Collision-induced depolarized scattering by CF 4 in a Raman vibrational band

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Collision-induced depolarized scattering by CF₄ in a Raman vibrational band

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Collision-induced scattering data have been recorded at room temperature for gaseous tetrafluoromethane in a frequency vicinity of the Raman vibrational line $\nu_1 = 908$ cm^{-1}. For the first time, corresponding binary depolarized intensities have been measured in absolute units for frequency shifts up to 110 cm^{-1} from the band center. Comparison with theoretical semiclassical intensities computed from dipole-induced dipole and dipole-multipole light scattering mechanisms leads to an evaluation of the first derivative of the dipole-quadrupole polarizability tensor A'. This result is in good agreement with recent *ab initio* quantum-chemistry calculations of the CF₄ multipolar polarizabilities. © *1998 American Institute of Physics.* [S0021-9606(98)51219-6]

I. INTRODUCTION

For the totally symmetric vibration ν_1 of an optically isotropic molecule, the Raman polarizability tensor is isotropic and the corresponding depolarized spectrum is forbidden if the molecule is isolated. However, if the molecule is perturbed by neighboring molecules in a compressed gas the Raman polarizability tensor becomes slightly anisotropic. This collision- (and/or interaction-)induced anisotropy leads to the emergence of a purely collision-induced depolarized Raman spectrum in the vicinity of the ν_1 normal vibration frequency. This type of spectra for the ν_1 vibrational Raman band of CF₄ and SF₆ has been reported by one of us[1,2] some time ago, when the CF₄ Raman spectrum was measured in arbitrary units in the frequency range 6–32 cm^{-1}. In this paper, for the first time, the depolarized scattering intensities are given in *absolute units* for the Raman ν_1 mode spectrum up to 110 cm^{-1} from the center of the vibrational line. The theoretical semiclassical spectrum was computed for multipolar induction operators up to the dipole-induced octopole.[3,4] Nonlinear light scattering mechanisms due to hyperpolarizabilities and permanent multipole moments were taken into account in the theoretical spectrum as well. Recent *ab initio* computations by Maroulis[5,6] of CF₄ multipolar- and hyper-polarizabilities, multipole moments and their derivatives enabled us to calculate the theoretical ν_1 Raman spectrum in absolute units. We found this spectrum to be in good agreement with our experimental data. From the best fit between the experimental and theoretical spectra, the experimental value of the first derivative of the dipole-quadrupole polarizability tensor A' was measured.

Our paper is organized as follows: experimental details are given in Sec. II. Section III deals with the theoretical description of the spectrum. A comparison of the experimental and theoretical spectra is given in Sec. IV.

II. EXPERIMENT AND RESULTS

The main part of the setup used for our experiment has been described elsewhere.[7] The setup was recently equipped with a multichannel CCD camera. However, the low dark-noise bialkali photomultiplier (PM) used previously was retained. Both PM and CCD camera were used in order to measure the scattered intensities of the vibrational Raman band ν_1 of CF₄. The CF₄ fluid, purchased from L'Air Liquide company, was further purified from its 99.995% commercial purity by thermal treatment. The gas was contained in a four-window high-pressure cell and its densities were evaluated from the PVT data compiled in Ref. 8. The sample was illuminated by the 2 W beam of an argon-ion laser operating on its green line ($\lambda_L = 514.5$ nm) and polarized either vertically or horizontally (by means of a half plate associated with a Glan polarizer). The light scattered at 90 degrees in the horizontal plane was collected without an analyzer within a solid angle of $\Theta = 6.2$ degrees. Experimental intensities were measured at frequency shifts ν from 3 to 110 cm^{-1} in relation to the ν_1 line of CF₄. The spectra were scanned by using a slit function of 4 cm^{-1} for the frequency shifts beyond $\nu = 10$ cm^{-1} and slit functions of 1.5 cm^{-1} or 2 cm^{-1} for data below (10 cm^{-1}). Two sets of data were recorded at each density ρ. The first set, $I_H(\nu,\rho)$ corresponds to a laser-beam polarization parallel to the scattering plane, whereas the second set, $I_V(\nu,\rho)$, is associated to vertical laser polarization. Since the collection angle Θ is finite, the *depolarized* intensity $I_d(\nu,\rho)$ is not only a function of $I_H(\nu,\rho)$ at a given frequency shift ν but moreover a function of $I_V(\nu,\rho)$. According to Refs. 9 and 10 and to the value of Θ, $I_d(\nu,\rho)$ may be expressed in arbitrary units as:

$$I_d(\nu,\rho) = 1.006 I_H(\nu,\rho) - 0.006 I_V(\nu,\rho). \tag{1}$$

Depolarized scattering intensities of the vibrational Raman band ν_1 of CF₄ were measured at 294.5 K for several den-
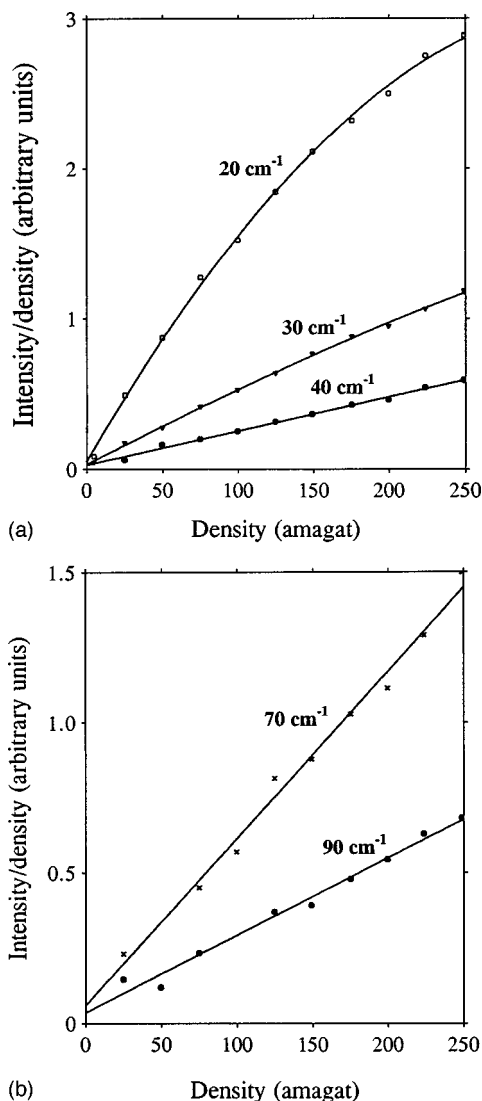
FIG. 1. Experimental depolarized Stokes intensities $I_d(\nu)$ of the ν_1 Raman band of gaseous CF$_4$ at 294.5 K divided by density (arbitrary units) *versus* the density ρ in amagat units for several characteristic frequency shifts. (a) 20 cm^{-1}, 30 cm^{-1}, 40 cm^{-1}; (b) 70 cm^{-1}, 90 cm^{-1}.

FIG. 2. Two-body depolarized absolute units scattering Stokes spectrum of the ν_1 Raman band of gaseous CF$_4$ at 294.5 K. Full circles ($\bullet$) indicate our experimental intensities when using CCD camera; crosses ($\times$) indicate our experimental points measured with a photomultiplier; open triangles (Δ) indicate the measurements made previously in relative units (Ref. 2) and adjusted to our measurements at $\nu = 20$ cm^{-1}.

band relatively to the integrated intensity of the $S_0(2)$ line of H$_2$ gas. Following a procedure described elsewhere,[12,13] we obtained for Raman CIS at $\nu = 15$ cm^{-1}: $I_d(15$ cm$^{-1})$ $= (2.03 \pm 0.35) 10^{-56}$ cm^6. The absolute spectrum obtained using a photomultiplier is very similar to that obtained using a CCD camera, as it can be noted in Fig. 2. Moreover, taking into account the uncertainties of the measurements, these spectra are compatible with the relative intensities obtained previously in the frequency range 6 to 32 cm^{-1} by one of us[2] (for comparison, we adjusted the latter to our measurements at $\nu = 20$ cm^{-1}).

III. THEORETICAL CONSIDERATIONS

In a dense medium, collisional effects as well as time- and space-fluctuations of multipolar molecular fields will in general lead to changes in the molecular polarizability tensor. Then the pair polarizability tensor of two molecules A and B, $\Pi_{\alpha\beta}$, is no longer simply a sum of intrinsic polarizabilities of both molecules $A_{\alpha\beta}(A)$ and $A_{\alpha\beta}(B)$ and acquires an incremental collision-induced polarizability of linear origin $\Delta A_{\alpha\beta}^{(L)}(AB)$ and of nonlinear origin $\Delta A_{\alpha\beta}^{(NL)}(AB)$:

$$\Pi_{\alpha\beta} = A_{\alpha\beta}(A) + A_{\alpha\beta}(B) + \Delta A_{\alpha\beta}^{(L)}(AB) + \Delta A_{\alpha\beta}^{(NL)}(AB).$$

(2)

The excess collision–induced pair polarizability of molecules A and B results as a self-consistent solution of a set of equations for local fields polarizing molecules A and B and the multipolar moments induced in molecules A and B. In a first approximation, the long range field-induced change in the pair polarizability, related to the linear multipolar polarizabilities of molecules is:[14]

sities up to 250 amagat and for frequency shifts up to 110 cm^{-1}. In the frequency range studied, the density behavior of the intensity depends on the frequency shift ν of the scattered light. In Fig. 1, the intensity divided by the density is plotted *versus* the density for several values of ν. Except for $\nu \leq 30$ cm^{-1}, the intensities increase as the square of the density up to 250 amagat. This shows that binary interactions predominate in these density and frequency ranges. However, it should be noted that a negative contribution due to three-body interactions appears for $\nu = 20$ cm^{-1} and $\nu = 30$ cm^{-1} at densities higher than 50 amagat and 100 amagat, respectively. In order to deduce the two-body spectrum accurately, a virial expansion in the density truncated to power 3 was made. As shown previously,[11] intensity contributions proportional to the density to power 4 need not be considered, in a first approximation, for CIS around a Raman vibrational band. The binary spectrum obtained in this way was calibrated in absolute units from measurements of the depolarized CIS at $\nu = 15$ cm^{-1} from the center of the ν_1
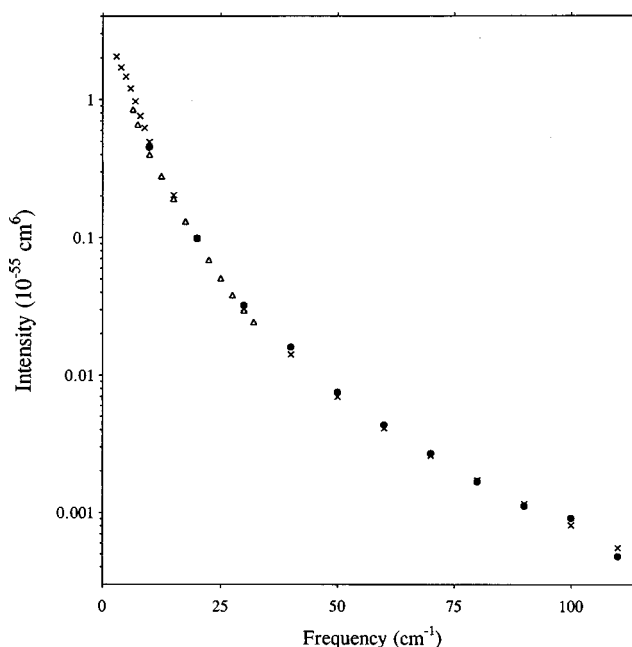
$$\Delta A_{\alpha\beta}^{(L)} = (1+\mathscr{P}_{AB})\left\{\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}(-1)^n\frac{2^{m+n}m!n!}{(2m)!(2n)!}\right.$$

$$\left.\times {}^{(1)}\mathbf{A}^{(m)}(\omega_A)[m]\,{}^{(m)}\mathbf{T}^{(n)}(\mathbf{R}_{AB})[n]\,{}^{(n)}\mathbf{A}^{(1)}(\omega_B)\right\}_{\alpha\beta},$$

(3)

where the tensor ${}^{(1)}\mathbf{A}^{(m)}(\omega_i)$ of rank $1+m$ determines the linear dipole-mth rank multipole polarizability due to dipole-$2^{**}m$-pole electric transitions in a molecule i, the symbol $[m]$ denotes m-fold contraction whereas $\mathscr{P}_{AB}$ permutes the indices A and B. Moreover the tensor

$${}^{(m)}\mathbf{T}^{(n)}(\mathbf{R}_{AB}) = \nabla_A^m \nabla_B^n\left(\frac{1}{R_{AB}}\right)$$

(4)

of $m+n$ rank defines $2^{**}m$-pole-$2^{**}n$-pole interaction between molecules A and B separated by a distance $\mathbf{R}_{AB}$.

The additional variation in the pair polarizability due to nonlinear molecular polarizabilities combined with permanent multipoles in a first approximation has the form:[14]

$$\Delta A_{\alpha\beta}^{(NL)} = (1+\mathscr{P}_{AB})\left\{\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}(-1)^n\frac{2^{m+n}m!n!}{(2m)!(2n)!}\right.$$

$$\times {}^{(1)}\mathbf{B}^{(1+m)}(\omega_A)[m]\,{}^{(m)}\mathbf{T}^{(n)}(\mathbf{R}_{AB})[n]$$

$$\left.\times \mathbf{Q}^{(n)}(\omega_B)\right\}_{\alpha\beta},$$

(5)

where the tensor ${}^{(1)}\mathbf{B}^{(1+m)}(\omega_i)$ of rank $2+m$ determines the nonlinear (second order) dipole-mth rank multipole hyperpolarizability due to dipole-dipole-$2^{**}m$-pole electric transitions in a molecule i. Moreover $\mathbf{Q}^{(n)}(\omega_i)$ defines the $2^{**}n$ order intrinsic molecular multipole moment of molecule i.

The formulas of Eq. (3) and Eq. (5) are of Cartesian form. Light scattering problems, however, often require the pair polarizability in the language of irreducible spherical tensors. Irreducible spherical tensor form of Eq. (3) has been presented in our previous papers[15,16] (see also Refs. 17 and 18). In the Appendix of this paper we develop the irreducible spherical tensor form of Eq. (5).

In Eq. (2) the Raman incremental pair polarizability tensor for the normal vibration ν_1 considered by us is

$$_{(RAM)}\Delta A_{\alpha\beta} = \frac{\partial\Delta A_{\alpha\beta}}{\partial Q_1^A}Q_1^A + \frac{\partial\Delta A_{\alpha\beta}}{\partial Q_1^B}Q_1^B,$$

(6)

where Q_1^p is the normal coordinate for the mode ν_1 and the molecule p. Moreover for the ν_1 vibration of CF_4, the Raman polarizability tensor of an isolated molecule is isotropic and, consequently, monomer polarizabilities of Eq. (2) do not contribute to depolarized Raman scattering considered in this work. For a laser beam polarized in the scattering plane and detected with no analyzer the theoretical anisotropic Raman ν_1 mode light scattering double differential cross section is given by[13,19]

$$\left(\frac{\partial^2\sigma}{\partial\Omega\,\partial\omega}\right)_H = \frac{1}{5}k_s^4\frac{1}{2\pi}\int\ \exp(-i\omega t)F_{22}^{\nu_1}(t)dt,$$

(7)

TABLE I. The anisotropic Raman light scattering correlation functions $F_{22}^{\nu_1}(t)$ for successive multipolar induction operators.

Mechanism	Raman case	$F_{22}^{\nu_1}(t)$
DID	$\alpha'\mathbf{T}\alpha + \alpha\mathbf{T}\alpha'$	$48(\alpha\alpha')^2 S_0(t)F_+$
DQ	$\alpha'\mathbf{TA} + \alpha\mathbf{TA}'$	$\frac{192}{7}[(\alpha'A)^2 + (\alpha A')^2]S_3(t)R_0(t)R_3(t)F_+$
DO	$\alpha'\mathbf{TE} + \alpha\mathbf{TE}'$	$\frac{220}{9}[(\alpha'E)^2 + (\alpha E')^2]S_4(t)R_0(t)R_4(t)F_+$
QQ	$\mathbf{A}'\mathbf{TA} + \mathbf{ATA}'$	$\frac{251648}{945}(AA')^2 S_4(t)R_3(t)R_3(t)F_+$
QO	$\mathbf{A}'\mathbf{TE} + \mathbf{ATE}'$	$\frac{9280}{21}[(AE')^2 + (A'E)^2]S_5(t)R_3(t)R_4(t)F_+$
OO	$\mathbf{E}'\mathbf{TE} + \mathbf{ETE}'$	$\frac{22660}{21}(EE')^2 S_6(t)R_4(t)R_4(t)F_+$

where

$$F_{22}^{\nu_1}(t) = \langle {}_{(RAM)}\Delta\mathbf{A}^{(2)}(0)\odot {}_{(RAM)}\Delta\mathbf{A}^{(2)}(t)\rangle$$

(8)

stands for the autocorrelation function of the anisotropic part of the induced Raman pair polarizability ${}_{(RAM)}\Delta\mathbf{A}^{(2)}$ of the system. The anisotropic ν_1 mode Raman light scattering correlation functions for dipole-induced dipole (DID) and successive multipolar induction operators are assembled in Table I.

(Multi)polarizabilities (dipolar α, dipole-quadrupole $\mathbf{A}$, dipole-octopole $\mathbf{E}$) and their normal coordinate derivatives (α', $\mathbf{A}'$ and $\mathbf{E}'$, respectively) are involved in these correlation functions. In Table I, A ($=A_{x,yz}$) and E ($=E_{z,zzz}$) stand for the independent components of the tensors $\mathbf{A}$ and $\mathbf{E}$, respectively, and each derivative of a (multi)polarizability $\mathscr{Z}$ is defined as $\mathscr{Z}' = \partial\mathscr{Z}/\partial Q_1^p$; the $R_a(t)$ and $S_b(t)$ functions were defined by us previously[13,16] whereas the F_+ function for the Raman Stokes side of the $\tilde{\nu}_1$ normal vibration is[19]

$$F_+ = \frac{b_{\nu_1}^2}{1 - e^{-[hc\tilde{\nu}_1/k_BT]}},$$

(9)

where $b_{\nu_1}[=(h/8\pi^2 c\tilde{\nu}_1)^{1/2}]$ is the zero point vibrational amplitude of the mode, and h stands for Planck's constant, c for the light velocity and $\tilde{\nu}_1$ for the normal mode frequency in cm^{-1}.

In general the pair polarizability, besides the multipolar induction operators already discussed by us and assembled in Table I, results as well from *nonlinear* light scattering mechanisms (induced by hyperpolarizabilities and permanent multipole moments). For tetrahedral molecules these nonlinear mechanisms contribute to some correlation functions of Table I — those governed by double rotational transitions. We have derived analytical formulae, Eqs. (10)–(12), for these nonlinear contributions. For correlation functions of $\mathbf{A}'\mathbf{TA} + \mathbf{ATA}'$ (QQ) of order (R_{12}^{-10}), corrections for nonlinear light scattering mechanisms (lsm) have the form:

$$\Delta F_{22}(t) = \left\{-\frac{768}{5}AA'(b'_{xyz}\Omega + b_{xyz}\Omega')\right.$$

$$+\frac{192}{7}[(b'_{xyz}\Omega)^2 + 2b_{xyz}b'_{xyz}\Omega\Omega'$$

$$\left.+(b_{xyz}\Omega')^2]\right\}S_4(t)R_3(t)R_3(t)F_+.$$

(10)

For correlation functions of $\mathbf{A}'\mathbf{TE} + \mathbf{ATE}'$ (QO) of order (R_{12}^{-12}) nonlinear lsm corrections become:

$$\Delta F_{22}(t) = \left\{ -\frac{576}{7}(A'E\Delta B\Omega' + AE'\Delta B'\Omega) + \frac{144}{25}[(\Delta B'\Omega)^2 + (\Delta B\Omega')^2] - 192(A'Eb'_{xyz}\Phi + AE'b_{xyz}\Phi') \right.$$

$$\left. + \frac{96}{7}(b'_{xyz}\Delta B\Omega'\Phi + b_{xyz}\Delta B'\Omega\Phi') + \frac{240}{7}[(b'_{xyz}\Phi)^2 + (b_{xyz}\Phi')^2] \right\} S_5(t)R_3(t)R_4(t)F_+ . \tag{11}$$

Finally, for lsm of $\mathbf{E'TE + ETE'}$ (OO) of order (R_{12}^{-14}) for these corrections we get:

$$\Delta F_{22}(t) = \left\{ -\frac{1056}{7}EE'(\Delta B'\Phi + \Delta B\Phi') \right.$$

$$+ \frac{88}{15}[(\Delta B'\Phi)^2 + 2\Delta B\Delta B'\Phi\Phi'$$

$$\left. + (\Delta B\Phi')^2] \right\} S_6(t)R_4(t)R_4(t)F_+ , \tag{12}$$

where b_{xyz} and $B_{\alpha\beta\gamma\delta}$ stand for the dipole-dipole-dipole and dipole-dipole-quadrupole hyperpolarizability tensors of the molecule, b'_{xyz} and the $B'_{\alpha\beta\gamma\delta}$ stand for their normal coordinate derivatives, $\Delta B = 3B_{zz,zz} - 4B_{xz,xz}$ and $\Delta B' = 3B'_{zz,zz} - 4B'_{xz,xz}$. In addition, Ω and Φ denote the independent components of the permanent octopole and hexadecapole moments, respectively, whereas Ω' and Φ' denote the corresponding derivatives.

We calculate the successive contributions to the resulting theoretical ν_1 Raman depolarized spectrum of CF₄ using the formulae of Table I and Eqs. (10)–(12). As in our previous papers[13,16] for each light scattering mechanism we calculate the rotational stick spectrum and then convolute it with the respective translational spectrum. For CF₄ with 4 equivalent bonds the relation between the bond length R derivative and the ν_1 mode normal vibration Q_1 polarizability derivative has the form:[19]

$$\left(\frac{\partial \alpha}{\partial Q_1}\right)_{molecule} = \frac{1}{2\sqrt{m_F}}\left(\frac{\partial \alpha}{\partial R}\right)_{molecule} . \tag{13}$$

This relation naturally extends to multipolar A, E, etc. polarizabilities as well as to hyperpolarizabilities and multipole moments. By way of Eq. (13) we connect the normal coordinate derivatives present in our light scattering formulae [Table I and Eqs. (10)–(12)] to bond length R derivatives computed *ab initio* by Maroulis.[5,6]

IV. DISCUSSION

A comparison between our experimental data given with error bars and the calculated spectra is presented in Figs. 3 and 4. To be consistent with our previous papers on depolarized and isotropic Rayleigh spectra of CF₄,[13,16] in our present computations we used the same Lennard-Jones potential.[20] The first-order DID spectrum was calculated from classical trajectories. The multipolar contributions to the spectrum were obtained by the method briefly described in Sec. III (more details on the computation principles of DID and dipole-multipole light scattering mechanisms as well as on the influence of quantum corrections are given in

Refs. 13 and 16). As results from Eqs. (10)–(12), the nonlinear light scattering mechanisms (due to hyperpolarizabilities and permanent multipole moments) affect the intensities of the double transition contributions due to the QQ, QO and OO mechanisms. To evaluate their relative influence, we used only available values of the nonlinear and multipolar CF₄ parameters, computed recently *ab initio* by Maroulis.[5,6] We found that nonlinear contributions at each frequency represent less than 5% of the intensity of each double rotational transition multipolar contribution. Moreover, the spectra due to QQ, QO and OO multipolar light scattering mechanisms alone do not contribute significantly to the total theoretical spectrum in the 0–110 cm^{-1} frequency range, as it can be seen in Figs. 3 and 4. Therefore, the nonlinear parameters can be safely neglected in the overall description of the theoretical spectrum. Concerning the CF₄ dipolar and multipolar polarizabilities and their derivatives, two sets of values are used in our theoretical computations of the spectrum. These values are assembled in Table II.

In both Figs. 3 and 4, a refractivity-experiment value of the dipolar polarizability α at $\lambda_L = 514.5$ nm is used.[21] In
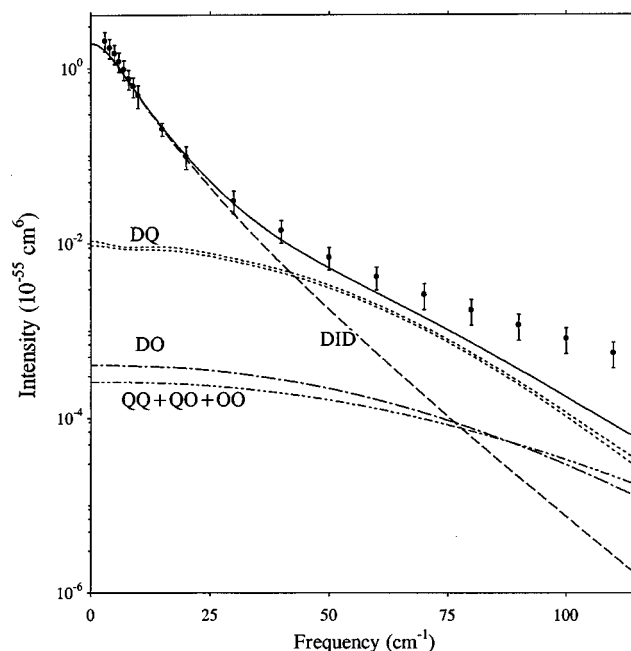

FIG. 3. Two-body depolarized absolute units scattering Stokes spectrum of the ν_1 Raman band of gaseous CF₄ at 294.5 K. Full circles (●) indicate our experimental data together with error bars. Theoretical curves (DID — — —, DQ - - - - -, DO — · —, QQ+QO+OO — · · — and total theoretical ———) are computed using a Lennard-Jones potential[20] and a set of (multi)polarizability values provided in Table II ($\alpha = 2.93$ Å³ and the *ab initio* values of Maroulis, Refs. 5, 6). In addition, we report a second DQ curve (the upper one) which has been computed using a recent CF₄ potential calculated by Palmer and Anchell (Ref. 27).
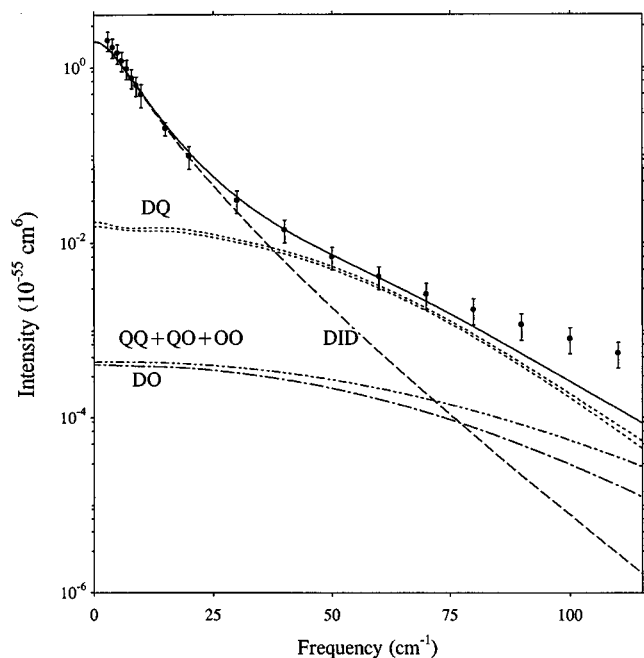
FIG. 4. The same as in Fig. 3, except for our theoretical curves computed here for the experimental values of the polarizabilities α, α', A and E and for a value of A' extrapolated from the present spectrum by way of a "best fit" procedure (see Table II). The value of E' computed by Maroulis (Refs. 5, 6) is maintained.

Fig. 3, the multipolarizabities and the polarizability derivatives used for calculations were recently published by Maroulis.[5,6] These data are the only *ab initio*-computed ones available for CF_4. In Fig. 4, the DID and dipole-multipole contributions are computed using an experimental value of α' measured in absolute Raman experiments.[19,22] Moreover, for this spectrum we used $|A|$ and $|E|$ values extrapolated from depolarized and isotropic CIS Rayleigh wings[16] whereas the value of $|A'|$ given in Table II is the one for which our experimental and theoretical Raman spectra fit

best in the 0–80 cm^{-1} frequency range. Note that Maroulis' value of E' is kept in Fig. 4 because $|E'|$ cannot be correctly fitted in a frequency range where the $\alpha'\mathbf{TE} + \alpha\mathbf{TE}'$ (DO) contribution is very weak (we may determine only the maximum value of $|E'|$ for which the DO contribution alone remains lower than or equal to the upper error-bar limits of the experimental spectrum whatever the frequency is: we found $E'_{max} = 28$ Å^4). On both Figures 3 and 4 the theoretical spectra lie lower than the experimental data in the 80–110 cm^{-1} frequency range. In our opinion, rather than a consequence of an invalid description of the DO mechanism, the discrepancy between theory and experiment in this very high frequency range results from neglecting here short range effects (such as overlap, exchange effects or molecular frame distortion) which are as yet unknown numerically in the case of CF_4. On the other hand, DID and $\alpha'\mathbf{TA} + \alpha\mathbf{TA}'$ (DQ) mechanisms are predominant in the 0–80 cm^{-1} frequency range. Below 12 cm^{-1}, the theoretical spectrum lies inside the error bars though near their lower limits. This slight divergence was expected because the low-frequency range spectral contribution of van der Waals dimers is not considered here.[23] Its integrated intensity can, however, be evaluated by Levine's method.[24] It shows that, for the DID Raman pair-polarizability tensor anisotropy $\beta_{DID}(r) = 6\sqrt{2}\alpha\alpha'/r^3$ coupled with the aforementioned Lennard-Jones potential,[20] van der Waals dimers contribute to 14.3 % of the integrated intensity of the theoretical depolarized DID spectrum. This means that the free-dimer DID spectrum represented in Figs. 3–4 contributes only to 85.7% of the integrated intensity due to the DID process. We may compare the experimental zero-order moment $M_0^{exp} = (15/2)(\lambda_{\nu_1}/2\pi)^4 \int_{-\infty}^{\infty} I_d(\nu)d\nu$ to its theoretical value $M_0^{theory} = \int_0^{\infty}\beta^2(r)\exp(-V(r)/k_BT)4\pi r^2 dr$, which includes contributions of free dimers as well as of van der Waals dimers. The theoretical zero-order moment may be obtained from Table I and Eq. (7) by putting:

TABLE II. Theoretical and experimental values of the polarizabilities and their bond length R derivatives for the CF_4 molecule. Those used in Fig. 3 are labelled by an asterisk (*) and those used in Fig. 4 are labeled by a diamond ($\diamond$). Values of the bond length derivatives are provided for the whole molecule and may be connected to the normal coordinate derivatives by way of Eq. 13. Theoretical values have been computed *ab initio* by Maroulis (Ref. 5, 6). Experimental values have been deduced either from CF_4 refractive indexes measured at optical frequencies, from Raman measurements or from collision-induced scattering (CIS) experiments (including this work).

Polarizability	Theory (Refs. 5, 6)	Experiment	Method	Reference
α	2.89 Å^3	2.93 Å$^{3*\diamond}$	Refractivity	21
$\alpha' = \left(\dfrac{\partial\alpha}{\partial R}\right)$	3.92 Å^{2*}	4.00 Å$^{2\diamond}$	Raman	19, 22
		3.68 Å^2	Raman	30
$|A|$	0.972 Å^{4*}	1 Å$^{4\diamond}$	CIS Rayleigh	16
$|A'| = \left|\dfrac{\partial A}{\partial R}\right|$	4.09 Å^{3*}	5.3 Å$^{3\diamond}$	CIS Raman	This work
$|E|$	1.15 Å^{5*}	1.5 Å$^{5\diamond}$	CIS Rayleigh	16
$|E'| = \left|\dfrac{\partial E}{\partial R}\right|$	5.53 Å$^{4*\diamond}$	<28 Å^4	CIS Raman	This work

TABLE III. Zero-order moments M_0 of the depolarized collision-induced spectrum for the vibrational ν_1 band of CF_4 at room temperature. Experimental moments are obtained from our CIS measurements and from previous depolarization ratio measurements using 7.54×10^{-31} cm^2 for the scattering cross section of the CF_4 polarized ν_1 band (Ref. 31). Theoretical moments are computed using a Lennard-Jones potential (Ref. 20) for two sets of (multi)polarizability values provided in Table II.

Experiment	M_0^{exp} (Å^9)	M_0^{theory} (Å^9)
This work	0.153 ± 0.040	0.144^a
References 1, 11	0.159 ± 0.023	0.152^b
Ref. 2	0.183 ± 0.036	

[a]Calculated with a set of (multi)polarizability values used in Fig. 3.
[b]Calculated with a set of (multi)polarizability values used in Fig. 4.

$$\beta^2(r) = 72 \frac{(\alpha\alpha')^2}{r^6} + \frac{288}{7} \frac{(\alpha A')^2 + (\alpha' A)^2}{r^8}$$
$$+ \frac{110}{3} \frac{(\alpha E')^2 + (\alpha' E)^2}{r^{10}} + \frac{125824}{315} \frac{(AA')^2}{r^{10}}$$
$$+ \frac{4640}{7} \frac{(AE')^2 + (A'E)^2}{r^{12}} + \frac{11330}{7} \frac{(EE')^2}{r^{14}}.$$

$$(14)$$

For the Maroulis' *ab initio*-computed polarizability data used in Fig. 3, we found $M_0^{theory} = 0.144$ Å^9. For those of Fig. 4 we got $M_0^{theory} = 0.152$ Å^9. These results are both very close to the experimental moment $M_0^{exp} = 0.153 \pm 0.040$ Å^9 calculated from our data and to those deduced from previous depolarization ratio measurements,[1,2,11] as it may be checked in Table III.

Moreover, the line shape agreement between theory and experiment is good beyond 12 cm^{-1} up to 80 cm^{-1}, in particular in the 40–80 cm^{-1} frequency range where the theoretical spectrum is mainly due to the DQ light scattering mechanism. This may be checked in Fig. 4 and even in the purely ''*ab initio*'' case of Fig. 3 (Maroulis' values), partly because Maroulis computed values of α', A and E are close to those deduced from previous experiments.[13,16,22] Concerning A', it is encouraging to note that Maroulis' value (4.09 Å^3) and our ''best fit'' value (5.3 Å^3) are close to each other too. Defining A'_{max} following a procedure similar to that used for E'_{max}, we found that $A'_{max} = 6.9$ Å^3 is also in the vicinity of the value computed by Maroulis. Besides, it is worth stressing that Maroulis computed *static* polarizabilities (at $\lambda = \infty$) whereas we measure dynamic ones (at $\lambda_L = 514.5$ nm). This may explain the slight discrepancy between his α value given in Table II (which does not include the so-called ''atomic part'' of the molecular dipolar polarizability) and the one measured at $\lambda_L = 514.5$ nm. Likewise, it may explain the discrepancy between his A' value and ours. The overall simplicity of the Lennard-Jones potential[20] used in our calculations may contribute to the discussed discrepancy as well. Other available CF_4 potentials have been tested too in our previous paper on CIS Rayleigh spectra.[16] None of them modifies significantly the spectral line shapes of the dipole-multipole contributions (which are mainly due to the rotational stick spectra of the successive light scattering

mechanisms[25]). However, the theoretical absolute spectral intensity and consequently its integrated intensity depend slightly on the potential. In this work, among the available CF_4 potentials we tested three (those which lead to values of the theoretical moments M_0^{theory} compatible with the experimental moments M_0^{exp}: at the same time for the CF_4 Raman depolarized spectrum studied here as well as for CF_4 Rayleigh spectra[13,16]). In addition to two Lennard-Jones' potentials (the one already used in this paper[20] and another given in Ref. 26), we computed the isotropic part of the potential which may be deduced from the *ab initio* intermolecular potential energy surfaces of CF_4 recently calculated by Palmer and Anchell.[27] As expected, the spectral line shape of the DQ contribution is not affected by the choice of the potential. This is shown in Figs. 3 and 4, where the DQ contribution computed using the Palmer and Anchell's potential is plotted together with that associated to the first Lennard-Jones potential.[20] Concerning the integrated intensity of this DQ contribution, we found that Palmer's potential and the second Lennard-Jones potential[26] increase its value by 8.5% and 14.3%, respectively. Since the DQ intensity is proportional to $\alpha^2 A'^2 + \alpha'^2 A^2$, the corresponding decreases of the fitted A'_{max} value are less than 4.3% and 7.2%, respectively. These results bring closer the fitted value of $|A'|$ and the A' computed by Maroulis. Nevertheless, this difference is not significant in consideration to the logarithmic scale of the figures and to the error bars of the experimental intensities ($\approx \pm 30\%$ at $\nu = 60$ cm^{-1}). Therefore, the discrepancy between the *ab initio* computed value of A' and the fitted value of $|A'|$ cannot be used as a decisive test between the three aforementioned potentials. Finally, regardless of which potential is used, both experimental and theoretical CIS depolarized spectra of the ν_1 vibrational band of CF_4 provide polarizability values which are compatible with the quantum chemistry calculations of Maroulis.

V. CONCLUSION

For the first time, the depolarized intensities of the CIS binary spectrum associated to the ν_1 vibrational Raman band of CF_4 have been measured in absolute units from 3 cm^{-1} up to 110 cm^{-1}. These experimental results have been compared to the contributions of both DID and dipole-multipole light scattering mechanisms to the CIS Raman depolarized spectrum, using the conclusions of our previous studies on the absolute-units CIS Rayleigh spectra of CF_4.[13,16] Due to the weakness of the dipole-octopole contribution, the associated parameter E' may not be fitted. Moreover, some short range effects modify the spectral line shape of the depolarized Raman spectrum beyond 80 cm^{-1}. Nevertheless, DID and DQ dipole-quadrupole light scattering mechanisms may be considered responsible for the depolarized intensities in the 0–40 cm^{-1} and in the 40–80 cm^{-1} frequency ranges, respectively. Comparison between theory and experiment leads to a fitted value of the derivative $A' = (\partial A/\partial R)_{molecule}$ of the dipole-quadrupole polarizability tensor close to the corresponding *ab initio* value computed by Maroulis.[5,6] Since in our previous papers[13,16] it was found that collision-induced spectra in the Rayleigh band permit the measure-

ment of multipolar polarizability tensors (A and E for CF_4), study of both Rayleigh and Raman CIS spectra appears to be a good way, presently the only way, to determine experimentally the multipolar polarizabilities as well as their derivatives for globular molecules such as CF_4.

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APPENDIX

Now, we develop the irreducible spherical tensor form of the excess pair polarizability of nonlinear origin. We start from the electrostatic interaction energy between molecules A and B in the form:[28]

$$U = \sum_{l_A l_B} \left(\frac{2^N}{(2l_A)!(2l_B)!} \right)^{1/2} \frac{X_N}{X_{l_B}} \sum_{m_A m_B, m} (-1)^{m_B} C(l_A, N, l_B;$$

$$m_A, n, m_B) Q_{l_A m_A} T_{Nn}^{(AB)} Q_{l_B - m_B}, \quad (A1)$$

where $N = l_A + l_B$, $Q_{l_i m_i}$ denotes the m_i component of the l_i-th order spherical electric multipole moment of the perturbed molecule i, T_N denotes the spherical interaction tensor, $C(abc; \alpha\beta\gamma)$ stands for the Clebsch-Gordan coefficient and $X_{ab \ldots f} = [(2a+1)(2b+1) \ldots (2f+1)]^{1/2}$. The multipole moment of perturbed molecule i reads[29]

$$Q_{l_i m_i} = Q_{l_i m_i}(0) + \sum_{l_2 n_2} \bar{\alpha}_{l_i l_2}^{m_i n_2}(0) V_{l_2}^{n_2 *}$$

$$+ \frac{1}{2!} \sum_{\substack{l_2, n_2 \\ l_3, n_3}} \bar{\beta}_{l_i l_2 l_3}^{m_i n_2 n_3}(0) V_{l_2}^{n_2 *} V_{l_3}^{n_3 *} + \ldots, \quad (A2)$$

where the V_l^n stand for the irreducible spherical tensor components of the external field. From (A1) we calculate the excess interaction-induced reducible dipole-dipole pair polarizability as the second derivative:

$$\Delta A_{1\ 1}^{m_1 m_2} = -\left(\frac{\partial^2 U}{\partial V_1^{m_1 *} \partial V_1^{m_2 *}} \right)_{V \to 0}. \quad (A3)$$

Bearing in mind the form of the second derivative of a product of two functions f and g:

$$\frac{\partial^2 (fg)}{\partial V_1 \partial V_2} = \frac{\partial f}{\partial V_1} \frac{\partial g}{\partial V_2} + \frac{\partial g}{\partial V_1} \frac{\partial f}{\partial V_2} + f \frac{\partial^2 g}{\partial V_1 \partial V_2} + g \frac{\partial^2 f}{\partial V_1 \partial V_2} \quad (A4)$$

from Eq. (A2) we note that first two terms of Eq. (A4) give us the pair polarizability of dipole-multipole origin, see Eq. (3). The last two terms contribute to the pair polarizability resulting from dipole-dipole-multipole hyperpolarizability–permanent multipole coupling between molecules A and B of the pair, see Eq. (5). Here we focus our attention on the latter one. Using Eq. (A2) and calculating respective derivatives for interaction-induced variation in the pair polarizability due to nonlinear molecular polarizabilities we have:

$$\Delta A_{1\ 1}^{m_1 m_2} = -\sum_{l_A l_B} \left\{ \left(\frac{2^N}{(2l_A)!(2l_B)!} \right)^{1/2} \frac{X_N}{X_{l_B}} \right.$$

$$\times \sum_{m_A m_B, n} [(-1)^{m_B} C(l_A, N, l_B; m_A, n, m_B)$$

$$\times (\bar{\beta}_{l_A\ 1\ 1}^{m_A m_1 m_2} T_{Nn}^{(AB)} Q_{l_B - m_B}$$

$$\left. + Q_{l_A m_A} T_{Nn}^{(AB)} \bar{\beta}_{l_B\ 1\ 1}^{-m_B m_1 m_2})] \right\}. \quad (A5)$$

In the following notation we drop the 0 appearing in Eq. (A2) in order to denote the multi(polarizability) and hyperpolarizability of the *unperturbed* molecule.

Reducible polarizability and hyperpolarizability tensors $\Delta A_{1\ 1}^{m_1 m_2}$ and $\bar{\beta}_{l_i\ 1\ 1}^{m_i m_1 m_2}$ transform into their irreducible counterparts by standard procedure:

$$A_{1\ 1}^{m_1 m_2} = \sum_{K,M} C(11K; m_2 m_1 M) \Delta A_{KM}[11], \quad (A6)$$

$$\bar{\beta}_{l_i\ 1\ 1}^{m_i m_1 m_2} = \sum_{a, \xi, J_i, M_i} C(11a; m_2 m_1 \xi) C(al_i J_i; \xi m_i M_i) \bar{\beta}_{J_i M_i}[(11)al_i], \quad (A7)$$

where $\bar{\beta}_{J_i M_i}[(11)al_i]$ is the irreducible J_i rank spherical tensor of dipole-dipole-$2^{**}a$-pole hyperpolarizability of molecule i in a coupling scheme where two dipoles are first connected and, subsequently the $2^{**}a$-pole multipolar moment.

Applying transformations (A6) and (A7) in Eq. (A5) and using orthogonality and symmetry relations for Clebsch-Gordan coefficients we easily arrive at the following formula

for the excess contribution to the pair polarizability due to nonlinear polarization of the molecules of a pair:

$$\Delta A_{KM}^{(NL)}[11] = -(1 + \mathscr{P}_{AB}) \sum_{J_A, l_A, l_B} \left(\frac{2^N}{(2l_A)!(2l_B)!} \right)^{1/2}$$

$$\times (-1)^{J_A + K + N} \frac{X_{NJ_A}}{X_{K l_A}} \{ \bar{\beta}_{J_A}[(11)Kl_A]$$

$$\otimes [T_N^{(AB)} \otimes Q_{l_B}]^{(l_A)} \}_{KM}. \quad (A8)$$

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