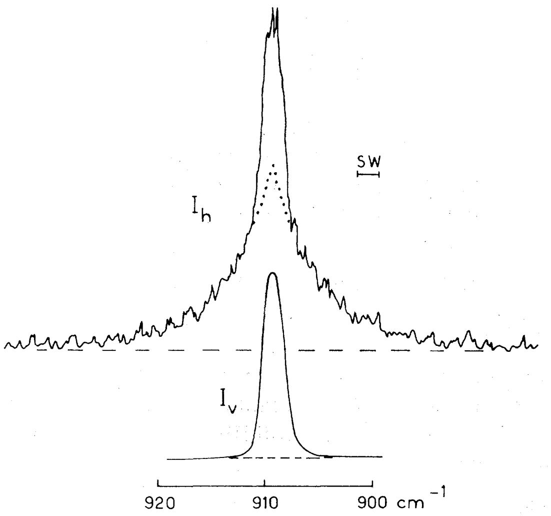

FIG. 1. I_h and I_v components of the ν_1 band of gas CF_4 at 89 amagat and 296 °K. The dotted line shows the exponential extrapolation for the center of the band. The dashed lines correspond to zero intensity. The spectral slit width (SW) is indicated.

responding to an incident beam polarized perpendicular and parallel to the direction of the scattered beam. Then η_s is calculated from

$$\eta_s \approx \frac{1}{2}\int I_h(\nu)\,d\nu \Big/ \int I_v(\nu)\,d\nu \ ,$$

which is correct for the low values of η_s.[4]

In the spectra $I_h(\nu)$ the low-frequency region at the center of the depolarized band is generally perturbed by false intensity from various sources. From this point of view Raman scattering has an advantage over the Rayleigh scattering since it is not affected by reflections of the laser beam inside the high-pressure cell. In the present work the leakage of the I_v component into the I_h component induces an additional contribution to η_r which we can estimate to a few parts in 10^{-4}. To eliminate the false intensity at the center of the Raman band at high pressure (>100 amagat) we have extrapolated the $I_h(\nu)$ spectra from the high frequencies using an exponential approximation in the interval 0–3 cm^{-1} (Fig. 1). For low densities (< 100 amagat) this method cannot be used because of the asymmetry of the band arising from the vibration-rotation coupling (at high pressure the motional narrowing effect[5] suppresses this asymmetry). So, for these low densities, we put a Glan prism inside the high-pressure cell in order to eliminate the false intensity induced by the pressure-dependent depolarization window effects (see Ref. 6).

III. RESULTS AND DISCUSSION

A. Integrated intensity

We show in Fig. 2 the measured integrated-depolarization-factor values for the ν_1 band of gaseous CF_4 for densities up to 280 amagat at 296 °K.

1. Low densities

From our results we have deduced the experimental value of the Raman slope $\Delta\eta_s^{\mathrm{Ram}}$ of the graph $\eta_s = f(\rho)$ at the low-density limit:

$$(\Delta\eta_s^{\mathrm{Ram}})_{\mathrm{expt}} = (4 \pm 0.8) \times 10^{-5}\ \mathrm{amagat}^{-1} .$$

This value is in agreement with previous data

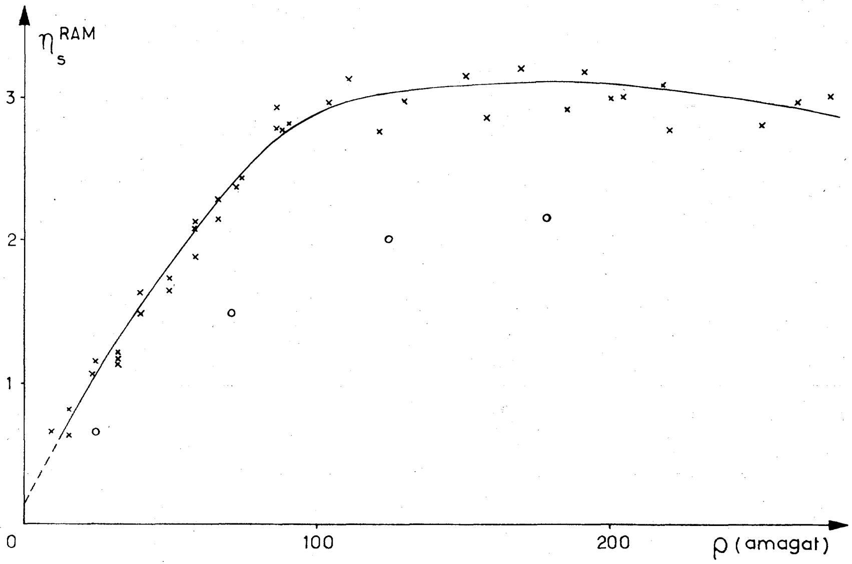

FIG. 2. Depolarization Raman factor η_s^{Ram} against density ρ for the ν_1 band of CF_4 at 296 °K. Crosses (×) are experimental points; circles (○) are relative to computer calculations using a Lennard-Jones potential (Ref. 16).

obtained for a more limited density range.[3] In the DID approximation we have calculated a theoretical value of $\Delta\eta_s^{\mathrm{Ram}}$ from relation (2). For the radial pair distribution function we used $g(r) = e^{-V(r)/KT}$ with the Lennard-Jones potential[7] for $V(r)$, and from the values of the integral $H_6\,[2(\epsilon/KT)^{1/2}]$ tabulated in Ref. 8 we deduced

$$(\Delta\eta_s^{\mathrm{Ram}})_{\mathrm{DID}} = 3.1\times 10^{-5}\ \mathrm{amagat}^{-1}\,.$$

The theoretical DID slope is lower than the experimental one as for previous CF_4 results (Table I) for the Rayleigh depolarization factor[9] and the second virial Kerr coefficient,[10] two effects related to the same polarizability anisotropy. Similar discrepancies have been observed for other molecules and various corrections were suggested: either including short-distance interactions[2,11] or improving the point-dipole DID model.[12,13] We show in Table I the ratio of the Raman $\Delta\eta_s$ relative to the Rayleigh $\Delta\eta_s$ using recent results for Rayleigh values of CF_4 and SF_6. We observe that this experimental ratio is 1.7 and 1.35 for CF_4 and SF_6, respectively. In agreement with theoretical results the Raman $\Delta\eta_s$ is higher than the Rayleigh value. However the experimental precision does not make significant the difference between this ratio and its theoretical DID of 2 according to relation (2).

2. *High densities*

As the density increases the pair approximation becomes inadequate. Using the fluctuating-local-field theory a more general description of Rayleigh and Raman CIS including multiple interactions has been proposed[14]: In a fluid a molecule i is perturbed by its neighbors j and one has to take into account an incremental polarizability

$$\delta\hat{\alpha}_i = \sum_{j(\neq i)} \alpha^i\alpha^j\,\hat{S}^{ij}\,, \tag{3}$$

where

$$S^{ij}_{XY} = \frac{1}{(r^{ij})^3}\left(3\,\frac{X^{ij}\,Y^{ij}}{(r^{ij})^2} - \delta_{XY}\right).$$

$X, Y = x, y, z$ are the position coordinates, δ is the Kronecker symbol, and r^{ij} is the distance between the molecules i and j. This $\delta\alpha_i$ induces Rayleigh and Raman scattering and one obtains the depolarization factors

$$\eta_s^{\mathrm{Ray}} = (\alpha_0^2/N)(V_M/RT\chi_T)S^{\mathrm{Ray}}\,, \tag{4}$$

$$\eta_s^{\mathrm{Ram}} = (\alpha_0^2/N)S^{\mathrm{Ram}}\,, \tag{5}$$

where N is the total number of molecules, R the ideal gas constant, T the absolute temperature, χ_T the isothermal compressibility, V_M the molar volume, and

$$\begin{aligned} S^{\mathrm{Ray}} &= \sum_{\substack{ijmn\\(i\neq j,\ m\neq n)}} \langle S^{ij}_{vh}\,S^{mn}_{vh}\rangle \\ &= \tfrac{3}{4}\,(N/\sigma^6)(2S_2^{zz} + 4\,S_3^{zz} + S_4^{zz})\,, \end{aligned} \tag{6}$$

$$\begin{aligned} S^{\mathrm{Ram}} &= \sum_{\substack{ijn\\(i\neq j,n)}} \langle S^{ij}_{vh}\,S^{in}_{vh}\rangle \\ &= \tfrac{3}{4}\,(N/\sigma^6)(4S_2^{zz} + 4S_3^{zz})\,. \end{aligned} \tag{7}$$

Here we use the notation of Ref. 15:

$$S_4^{zz} = \frac{4}{3}\,\frac{\sigma^6}{N}\sum_{i\neq j\neq m\neq n}\langle S^{ij}_{vh}\,S^{mn}_{vh}\rangle$$

and a similar expression for S_3^{zz} with $i=m$ and for S_2^{zz} with $i=m$ and $j=n$. σ is the Lennard-Jones diameter. For low densities the three- and four-particle contributions S_3^{zz} and S_4^{zz} may be neglected and one finds again[3] that $\eta_s^{\mathrm{Ram}}/\eta_s^{\mathrm{Ray}} = 2$.

In order to calculate η_s^{Ram} different methods may be used. With the lattice model,[14] where the possible positions of the molecules are restricted to the sites of a regular undeformable lattice, we have

$$\eta_s^{\mathrm{Ram}} = C(\rho/\rho_0)(1-\rho/\rho_0)\,. \tag{8}$$

C is a density-independent constant and ρ_0 is a

TABLE I. Ratio of experimental result divided by the DID theoretical value for the Raman and Rayleigh depolarization factor $\Delta\eta_s$ at 1 amagat and for the second virial Kerr coefficient (Ref. 10) B_K.

	$(B_K)_{\mathrm{expt}}/(B_K)_{\mathrm{DID}}$	$(\Delta\eta_s)_{\mathrm{expt}}/(\Delta\eta_s)_{\mathrm{DID}}$		$\Delta\eta_s^{\mathrm{Ram}}/\Delta\eta_s^{\mathrm{Ray}}$	
		Rayleigh [a]	Raman	Expt.	DID
CF_4	1.50 ± 0.14	1.52 ± 0.30	1.29 ± 0.26	1.7	2
SF_6 [b]	1.76 ± 0.23	1.99 ± 0.27	1.34 ± 0.20	1.35	2

[a] From Ref. 9.

[b] From Ref. 3.

density corresponding roughly to the maximum density (≈solid density). Since, due to the uncertainty in constants C and ρ_0, the evaluation of η_s^{Ram} from expression (8) is difficult, we calculated the Raman and Rayleigh depolarization factors using machine computations for S_2^{zz}, S_3^{zz}, and S_4^{zz}.[15,16] In particular we have calculated $S_2^{zz}+S_3^{zz}$ and therefore η_s^{Ram} from the results about the dielectric properties of fluids.[16] These calculated values are shown in Fig. 2 and demonstrate that, for the densities studied, the computer calculations give a correct order of magnitude for the intensity and reproduce the shape of the experimental graph $\eta_s^{\mathrm{Ram}} = f(\rho)$. However, the experimental intensities are systematically higher than the computer values. In order to go further into comparison between experimental and computer results we define an interference factor F not depending on molecular parameters and the equation of state

$$F^{\mathrm{Ram}}(\rho) = \eta_s^{\mathrm{Ram}}/\rho\eta_{s,0}^{\mathrm{Ram}} , \qquad (9)$$

$$F^{\mathrm{Ray}}(\rho) = (RT\chi_T/V_M)(\eta_s^{\mathrm{Ray}}/\rho\eta_{s,0}^{\mathrm{Ray}}) , \qquad (10)$$

where ρ is the density in amagats and $\eta_{s,0}$ the depolarization factor for 1 amagat.

For the DID approximation, we deduce from expressions (6) and (7)

$$F^{\mathrm{Ram}}(\rho) = (S_2^{zz}+S_3^{zz})/\rho S_{2,0}^{zz} , \qquad (11)$$

$$F^{\mathrm{Ray}}(\rho) = (2S_2^{zz}+4S_3^{zz}+S_4^{zz})/2\rho S_{2,0}^{zz} , \qquad (12)$$

where $S_{2,0}^{zz}$ is the S_2^{zz} value for 1 amagat. Without three- and four-particle effects and with a density-independent pair distribution function the factor F would reduce to 1 for all densities.

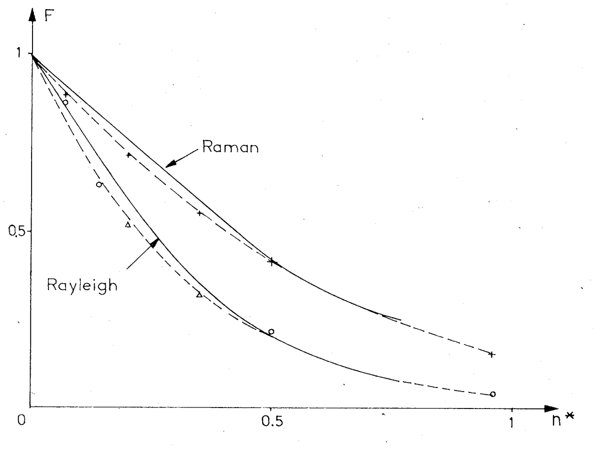

FIG. 3. Interference factor F against reduced density ($n^*=n\sigma^3$) for CF_4 at 296 °K. The solid lines are the experimental results (above: Raman, below: Rayleigh). The dashed lines are drawn from computer calculations using Lennard-Jones potential (Refs. 15 and 16): crosses (+) are for Raman; circles (○) and triangles (△) are for Rayleigh [triangles (△) are extrapolations from hard-sphere potential results].

In Fig. 3 the experimental Raman and Rayleigh[9] factors F are plotted against reduced density n^* ($n^*=n\sigma^3$). We observe that (i) F^{Ram} is higher than F^{Ray} for all densities studied, (ii) the ratio $F^{\mathrm{Ram}}/F^{\mathrm{Ray}}$ increases with density. Thus for 270 amagat ($n^*\approx 0.76$) $F^{\mathrm{Ram}}/F^{\mathrm{Ray}}=3$; so if we consider that the ratio $\eta^{\mathrm{Ram}}/\eta^{\mathrm{Ray}}=1.7$ for low densities, the Raman depolarization factor at 270 amagat is five times the Rayleigh one if we do not take into account the factor $RT\chi_T/V_M$.

These features experimentally demonstrate that the multiple-interaction contributions are relatively smaller for Raman than for Rayleigh scattering. On the other hand, we see in Fig. 3 that experimental graphs $F^{\mathrm{Ram}}(\rho)$ and $F^{\mathrm{Ray}}(\rho)$ are in good agreement for all densities with the computer calculations[16] using the Lennard-Jones potential. We conclude that the point-dipole DID model used for these machine calculations describes fairly well the change with density of the Raman and Rayleigh CIS intensities even for densities as high as $n^*=0.75$.

B. Line shape

We have studied the line shape of the depolarized ν_1 band of CF_4 for densities up to 270 amagat at 296 °K. Our analysis is limited to the Stokes side of the Raman band in order to avoid hot-band problems and perturbations coming from the rotation-vibration coupling which mainly influences the anti-Stokes side.

1. Low densities

At the low-density limit the high-order interactions are negligible and we observe a two-body spectrum. Experimentally, because of the small intensity of the Raman CIS, the recorded spectra for a few amagat have bad signal to noise ratio. In this work we calculated the two-body spectrum from spectra recorded for densities up to 200 amagat. For this we have deduced the $I_2(\nu)$ value at every frequency ν by expanding the intensity as a power series in the density limited to the third-order term[17]:

$$I(\nu) = I_1(\nu)\rho + I_2(\nu)\rho^2 + I_3(\nu)\rho^3 . \qquad (13)$$

The calculated $I_2(\nu)$ spectrum is shown in Fig. 4 from 6 to 32 cm^{-1}. In order to facilitate the discussion we characterize the line shape at any given frequency ν by the coefficient ν_0 of the exponential $e^{-\nu/\nu_0}$ which locally fits the data for this frequency. In fact we see in Fig. 4 that ν_0 changes with frequency. For the low-frequency region of $I_2(\nu)$, at $\nu = 10$ cm^{-1}, we get $\nu_0 = 6.1 \pm 0.6$ cm^{-1}.

We can calculate a theoretical width for Raman

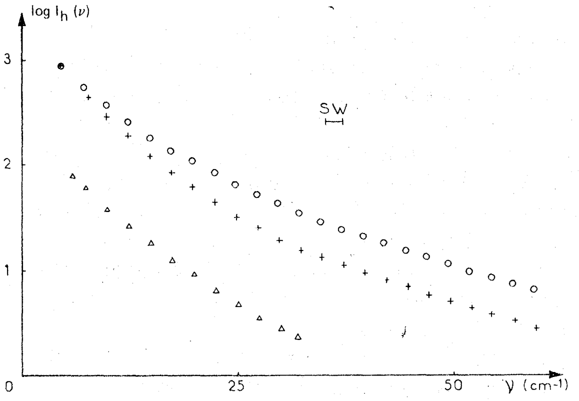

FIG. 4. Logarithm of the experimental intensity $\log I_h$ (arbitrary units) against frequency for the Stokes wing of the Raman depolarized component of the ν_1 band of gas CF_4 at 296 °K. Circles (O) are for 267 amagat; Crosses (+) are for 132 amagat and triangles (Δ) are for the two-body spectrum $I_2(\nu)$. The spectral slit width (SW) is indicated. For display purposes the curves are arbitrarily shifted along the vertical scale.

CIS in the DID approximation: assuming an exponential shape for the intensity[18] ($I(\nu)\alpha e^{-\nu/\nu_0}$) the ratio of the second spectral moment[11] Φ_2 to the zero-order moment Φ_0 is

$$\Phi_2/\Phi_0 = -2\nu_0^2 . \tag{14}$$

From this relation and using the expression[11] of the spectral moments in terms of the polarizability β' we calculated

$$\nu_0^{\mathrm{DID}} = 6\ \mathrm{cm}^{-1}$$

which is in good agreement with the experimental value. On the other hand, for the CF_4 Rayleigh CIS we have measured previously,[19] at 10 cm^{-1} from the laser frequency, $\nu_0 = 5.6 \pm 0.6$ cm^{-1}. So the Raman and Rayleigh experimental low-frequency slopes are similar. This is in agreement with the low-density DID theory since due to the term r^{-3} in Eq. (1) the Raman and Rayleigh polarizability anisotropies have the same time dependence.

Using Eq. (13) we have also deduced an experimental spectrum $I_3(\nu)$ which may be represented for $\nu \lesssim 20$ cm^{-1} by a single exponential $e^{-\nu/\nu_0}$ with a coefficient $\nu_0 \approx 5$ cm^{-1} in reasonable agreement with a recent theoretical DID calculation.[20] And the ratio, at 1 amagat, of the three-body total contribution I_3 by the two-body total contribution I_2 may be estimated to be $I_3/I_2 \approx 3 \times 10^{-3}$; the same ratio calculated from the graph of the integrated intensity against the density (Fig. 2) gives a similar result. For CF_4 Rayleigh CIS[19] this ratio is about $I_3/I_2 = 5.9 \times 10^{-3}$. Thus this is in agreement with the Eqs. (6) and (7) which give a theoretical value of I_3/I_2 which is twice as high for Rayleigh than the Raman value.

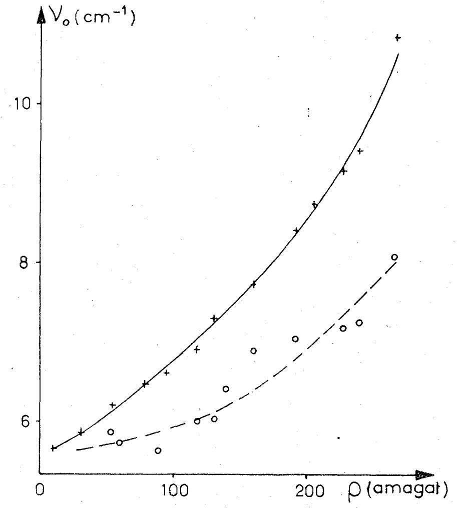

FIG. 5. Experimental values of the exponential coefficient ν_0 for the Stokes depolarized wing of CF_4 at 14 cm^{-1} from the center of the CIS band. Crosses (+) are the Rayleigh results (Ref. 19) and circles (O) the results for the Raman band ν_1.

2. *High densities*

For Rayleigh CIS of CF_4 we have previously observed[19] that the low-frequency slope increases when density increases up to 270 amagat. A similar but slower variation is shown for Raman CIS in Fig. 5 (ν_0 being measured at 14 cm^{-1} from the center of the band). For instance at 270 amagat

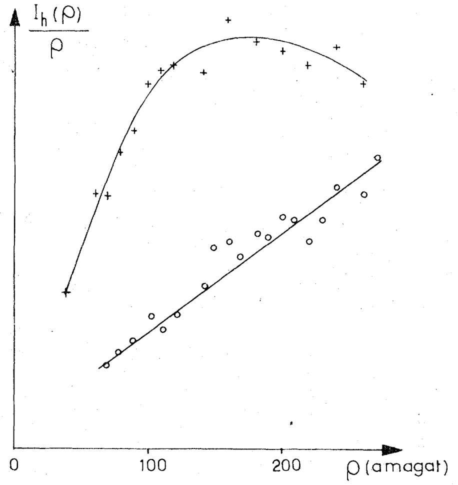

FIG. 6. Intensity (arbitrary units) $I_h(\rho)/\rho$ for the Stokes depolarized wing of the ν_1 band of CF_4 gas (296 °K) against density. Crosses (+) are for the intensities at $\nu = 7$ cm^{-1} and circles (O) at $\nu = 28$ cm^{-1} from the center of the band.

this coefficient ν_0 is about 11 cm^{-1} for Rayleigh and 8 cm^{-1} for Raman, the two slopes being the same at low densities. It is suggested that this difference is partially due to the multiple-interaction contributions which are relatively smaller for Raman than for Rayleigh scattering as is shown in Eqs. (6) and (7).

We may also observe in the Raman CIS the influence of the multiple interaction at different frequencies from the function $I(\nu)=f(\rho)$. We show in Fig. 6 that for low frequencies ($\nu = 7$ cm^{-1}) the intensity includes a negative contribution due to three-body interactions; this contribution vanishes progressively as the frequency increases and for $\nu = 28$ cm^{-1} Fig. 6 shows that the depolarized Raman intensity varies as ρ^2 indicating that the scattering is due to molecular pairs.

For CF_4 Rayleigh CIS[19] we have shown that the high-frequency scattering ($\nu \gtrsim 70$ cm^{-1}) may be described by a short-distance (non-DID) induced-binary-collision model (IBC) previously used for liquids.[21] For Raman CIS of CF_4 the intensity is too weak to know with sufficient precision the spectrum at frequencies as high as 70 cm^{-1}. We have measured for the coefficient ν_0 at $\nu = 45$ cm^{-1} and 267 amagat (Fig. 4): $\nu_0 = 17 \pm 3$ cm^{-1} to be compared with the corresponding Rayleigh result[19] of about 16 cm^{-1}. In order to correctly describe this high-frequency part of the spectrum it is probably necessary to use a more complete theory including an improved DID approximation as well as short-distance interactions (electron overlap, frame distortion).

IV. CONCLUSION

The study of Raman CIS data for CF_4 and the comparison with similar Rayleigh results show that for this molecule the point-dipole DID approximation may explain, up to densities close to the liquid-state density. (i) the change of the integrated intensity with the density and (ii) the low-frequency line shape for low densities.

However, the calculation of the absolute value of the integrated intensity in this approximation is unsatisfactory. A more correct theory must probably take into account the spatial distribution of the polarizability within each molecule and its dependence on the intermolecular distance. Such calculations for the CIS of argon[13] have improved the agreement between experiment and theory.

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[17] The relation (13) which is suggested by relation (7) is incorrect at sufficiently high densities. In particular it is modified by the change with density of the two- and three-body distribution function.

[18] This assumption is almost verified for the experimental spectrum $I_2(\nu)$ in Fig. 4 ($\nu \lesssim 30$ cm^{-1}).

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