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Isotropic and anisotropic collision-induced light scattering by gaseous sulfur hexafluoride at the frequency region of the $\nu_1$ vibrational Raman line

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Experimental binary isotropic and anisotropic Stokes spectra of the collision-induced light scattered by gaseous sulfur hexafluoride are measured at the frequency region of the $\nu_1$ vibrational Raman line. They are compared to theoretical intensities due to dipole–multipole interactions. Taking into account the results of a previous study on the interaction-induced intensities in the Rayleigh wings of gaseous sulfur hexafluoride, an experimental value of the derivative of the dipole–octopole polarizability associated with the $\nu_1$ vibrational mode is provided and compared to the result of a recent ab initio calculation. © 2003 American Institute of Physics. [DOI: 10.1063/1.1575733]

I. INTRODUCTION

Collision-induced light scattering (CILS) arises in the scattering from dense media through molecular interactions. Most of the studies on this effect have concerned the Rayleigh wings of gases or liquids.1–3 However, CILS contributes also to the scattering intensities in the frequency region of vibrational Raman bands.4–8 In this last case, the scattering of collisional origin is generally less intense than the whole scattering generated by monomers all together, and within vibrational Raman bands CILS has been only measured for few molecules.4,6–8 For the sulfur hexafluoride molecule, which belongs to the symmetry group $O_h$, the derivative of the polarizability tensor with respect to the normal coordinate of the symmetric vibration $\nu_1$ is isotropic in the absence of any molecular interaction. On the contrary, when collisional effects are considered, the collisional-induced component of this Raman derivative polarizability tensor has an anisotropic part4,5 which induces a purely collision-induced component of this Raman derivative polarizability tensor when collisional effects are considered, the collision-induced anisotropic scattering spectrum. Therefore, the study of this $\nu_1$ Raman band is a good opportunity to measure CILS at the frequency region of a vibrational Raman line. In previous work,4 the frequency-integrated CILS anisotropic intensity in the vicinity of the $\nu_1$ line has been studied for gaseous SF$_6$ at room temperature.

II. EXPERIMENT

Data were collected using a typical scattering setup described previously in detail.13 We used the green line ($\lambda_L=514.5$ nm) of an argon ion laser to illuminate the gaseous sample contained in a four-window high-pressure cell. The light scattered at 90° was analyzed using a double monochromator whose output signals were measured using either a low-noise photomultiplier or a charge-coupled device (CCD) cooled at 140 K. Gas SF$_6$ was provided by the Praxair Company with a purity of 99.995%. Gas densities were determined from pressure measurements performed to an accuracy of 1% and pressure volume temperature (PVT) data compiled in Ref. 14. Our scattering data were collected for a temperature of the sample stabilized at 294.5±1 K. The scattering intensities reported in this work correspond to the Stokes side of the $\nu_1$ Raman band centered at about 775 cm$^{-1}$. The value of this frequency may change slightly according to the gas pressure. Two types of scattering intensities, $I_{\parallel}$ and $I_{\perp}$, were measured. They were obtained with the polarization of the laser beam parallel or perpendicular, respectively, to the scattering plane.15 Each intensity value was corrected to take into account the spectral sensitivity of our apparatus as well as the aperture of the scattering beam collected at the entrance of the monochromator. A typical spectrum, displayed in Fig. 1, shows the Stokes side of the $\nu_1$ band of gaseous SF$_6$ at 19 bars. A weak Raman band at the frequency region of the $\nu_1$ mode is visible in the high-frequency part of the wing with a maximum intensity at about 950 cm$^{-1}$. In order to obtain binary intensities, which is the purpose of this work, we measured scattering intensities at several gaseous densities $\rho$, up to 27 amagats. Then, for each frequency shift $\nu$ considered, we fitted total intensities $I_{\nu}(\nu)$ to a power series of the form
\[ I_t(n) = I_0(n) + I_1(n) + I_2(n) + I_3(n), \]

where \( I_2(n) \) and \( I_3(n) \) are the two- and three-body correlation terms, respectively. \( I_1(n) \) stands for the monomers contribution, and \( I_0(n) \) is the intensity independent of the gas density. In this way, we obtained the parallel and perpendicular pair intensities \( I_i(n) \) and \( I_{\perp}(n) \), respectively, according to the polarization of the laser. To illustrate this procedure, typical curves \( I_r(n) \) are displayed in Fig. 2 for several frequency shifts \( n = 10, 20, \) and \( 30 \) cm\(^{-1} \). The reduced intensity \( I_r(n) \) is defined by

\[ I_r(n) = \frac{I_{\perp}(n)}{I_0(n) + I_{\perp}(n)}, \]

where \( I_{\perp}(n) \) is the integrated perpendicular intensity of the \( \nu_1 \) Raman band. Pair intensities \( I_2(n) \) are deduced from the slopes of the curves \( I_r(n) \) at the zero-density limit. Finally, the binary anisotropic spectrum \( I_{\text{ani}}(n) \) and the binary isotropic spectrum \( I_{\text{iso}}(n) \) were obtained from

\[ I_{\text{ani}}(n) = I_{\perp}(n), \]

\[ I_{\text{iso}}(n) = I_{\perp}(n) - \frac{2}{3} I_{\perp}(n). \]

All the intensities were calibrated on an absolute scale, on the basis of a comparison with the intensity of the \( S_0(1) \) rotational line of hydrogen used as an external reference. 16

### III. THEORY

#### A. General considerations

We consider a macroscopically isotropic system composed of \( N \)-like globular molecules in an active scattering volume \( V \) illuminated by laser radiation of angular frequency \( \omega_L = 2\pi v_L \), polarized linearly in the direction \( e \). We analyze the secondary purely collision-induced \( \nu_1 \) vibration Raman electromagnetic radiation emitted by the system in response to that perturbation. At a point \( R \) distant from the center of the sample, the radiation scattered at \( \omega_s = 2\pi(v_L - v_1 - v) \) is measured on traversal of an analyzer with polarization \( n \). Then the quantum-mechanical expression for the pair differential scattering cross section has the form

\[ \frac{\partial^2 \sigma}{\partial \omega \partial \Omega} = \frac{\omega_s^4}{c^2} \int_{-\infty}^{\infty} dt e^{-i\omega t} \frac{\langle n \cdot \Delta \Lambda^{(\nu_1)}(t) \cdot e \rangle}{\langle W: \Delta \Lambda^{(\nu_1)}(0) \rangle \cdot \langle W: \Delta \Lambda^{(\nu_1)}(t) \rangle}, \]

where \( \Delta \Lambda^{(\nu_1)} \) states for the interaction-induced Raman \( \nu_1 \) vibration pair polarizability and \( \langle \rangle \) denotes a canonical average. Introducing the tensor (dyad)

\[ W = n e, \]

the pair correlation function \( F^{(\nu_1)}(t) \) of Eq. (5) can be rewritten

\[ F^{(\nu_1)}(t) = \langle [W: \Delta \Lambda^{(\nu_1)}(0)] [W: \Delta \Lambda^{(\nu_1)}(t)] \rangle, \]
TABLE I. Excess Rayleigh nonlinear origin anisotropic pair polarizability $\Delta A_{12M}^{(NLI)}$ tensor for octahedral molecules.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>$j_A$</th>
<th>$j_B$</th>
<th>$l_A$</th>
<th>$l_B$</th>
<th>$N$</th>
<th>$\Delta A_{12M}^{(NLI)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1 T_e \Phi$</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>[-\sqrt{\frac{13}{60}}]</td>
</tr>
<tr>
<td>$B_1 T_e \Phi$</td>
<td>0</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>[-\sqrt{\frac{13}{60}}]</td>
</tr>
</tbody>
</table>

where the symbol: denotes the twofold scalar tensor product. Using the reduction scheme of the symmetric second-rank tensor $T_{ij}$ in its irreducible Cartesian form

$$T_{ij} = T_{ij}^{(0)} + T_{ij}^{(2)},$$

where

$$T_{ij}^{(0)} = \frac{1}{2} T_{kk} \delta_{ij}, \quad T_{ij}^{(2)} = \frac{1}{2} (T_{ij} + T_{ji}) - \frac{1}{2} T_{kk} \delta_{ij},$$

we transform the $W$ and $\Delta A^{(r_1)}$ tensors into their irreducible forms and we change their coupling schemes. Next we group the geometrical and molecular parts and we assume that for an isotropic fluid the mean value occurring in Eq. (7) has to be a rotational invariant. Then for the pair correlation function $F^{(r_1)}(t)$ we obtain

$$F^{(r_1)}(t) = \sum_j \frac{1}{2j+1} \left\langle W_{(j)} \cdot W_{(j)} \right\rangle (\Delta A_{(j)}^{(r_1)}(0); \Delta A_{(j)}^{(r_1)}(t)).$$

(10)

We note that our pair correlation function $F^{(r_1)}(t)$ for the isotropic ($j = 0$) as well as the anisotropic part ($j = 2$) of the scattered light is a product of the geometrical factor

$$\phi_{ij} = \frac{1}{2j+1} \left\langle W_{(j)} \cdot W_{(j)} \right\rangle$$

and the molecular factor

$$F^{(r_1)}_{jj}(t) = \langle \Delta A_{(j)}^{(r_1)}(0); \Delta A_{(j)}^{(r_1)}(t) \rangle.$$  

(12)

Taking into account the form of the dyad $W$, using Eqs. (6), (8), and (9), for the pair double-differential cross sections of the isotropic and anisotropic collision-induced Raman light scattering we finally obtain

$$\frac{\partial^2 \sigma}{\partial \omega \partial \Omega} \big|_{150} = \frac{(e \cdot n)^2}{3} \omega_s^4 \int_{-\infty}^{\infty} dt \, e^{-i\omega t} F_{(0)}^{(r_1)}(t),$$

$$\frac{\partial^2 \sigma}{\partial \omega \partial \Omega} \big|_{222} = \frac{3}{30} (e \cdot n)^2 \omega_s^4 \int_{-\infty}^{\infty} dt \, e^{-i\omega t} F_{222}^{(r_1)}(t).$$

(13)

For the $A-B$ molecular pair the incrementual pair Raman polarizability tensor $\Delta A^{(r_1)}_{AB}$ for the normal vibration $v_1$ reads

$$\Delta A_{AB}^{(r_1)} = \frac{\partial A_{AB}^{(r_1)}}{\partial Q_A} Q_A + \frac{\partial A_{AB}^{(r_1)}}{\partial Q_B} Q_B,$$

(15)

where $\Delta A_{AB}^{(r_1)}$ is the pair Rayleigh excess polarizability and $Q_p$ is the normal coordinate for the mode $v_1$ and molecule $p$. Moreover, for the $v_1$ vibration of SF$_6$, the Raman polarizability tensor of an isolated molecule is isotropic and, consequently, monomer polarizabilities do not contribute to the depolarized Raman scattering considered in this work. The analytical expressions for the pair Rayleigh-multipolar first-order isotropic and anisotropic parts of the pair polarizability for octahedral molecules have been given elsewhere.\textsuperscript{11,18}

B. Second-order isotropic Raman scattering

Now let us consider the second-order isotropic Raman $v_1$ mode light scattering correlation function in detail. For the $A-B$ pair the Rayleigh second-order DID incremental (excess) pair polarizability tensor reads\textsuperscript{19,20}

$$\Delta A_{AB}^{(r_1)} = \frac{\partial A_{AB}^{(r_1)}}{\partial Q_A} Q_A + \frac{\partial A_{AB}^{(r_1)}}{\partial Q_B} Q_B.$$

(16)

In the case of small vibrations of the nuclei, the polarizability can be expanded into a Taylor series

$$\alpha(Q_p) = \alpha_0 + \alpha_{p}^{(r_1)} Q_p + \cdots,$$

(17)

where

$$\alpha_{p}^{(r_1)} = \left. \frac{\partial \alpha}{\partial Q_p} \right|_0.$$  

(18)

Then according to Eq. (15) for the collision-induced Raman polarizability we obtain

$$\Delta A_{AB}^{(r_1)} = [(2 \alpha_A \alpha_B A_{AB} + \alpha_A^2 AB) Q_A + (2 \alpha_A \alpha_B B_{AB} + \alpha_B^2 AB) Q_B)] Q_{T^{AB}}.$$

(19)

Taking into account that $T_{T^{AB}} = 6 R_{AB}^{-1}$ and assuming that we deal with the gas composed of identical molecules, for the isotropic Raman second-order pair polarizability we obtain

$$\Delta A_{AB}^{(r_1)} = \frac{2 \Delta A_{AB}^{(r_1)}}{3} = \frac{6 \alpha^2 (r_1)}{R_{AB}^2} (Q_A + Q_B).$$

(20)
The pair polarizability $\Delta A_{\alpha\beta}^{(r)}(t)$ depends on the translational and vibrational variables of molecules. It is generally assumed that the vibrational variables $Q$ are independent of the others and that the vibrational motions of two molecules are uncorrelated. The vibrational lifetime is very long with respect to the induction phenomena. Then we can write

$$\langle Q_A(0)Q_B(t) \rangle = \delta_{AB}(Q^2)\cos \omega_1 t, \quad (21)$$

where $\omega_1$ is the vibrational frequency. Finally, for the isotropic Raman spectrum due to the second-order DID light scattering mechanism we obtain from Eq. (12)

$$F_{00}^{(r)}(t) = \langle \Delta A_{\alpha\beta}^{(r)}(0) \Delta A_{\alpha\beta}^{(r)}(t) \rangle$$

$$= 72\alpha^4 (\alpha^{(r)})^2 (R_{AB}^6(0)R_{AB}^6(t))(\langle Q^2 \rangle^2). \quad (22)$$

C. Contributions from nonlinear polarizabilities

In order to obtain contributions to the Raman spectrum from nonlinear origin polarizabilities, the Rayleigh form of the respective pair nonlinear polarizability $\Delta A_{\alpha\beta}^{(NL)}$ is necessary [see Eq. (15)]. We arrived at the following formula for the excess pair Rayleigh polarizability due to nonlinear polarization of the molecules of a pair:

$$\Delta A_{\alpha\beta}^{(NL)}[11]$$

$$= (1 + P_{AB}) \sum_{j_A,k_B} (-1)^{(K+N+l_B+x+1)}$$

$$\times \left\{ \frac{2N}{(2l_A)!} \frac{N!}{(2l_B)!} \right\}^{1/2} \frac{X^{l_B} K}{X^{l_A} K} \times$$

$$\times \{ T_N^{(AB)} (B_{j_A}(11)Kl_A) \otimes Q_{j_B}^{(11)KM} \}. \quad (23)$$

For the $v_1$ vibration of sulphur hexafluoride, the lowest-order contribution to this mechanism results from the dipole$^2$-quadrupole hyperpolarizability tensor $B_{\alpha\beta\gamma\delta}$ of one SF$_6$ molecule combined with the permanent hexadecapole moment $F$ of the other SF$_6$ molecule. For SF$_6$ in the frame of the main reference axes, the $B_{\alpha\beta\gamma\delta}$ tensor has two independent Cartesian components $B_{zzzz}$ and $B_{xzzz}$. For this tensor the following relations between its irreducible spherical and Cartesian components hold:

$$B_{00}(11)22 = \sqrt{\frac{6}{5}} B_0, \quad B_{a0}(11)22 = \sqrt{\frac{7}{15}} \Delta B, \quad (24)$$

$$B_{44}(11)22 = \frac{\Delta B}{2\sqrt{6}}, \quad B_{44}(11)22 = \Delta B \frac{\Delta B}{2\sqrt{6}},$$

where $B_0 = B_{zzzz} + 2B_{xzzz}$ and $\Delta B = B_{zzzz} - 4B_{xzzz}$, whereas for the hexadecapole moment we have

$$Q_{a0} = F, \quad Q_{44} = \frac{\sqrt{5}}{14} F. \quad (25)$$

Table I gives the form of the SF$_6$ excess Rayleigh nonlinear origin anisotropic pair polarizability $\Delta A_{\alpha\beta}^{(NL)}$ tensor derived using Eq. (23).

In our considerations of the light scattering correlation function, Eq. (12), we assume that rotational and translational motions of SF$_6$ molecules are not coupled. Moreover, we assume that the molecules in the scattering volume are correlated radially but uncorrelated orientationally. We use the following formula to calculate the successive components of the tensorial part of the correlation function $F_{22}^{(r)}(t)$, Eq. (12):

$$\langle [T_N(0) \otimes [A_{j_A}(0) \otimes B_{j_B}(0)]_l \rangle \rangle$$

$$\otimes [T_N(t) \otimes [C_{j_A}(t) \otimes D_{j_B}(t)]_l \rangle \rangle$$

$$= (-1)^{L+N+j_B} \gamma_{AB}^l \frac{X^2}{X_{j_B} X_{j_A}} \langle [T_N(0) \otimes T_N(t)] \rangle$$

$$\times (\langle [A_{j_A}(0) \otimes C_{j_A}(t)] \rangle \langle [B_{j_B}(0) \otimes D_{j_B}(t)] \rangle)$$

$$= (-1)^{L+N+j_B} \gamma_{AB}^l \frac{X^2}{X_{j_B} X_{j_A}} \frac{2N}{(2N)!}$$

$$\times (\overrightarrow{A}_{j_A} \otimes \overrightarrow{C}_{j_A})(\overrightarrow{B}_{j_B} \otimes \overrightarrow{D}_{j_B}) S_N(t) R_{j_A}(t) R_{j_B}(t). \quad (26)$$

where the tilde denotes the polarizability or the permanent multipole moment in its molecular frame reference system. For the nonlinear polarizabilities discussed here, the respective scalar tensor products appearing in Eq. (26) are of the form

$$\langle \overrightarrow{B}_0 \otimes \overrightarrow{B}_0 \rangle = \frac{6}{5} B_0^2, \quad \langle \overrightarrow{B}_4 \otimes \overrightarrow{B}_4 \rangle = \frac{1}{5} \Delta B^2, \quad \langle \overrightarrow{E}_6 \otimes E_6 \rangle = \frac{12}{7} \Phi^2, \quad \langle \overrightarrow{E}_4 \otimes E_4 \rangle = 2 \sqrt{\frac{3}{35}} \Delta B \Phi, \quad \langle \overrightarrow{E}_4 \otimes E_6 \rangle = \sqrt{\frac{7}{3}} E \Phi, \quad \langle \overrightarrow{E}_4 \otimes E_4 \rangle = \sqrt{\frac{3}{5}} E \Delta B. \quad (27)$$

The autocorrelation functions of the isotropic and anisotropic parts of the Raman pair polarizability are provided in Table II for successive multipolar and nonlinear induction operators. In Table II, the $F_+$ function for the Raman Stokes side of the $\nu_1$ normal vibration refers to

$$F_+ = \frac{b_{r_1}^2}{1 - e^{-[(h/8\pi^2 c) \nu_1 (R_B)]}}, \quad (28)$$

where $b_{r_1} = [(h/8\pi^2 c) \nu_1]^{1/2}$ is the zero-point vibrational amplitude of the $\nu_1$ mode ($h$ being Planck’s constant, $c$ the light velocity, and $\nu_1$ the normal-mode frequency in cm$^{-1}$). Moreover, in Table II, $E$ and $\Phi$ stand for the independent component of the tensor $\overrightarrow{E}$ and the hexadecapole moment $\Phi$, whereas their normal vibration derivative is defined as $Z'$ = $\partial Z/\partial Q^2$. It is noteworthy that the normal vibration derivative is related to a corresponding bond length $R$ derivative. For SF$_6$ with six equivalent bonds this relation has the form

$$\frac{\partial Z}{\partial Q^2} = \frac{1}{6} \frac{\partial R}{\partial Q^2}. \quad (29)$$
Experimental intensities are given on an absolute scale for Raman spectra, larizability, or multipole moment, which may be extended to any multipolarizability, hyperpolarizability, or multipole moment.

IV. RESULTS AND DISCUSSION

Experimental anisotropic and isotropic CILS spectra of SF₆ in the vicinity of the ν₁ Raman line (pointed hereafter as “Raman spectra”) are reported in Figs. 3 and 4, respectively. Experimental intensities are given on an absolute scale for the Stokes side of the ν₁ lineup to ν = 100 cm⁻¹, where ν is the frequency shift measured from the center of the ν₁ line. They are compared with the theoretical double-differential cross sections, taking into account translational and rotranslational contributions computed with the SF₆ intermolecular potential Z of Zarkova. According to Eq. (5) these theoretical intensities are proportional to the Fourier transform of the autocorrelation functions provided in Table II. In Fig. 4, the isotropic translational contribution (ITC) is calculated from the second-order DID mechanism by using classical trajectories of two molecules in interaction. In Fig. 3, the anisotropic translational contribution (ATC) to the Raman spectrum is deduced from the experimental anisotropic Rayleigh spectrum. Indeed, considering this Rayleigh spec-

\[
\frac{\partial \alpha}{\partial Q^1_{\text{molecule}}} = \frac{1}{\sqrt{6m_F}} \frac{\partial \alpha}{\partial R_{\text{molecule}}},
\]

which may be extended to any multipolarizability, hyperpolarizability, or multipole moment.

![FIG. 3. Two-body anisotropic scattering spectra on an absolute intensity scale (cm⁶) for the Stokes wing of the ν₁ Raman band of SF₆ at 294.5 K. Frequency shifts are measured in cm⁻¹ from the center of the ν₁ line. Our experimental data [solid circles (●)] are given with error bars. The partial and total theoretical spectra are computed for the Z potential (Ref. 23), α = 4.549 Å⁻¹ (Ref. 32), α = 7.38 Å⁻¹ (Ref. 33), E = 3.1 Å² (Ref. 11), and E' = 46 Å²: anisotropic translational contribution (ATC: ---), dipole-induced octopole (DIO: - - - - - - -), nonlinear-origin contribution (NLC: - - - - - - -), and total (——). We also provide the dipole-induced dipole (DID) contribution (--- ---) due to the free dimers in the 10–100 cm⁻¹ frequency range.](image)

![FIG. 4. Two-body isotropic scattering spectra on an absolute intensity scale (cm⁶) for the Stokes wing of the ν₁ Raman band of SF₆ at 294.5 K. Frequency shifts are measured in cm⁻¹ from the center of the ν₁ line. Our experimental data [solid circles (●)] are given with error bars. The partial and total theoretical spectra are computed for the Z potential (Ref. 23), α = 4.549 Å⁻¹ (Ref. 32), α = 7.38 Å⁻¹ (Ref. 33), E = 3.1 Å² (Ref. 11), and E' = 46 Å²: dipole-induced dipole (DIO: - - - - - - -), dipole-induced octopole (DIO: - - - - - - -), octopole-induced octopole (OIO: --- - -), and total (——).](image)
trum, it is possible to subtract the theoretical rototranslational intensities \( I_{\text{rot}}^{\text{Rayleigh}}(n) \) from the experimental intensities \( I_{\text{expt}}^{\text{Rayleigh}}(n) \) to get the translational intensities \( I_{\text{ATC}}^{\text{Rayleigh}}(n) \):

\[
I_{\text{ATC}}^{\text{Rayleigh}}(n) = I_{\text{expt}}^{\text{Rayleigh}}(n) - I_{\text{rot}}^{\text{Rayleigh}}(n).
\]

On the other hand, according to Table II and the autocorrelation functions given in Ref. 11, we can write

\[
I_{\text{ATC}}^{\text{Raman}}(n) = \frac{2}{\alpha^2} \left( \frac{\partial \alpha}{\partial Q_1} \right)^2 \left( \frac{v_L - v_1 - v}{v_L} \right)^4 I_{\text{ATC}}^{\text{Rayleigh}}(n),
\]

where \( n \) is the frequency shift measured from the center of either the Rayleigh line for the Rayleigh spectrum or the Raman line for the Raman spectrum. The computation of the rototranslational dipole-induced octopole (DIO), octopole-induced octopole (OIO), and nonlinear (NLC) contributions has been previously described. To provide them on an absolute intensity scale, several values for polarizabilities and multipoles must be known. As far as the nonlinear contribution given in Fig. 3 is concerned, we used the values of \( \Phi, \Delta B, B_0, \) and of their \( R \) derivatives computed by Maroulis. The value chosen for the dipole–octopole polarizability \( E (E=3.1 \text{ Å}^5) \) is the one proposed in our previous paper on the Rayleigh spectra of SF\(_6\) for the aforementioned potential. The \( E' \) values (\( E' = 46 \text{ Å}^4 \)) are obtained by fitting the theoretical anisotropic Raman spectrum to the experimental data in the 30–70 cm\(^{-1} \) frequency range in which the multipolar contributions play the leading role. Because of the competition between \( E \) and \( E' \) in the coefficients involved in the different correlation functions given in Table II, several values of the pair \((E,E')\) may correspond to similar theoretical intensities. The ensemble of such solutions forms an area, as shown in Fig. 5 for the potential \( Z \) in the plane defined by \( E \in \{2.2, 4.0 \text{ Å}^5\} \) and \( E' \in \{43, 49 \text{ Å}^4\} \). This area has been obtained through set inversion by considering both the Rayleigh isotropic spectrum (used in Ref. 11 for the measurement of \( E \)) and Raman anisotropic spectrum. For any point \((E,E')\) in this area, theoretical intensities lie inside the error bars of all experimental data in the frequency ranges for which multipolar effects may be considered as predominant (30–85 cm\(^{-1} \) for the isotropic Rayleigh spectrum and 30–70 cm\(^{-1} \) for the anisotropic Raman spectrum). The pair of values \((E=3.1 \text{ Å}^5, E'=46 \text{ Å}^4)\) used in Figs. 3 and 4 is set at the center of the area of solutions provided in Fig. 5 for the potential \( Z \). As far as the isotropic Raman spectrum reported in Fig. 4 is concerned, it can be noticed that in this case theoretical spectrum is far below experimental data. Moreover, as follows from Fig. 5 the value of \( E' \) cannot exceed 48.2 Å\(^4\) for the potential \( Z \). The choice of this maximum value would not be sufficient to obtain theoretical isotropic intensities as high as experimental ones. Similar discrepancies have been observed in the case of CF\(_4\). They are connected to the surprisingly low values reported in Fig. 6 for the depolarization ratio \( \eta(v) = I_{\perp}(v)/I_{\parallel}(v) \) of SF\(_6\). Even at low frequencies, the depolarization ratio is lower than the value expected for the intensities generated by the dipole–octopole mechanism alone (\( \eta = 22/63 = 0.35 \)). This shows that the experimental isotropic intensities are greater than those produced by multipolar mechanisms. Therefore, we may conclude that the intensities \( I_{\text{iso}}(v) \) result not only from the dipole–multipole mechanisms but also from another contribution.

Several effects may be mentioned in order to explain this behavior. The first one is connected to the inaccuracy of the potentials available for globular molecules such as CF\(_4\) or SF\(_6\). In Table III, we provide the pairs of values \((E,E')\) obtained by using different SF\(_6\) potentials. The use of a different potential slightly affects the values of \( E \) and \( E' \) as may be noticed in Table III, but cannot allow any increase in the theoretical isotropic intensities without a simultaneous (and here forbidden) increase in the theoretical anisotropic intensities in the midfrequency range used to obtain the values of \( E \) and \( E' \). On the other hand, there are SF\(_6\) potentials (e.g., the MMSV potential given in Ref. 28) which induce an enhancement of the spectral line shape of the multipolar contributions beyond 100 cm\(^{-1} \). Nevertheless, this enhancement does not concern the frequency range of our Raman experimental data and cannot alone explain the lack of the theoretical intensities beyond 70 cm\(^{-1} \) for both anisotropic and isotropic Raman spectra.

The second effect refers to short-range interactions such as the overlap and exchange mechanisms, molecular frame distortion, and the effect of the nonpointlike size of the molecule. They play a role at high frequencies, but are not well known for SF\(_6\). On the one hand, in the anisotropic case, the extrapolation of the translational contribution from the Rayleigh anisotropic spectrum is a way to take them into account. Comparing the deduced Raman translational curve (ATC) of Eq. (31) with the pure DID contribution (computed...
The splitting of the \( Q(J) \) lines of the \( v_1 \) band due to the vibrational–rotational coupling could be the third effect to consider. The consequence of this effect decreases when the density or frequency increases and may be regarded as negligible for our binary isotropic spectrum, in the frequency range scanned. Similarly, the influence of the nonlinear contributions, which, in the linear approximation of \( T_\gamma \), exists in the anisotropic spectrum and not in the isotropic spectrum, can be considered. In the case of the forbidden \( SF_6 \) vibrational line \( \nu_3 \) (symmetry species: \( F^{(1)}_{1u} \)) the dipole moment belongs to the \( F^{(1)}_{1u} \) representation too, so the off-diagonal matrix elements of the dipole moment are nonzero for this symmetry and then contribute to the Raman nonlinear origin polarizability. In this case the nonlinear origin light scattering mechanism is of the the same order as multipolar contributions in computations of the intensity of the \( \nu_3 \) Raman line, as suggested by Samson and Ben-Reuven. 29 However, in our case the nonlinear origin contributions to the Raman spectrum of the \( \nu_3 \) band of \( SF_6 \) are relatively small (see Fig. 3 for values computed by Maroulis12). We deal with the diagonal (ground-state) matrix elements of the hexadecapole moment and the nonlinear hyperpolarizability \( B \) as well as their off-diagonal matrix elements of the totally symmetric representation \( A_{1g} \). For this symmetry the hexadecapole is the first nonzero electric moment. Then this high-order moment coupled with dipole–quadrupole hyperpolarizability \( B \) gives a small contribution. Its influence on the measurement of \( E' \) may be neglected and cannot explain the discrepancies observed.

Finally, the discrepancies between the experimental and theoretical isotropic spectra are probably more connected to the far wings of the \( \nu_1 Q \) branch. Although the integrated intensity of this \( Q \) branch is proportional to the density \( \rho \), the dependence on the density of the spectral intensities in the wings may be different. Indeed, the intensity in the far wings of allowed spectral lines comes mainly from short-time interactions in binary collisions and is therefore quadratic in the density. Thus, the wing intensities of the \( \nu_1 \) line generated by the monomers may contribute to the experimental pair isotropic spectrum \( I_{iso}(\nu) \) measured in this work using the virial expansion described above in Eq. (1).

Consequently, the frame of our analysis is very different from the one described in our previous work about the Rayleigh wings of \( SF_6 \). 11 In the Rayleigh case, the strong translational contribution \( I_{Rayleigh}^{ATC} \) to the anisotropic spectrum predominates in the \( 0–100 \text{ cm}^{-1} \) frequency range scanned. 11 It is thus more advisable to deduce the measured value of \( E \) from the Rayleigh isotropic spectrum for which the DID contribution is of second order and lower than multipolar contributions. 11 On the contrary, because of the probable influence of the far wings of the \( \nu_1 \) line on the isotropic Raman spectrum, the latter is not adequate to measure the influence of multipolar mechanisms. Fortunately, in the Rayleigh case, the translational contribution to the anisotropic spectrum is relatively less important than the one found in the Rayleigh case. In Fig. 3, the dipole–octopole contribution becomes predominant beyond \( 30 \text{ cm}^{-1} \) where it never reaches 10% of the total intensity in the \( 0–220 \text{ cm}^{-1} \) frequency range of the anisotropic Rayleigh spectrum. Conse-

### Table III: Dipole–octopole polarizability \( E \) of \( SF_6 \) and its \( R \) derivative \( E' \) for the \( \nu_1 \) mode of \( SF_6 \).

<table>
<thead>
<tr>
<th>Theory</th>
<th>( E (\text{Å}^4) )</th>
<th>( E' (\text{Å}^4) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{Ab initio} (Ref. 12)</td>
<td>4.2</td>
<td>22.6</td>
</tr>
<tr>
<td>Experiment (CILS)</td>
<td>( E (\text{Å}^4) )</td>
<td>( E' (\text{Å}^4) )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Potential</th>
<th>Ref. 11</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>28-7 LJ</td>
<td>2.7±0.6</td>
<td>42±3</td>
</tr>
<tr>
<td>MMSV (Ref. 28)</td>
<td>2.6±0.6</td>
<td>40±2</td>
</tr>
<tr>
<td>HFD (Ref. 25)</td>
<td>3.8±0.8</td>
<td>55±2</td>
</tr>
<tr>
<td>Z (Ref. 23)</td>
<td>3.1±0.7</td>
<td>46±2</td>
</tr>
<tr>
<td>Best/recommended</td>
<td>3.0±1.5</td>
<td>47±10</td>
</tr>
</tbody>
</table>

FIG. 6. Experimental pair depolarization ratio \( \eta(\nu)=I_{2,1}(\nu)/I_{1,2}(\nu) \) vs frequency shifts \( \nu \) in \text{cm}^{-1} for the Stokes side of the \( \nu_1 \) Raman band of gaseous \( SF_6 \) at 294.5 K. The theoretical depolarization ratio \( \eta_{theo}(\nu) \) = 22/7 associated to the dipole-induced octopole mechanism is represented by a dashed horizontal line (— — —).

from classical trajectories), we found that they are close below \( \nu=30 \text{ cm}^{-1} \) (for the potential \( Z \), differences are less than 15% whatever the frequency is). This shows that DID mechanism is predominant in this frequency region. Beyond \( 30 \text{ cm}^{-1} \), the ATC intensities become lower than the computed DID intensities, due to short-range effects. Taking into account the ATC instead of DID intensities leads to a slight enhancement of the measured \( E' \) value (less than 10%). On the other hand, in the Raman isotropic case, the lack of the theoretical intensity is not limited to the highest frequencies and concerns the whole frequency range of the spectrum. Moreover, consideration of all translational contributions yields scattering intensities generally lower than the DID ones. This behavior cannot explain the difference observed between theoretical and experimental data for isotropic intensities.
quences of the uncertainties due to short-range effects on the shape of the translational contribution are therefore less important for the measurement of $E'$. Moreover, these effects are taken into account in the ATC shape deduced from the experimental Rayleigh anisotropic spectrum.

The pairs of values $(E, E')$ which are given in Table III relate to various potentials and deduced from the two spectra in which the dipole–multipole mechanisms can play a leading role: the Rayleigh isotropic spectrum and the Raman anisotropic spectrum. The reported values of $E'$ vary from 38 to 57 Å$^4$. From these results, we propose a best and recommended value $E' = 47 \pm 10$ Å$^4$. It is close to the one obtained with the potential $Z$ of Zarkova,$^23$ similarly to the situation discussed previously in the Rayleigh wings.$^{11}$ This experimental result is of the same order of magnitude as the theoretical value of $E'$ computed by Maroulis,$^12$ $E' = 22.6$ Å$^4$. However, it is noticeable that the experimental value is measured at an optical frequency when the theoretical one is a static value ($\nu = 0$).

V. CONCLUSION

We have shown that the derivative $E'$ of the dipole–octopole polarizability $E$ of the molecule SF$_6$ may be deduced from the Raman scattering spectra. This result has been achieved thanks to a detailed analysis of both isotropic and anisotropic spectra recorded in the Rayleigh wings and within the $\nu_1$ Raman band. In spite of the contribution of several effects to scattering intensities, the multipolar mechanisms were found predominant in some specific frequency regions, which allows us to deduce the values of $E$ and $E'$ for SF$_6$. Thus, this work points out that, as shown for CF$_4$, the study of Raman scattering in different polarization configurations is a suitable method, up to now the only one, to measure several of the multipolar polarizabilities and their derivatives for globular molecules.

1 Phenomena Induced by Intermolecular Interactions, NATO ASI Series, edited by G. Birnbaum (Plenum, New York, 1985).
15 The scattering plane is the plane defined by the laser beam and the axis of the scattering beam.