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# Collision-induced hyper-Rayleigh spectrum of octahedral molecules: The case of SF<sub>6</sub>

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A theoretical expression giving the collision-induced hyper-Rayleigh (CI HR) spectrum due to pairs of centrosymmetric molecules of octahedral symmetry has been derived. The dipole<sup>2</sup>-quadrupole hyperpolarizability light scattering mechanism of collision-induced hyperpolarizability  $\Delta\beta_{LM}$  is discussed in detail and proposed to explain the CI HR spectrum. Numerically we have applied our analytical formulas to binary CI HR spectrum of sulfur-hexafluoride. We have normalized our SF<sub>6</sub> CI HR spectrum to the monomer HR spectrum of CCl<sub>4</sub>. The spectral contribution due to second hyperpolarizability-permanent hexadecapole HR light scattering mechanism has been estimated and showed to be negligible. © 2001 American Institute of Physics. [DOI: 10.1063/1.1410979]

## I. INTRODUCTION

Hyper-Rayleigh (HR) scattering is a three-photon process in which a system is excited with two photons of laser frequency  $\omega_L$  and emits one photon at a frequency of about  $2\omega_L$ . The first theoretical inkling of this effect goes back to Dirac<sup>1</sup> and Mayer.<sup>2</sup> The full theoretical treatment of HR phenomenon was given at the same period by several authors.<sup>3–6</sup> Terhune, Maker and Savage<sup>7</sup> succeeded in observing HR scattering in H<sub>2</sub>O, CCl<sub>4</sub>, CH<sub>3</sub>CN and fused quartz. For further studies see Refs. 8–16. In his pioneering work<sup>3,4,17</sup> Kielich indicated that HR process arises in a molecule mainly due to its third-order dipolar hyperpolarizability tensor  $\beta_{ijk}$ .

Recent technological demands of new efficient materials for nonlinear optics have provoked great interest in nonlinear and multipolar polarizabilities of molecules. Hyper-Rayleigh scattering has been developed as the best experimental technique for determination of the first hyperpolarizability tensor  $\beta_{ijk}$  of molecules.<sup>18–23</sup>

Search for a precise value of the dipolar first hyperpolarizabilities  $\beta_{ijk}$  of molecules raised interest in the literature in the collision-induced hyper-Rayleigh scattering.<sup>24–26</sup> These studies indicate that collision (interaction)-induced contributions account for more than half of the hyper-Rayleigh intensity from the liquid phase of CCl<sub>4</sub>. For centrosymmetric systems the  $\beta_{ijk}$  tensor vanishes identically so no HR scattering is expected. Nevertheless, intensities at frequencies around the double incident frequency  $2\omega_L$  and due to collision-induced (CI) interactions have been observed for molecules with a center of inversion.<sup>27–29</sup> In this paper we discuss theoretical foundations of the collision-induced HR scattering spectral signal resulting from a pair of centrosymmetric molecules of octahedral symmetry. We note that

sometimes in linear regime the kind of a spectrum considered by us is called as collision-induced rotational Raman scattering.<sup>30</sup> Numerically we apply our analytical formulas to HR spectrum of gaseous sulfur-hexafluoride. Our study indicates that the collision-induced HR method opens a new way to study molecular interactions and dynamics as well as is the only technique allowing a measurement of several kinds of dipole-multipole hyperpolarizabilities of a system.

## II. HYPER-RAYLEIGH TIME CORRELATION FUNCTION

In a dense medium, collisional effects as well as time- and space-fluctuations will in general lead to changes in the molecular hyperpolarizability tensor. In the notation of the irreducible spherical tensors the lowest order multipolar collision-induced pair hyperpolarizability tensor reads<sup>31</sup>

$$\begin{aligned} \Delta\beta_{LM}[(11)a1] = & 3(1 + \mathcal{P}^{AB}) \sum_{\text{all but } L, M, a} (-1)^{j_B} \\ & \times \left( \frac{2^N}{(2l_A)!(2l_B)!} \right)^{1/2} X_{j_A j_B N x} \\ & \times \left\{ \begin{matrix} j_A & j_B & x \\ a & 1 & L \\ l_A & l_B & N \end{matrix} \right\} \{ \mathbf{T}_N^{(AB)} \otimes [\beta_{j_A}[(11)a l_A] \\ & \otimes \alpha_{j_B}[1 l_B]]^{(x)} \}_{LM}, \end{aligned} \quad (1)$$

where  $\alpha_{j_p M_p}[(1)l_p]$  is the irreducible dipole- $2^{l_p}$ -pole (multipolarizability tensor of a molecule  $p$  and  $\beta_{j_p M_p}[(11)a l_p]$  denotes the irreducible  $J_p$ -rank spherical tensor of the first order dipole<sup>2</sup>- $2^{l_p}$ -pole hyperpolarizability of a molecule  $p$  in a coupling scheme where two dipoles are first connected

and, subsequently, the  $2^j$ -pole multipolar moment. Moreover  $\mathbf{T}_N^{(AB)}$  is the spherical interaction tensor and  $\{\dots\}$  stands for the 9-j Wigner symbol whereas  $\mathcal{P}^{AB}$  permutes the indices  $A$  and  $B$ . In our considerations we assume the Kleinman<sup>32</sup> (full index) symmetry of the collision-induced pair hyperpolarizability tensor  $\Delta\beta_{ijk}$  and the same symmetry of polarizabilities and hyperpolarizabilities of monomers. In our formulas  $\odot$  and  $\otimes$  symbols stand for scalar and tensor products, respectively.

We apply Eq. (1) to a pair of octahedral molecules and we consider the  $\alpha_0\mathbf{T}_3\beta_j[(11)a2]$  (first nonzero) light scattering mechanism. To describe this mechanism, let's consider a pair of octahedral molecules  $A$  and  $B$ . A linearly polarized laser light  $\mathbf{E}^L$  is incident upon the pair. The laser light induces in each molecule a dipole moment at a frequency  $\omega_L$ :  $\mu_\alpha = \alpha_{\alpha\beta}E_\beta^L$  and a quadrupole moment at a frequency  $2\omega_L$  of the form

$$\Theta_{\alpha\beta}^{2\omega_L} = \frac{1}{2}\beta_{\gamma,\delta,\alpha\beta}E_\gamma^LE_\delta^L. \quad (2)$$

Then the dipole moment at a frequency  $2\omega_L$  induces in the molecule  $A$  in two-fold complementary ways: (1) through the dipole<sup>2</sup>-quadrupole hyperpolarizability  $\beta$  tensor of molecule  $A$ , laser field  $\mathbf{E}^L$  together with the field gradient of induced dipole moment of molecule  $B$  (2) due to the molecular field (at the frequency  $2\omega_L$ ) of the quadrupole moment of Eq. (2) induced in molecule  $B$  by laser field and the dipole<sup>2</sup> polarizability tensor  $\alpha$  of molecule  $A$  now acting at frequency  $2\omega_L$ .<sup>15</sup> Analogous considerations apply to molecule  $B$ . Then the rank one and three components of the pair hyperpolarizability tensor are of the form:

$$\Delta\beta_{1M}[(11)21] = -3\sqrt{\frac{3}{10}}\{\alpha^{(B)}[\mathbf{T}_3^{(AB)} \otimes \beta_4^{(A)}[(11)22]] - \alpha^{(A)}[\mathbf{T}_3^{(AB)} \otimes \beta_4^{(B)}[(11)22]]\}_{1M}, \quad (3)$$

$$\Delta\beta_{3M}[(11)21] = -\sqrt{\frac{33}{70}}\{\alpha^{(B)}[\mathbf{T}_3^{(AB)} \otimes \beta_4^{(A)}[(11)22]] - \alpha^{(A)}[\mathbf{T}_3^{(AB)} \otimes \beta_4^{(B)}[(11)22]]\}_{3M}. \quad (4)$$

For the octahedral symmetry molecules considered, the spherical irreducible dipole<sup>2</sup> polarizability tensor  $\alpha_j^{(i)}[11]$  of Eq. (1) is isotropic ( $j=0$ ) and the following relation holds  $\alpha_0^{(i)}[11] = -\sqrt{3}\alpha^{(i)}$ , where  $\alpha^{(i)}$  is the conventional dipole polarizability of molecule  $i$ . In Eq. (1)  $\beta_j^{(i)}[(11)22]$  stands for dipole<sup>2</sup>-quadrupole hyperpolarizability tensor of molecule  $i$ . In Buckingham<sup>33</sup> and Kielich<sup>13</sup> convention this tensor is denoted by  $\mathbf{B}$ .<sup>34</sup> In order to make our formulas more compatible with previous papers we follow this notation. For the octahedral symmetry molecules, only the irreducible tensors  $\mathbf{B}_j$  of ranks  $j=0$  and  $j=4$  are nonzero.<sup>31</sup> Generally our formulas (1)–(4) apply to a pair of different molecules  $A$  and  $B$ . However, when we consider scattering from one component fluid ( $A=B$ ) we easily note that in this case the contribution to the pair hyperpolarizability  $\Delta\beta_{LM}[(11)a1]$  due to  $\mathbf{B}_0$  vanishes. Moreover we note that the discussed here mechanism  $\alpha\mathbf{T}_3\mathbf{B}$  can be considered as *nonlinear* analogue of the  $\alpha\mathbf{T}_3\mathbf{A}$  light scattering mechanism, so successfully used in the collision-induced linear light scattering.<sup>30,35,36</sup>

The autocorrelation function

$$F_{LL}(t) = \langle \Delta\beta_L(0) \odot \Delta\beta_L(t) \rangle \quad (5)$$

is the key quantity required in the spectral analysis of the scattered light. We calculate the autocorrelation function Eq. (5) assuming that we consider one component fluid. The correlation function Eq. (5) generally deals with a situation when the rotational and translational degrees of freedom are coupled. However, when considering radiation scattered by low density gaseous systems we usually are justified in assuming that the molecules of the scattering volume are correlated radially but uncorrelated orientationally.<sup>30,35,36</sup> We use the notation

$$S_N(t) = \langle D_{00}^N(\delta\Omega_{12}(t)) R_{12}(0)^{-(N+1)} R_{12}(t)^{-(N+1)} \rangle, \quad (6)$$

$$R_j(t) = \langle D_{nn}^j(\delta\Omega(t)) \rangle, \quad (7)$$

where  $\delta\Omega(t)$  and  $\delta\Omega_{12}(t)$  denote the reorientation angles of the molecule and intermolecular vector, respectively, at the time  $t$ . According to our model we assume that the molecules of the system rotate freely. In this case the reorientational correlation function  $R_j(t) = \langle D_{nn}^j(\delta\Omega(t)) \rangle$  is independent of the magnetic quantum number  $n$  of the Wigner function involved,  $D_{nn}^j(\delta\Omega(t))$ . With this notation we have:

$$\langle \mathbf{T}_N^{(AB)}(0) \odot \mathbf{T}_N^{(AB)}(t) \rangle = \frac{(2N)!}{2^N} S_N(t), \quad (8)$$

$$\langle \mathbf{B}_j(0) \odot \mathbf{B}_j(t) \rangle = R_j(t) (\tilde{\mathbf{B}}_j \odot \tilde{\mathbf{B}}_j), \quad (9)$$

where  $\tilde{\mathbf{B}}_j$  denotes the dipole<sup>2</sup>-quadrupole hyperpolarizability tensor in its molecular frame reference system.

Using the irreducible spherical tensors decoupling procedure<sup>37</sup> for isotropic one component fluid we have:

$$\begin{aligned} \langle \alpha[\mathbf{T}_3^{(AB)}(0) \otimes \mathbf{B}_4(0)]_L \odot \alpha[\mathbf{T}_3^{(AB)}(t) \otimes \mathbf{B}_4(t)]_L \rangle \\ = \frac{(-1)^{(L+1)}(2L+1)}{63} \alpha^2 \langle \mathbf{T}_3^{(AB)}(0) \odot \mathbf{T}_3^{(AB)}(t) \rangle \\ \times \langle \mathbf{B}_4(0) \odot \mathbf{B}_4(t) \rangle \\ = (-1)^{(L+1)} \frac{10}{7} (2L+1) \alpha^2 (\tilde{\mathbf{B}}_4 \odot \tilde{\mathbf{B}}_4) S_3(t) R_0(t) R_4(t). \end{aligned} \quad (10)$$

We consider molecules of  $O_h$  symmetry in their nuclei equilibrium. Then the polarizability tensor  $\alpha$  is isotropic, whereas for the components of the dipole<sup>2</sup>-quadrupole tensor  $\mathbf{B}$ , the following relations hold<sup>38</sup>

$$\begin{aligned} \tilde{B}_{x,x,xx} = \tilde{B}_{y,y,yy} = \tilde{B}_{z,z,zz} = -2\tilde{B}_{x,x,yy} = -2\tilde{B}_{y,y,xx} \\ = -2\tilde{B}_{x,x,zz} = -2\tilde{B}_{z,z,xx} = -2\tilde{B}_{y,y,zz} \\ = -2\tilde{B}_{z,z,yy} = B_1, \end{aligned} \quad (11)$$

$$\hat{C}\tilde{B}_{x,y,xy} = \hat{C}\tilde{B}_{y,z,yz} = \hat{C}\tilde{B}_{x,z,xz} = B_2, \quad (12)$$

where the operator  $\hat{C}$  permutes the dipolar indices  $\alpha$  and  $\beta$  and quadrupolar pair of indices  $\gamma\delta$  of the tensor  $\tilde{B}_{\alpha,\beta,\gamma\delta}$ . The permutation within the pair  $\gamma\delta$  is also allowed. Taking into account Eqs. (11) and (12) we find the following relations between the molecule-frame irreducible spherical components of the dipole<sup>2</sup>-quadrupole tensor  $\tilde{B}_{jm}[(11)2a]$  and their Cartesian counterpart:

$$\tilde{B}_{00}[(11)22] = \sqrt{6/5}(B_1 + 2B_2),$$

$$\tilde{B}_{40}[(11)22] = \frac{\sqrt{7/15}(3B_1 - 4B_2)}{2},$$

$$\tilde{B}_{44}[(11)22] = \tilde{B}_{4-4}[(11)22] = \sqrt{5/14}\tilde{B}_{40}[(11)22]. \quad (13)$$

Using formulas (5)–(13) we calculate the respective time correlation functions of the hyper-Rayleigh scattered light:

$$\begin{aligned} F_{11}(t) &= \langle \Delta\beta_1[(11)21](0) \odot \Delta\beta_1[(11)21](t) \rangle \\ &= \frac{162}{35} \alpha^2 (3B_1 - 4B_2)^2 S_3(t) R_0(t) R_4(t), \end{aligned} \quad (14)$$

$$\begin{aligned} F_{33}(t) &= \langle \Delta\beta_3[(11)21](0) \odot \Delta\beta_3[(11)21](t) \rangle \\ &= \frac{66}{35} \alpha^2 (3B_1 - 4B_2)^2 S_3(t) R_0(t) R_4(t). \end{aligned} \quad (15)$$

### III. HYPER-RAYLEIGH LIGHT SCATTERING SPECTRUM

Consider a system of  $N$  molecules in a volume  $V$  on which is incident a linearly direction  $\mathbf{e}$  polarized light wave with the electric vector

$$\mathbf{E}^L(\mathbf{r}, t) = \mathbf{e} E_0^L \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega_L t)\}. \quad (16)$$

Then the time correlation function of hyper-Rayleigh scattered light analyzed at the point  $\mathbf{R} = \mathbf{k}_s$   $R$  (of the wave zone  $R \gg \lambda_0$ ) with an analyzer transmitting waves with polarization  $\mathbf{n}$  ( $\mathbf{n} \perp \mathbf{k}_s$ ) is of the form<sup>14</sup>

$$I_{\mathbf{n}}(t) = A^{2\omega} \left\{ \frac{8(\mathbf{n} \cdot \mathbf{e})^2 + 1}{45} F_{11}(t) + \frac{2(\mathbf{n} \cdot \mathbf{e})^2 + 4}{105} F_{33}(t) \right\} \quad (17)$$

when the factor  $A^{2\omega}$  contains  $\omega_s^4$  (where  $\omega_s$  is the scattered frequency) and  $\langle |E^L(0)E^L(t)|^2 \rangle$  in addition to other quantities.<sup>13</sup> In order to get spectral distribution of HR scattered light we take the Fourier transform ( $\mathcal{F}_t$ ) of Eq. (17).

We assume right-angle light scattering geometry and incident beam polarized perpendicularly to the scattering plane. We calculate the frequency dependent depolarization ratio of HR scattering as a ratio of the horizontal component  $I_{VH}(\nu)$  (when  $\mathbf{n} \perp \mathbf{e}$ ) of scattered spectrum to its vertical component  $I_{VV}(\nu)$  (when  $\mathbf{n} \parallel \mathbf{e}$ ):

$$\eta(\nu) = \frac{I_{VH}(\nu)}{I_{VV}(\nu)}. \quad (18)$$

Taking into account Eqs. (14)–(17) we obtain

TABLE I. Numerical values of the sulphur-hexafluoride and carbon-tetrachloride polarizability and hyperpolarizabilities used in our calculations (polarizability and hyperpolarizability values are in atomic units a.u.).

	Sulphur-hexafluoride	Carbon-tetrachloride
$\alpha$	30.35 <sup>a</sup>	
$B_{zz,zz}$	−134 <sup>b</sup>	
$B_{xz,xz}$	−156 <sup>b</sup>	
$\beta$		11.0 <sup>c</sup>
$\Gamma(\text{cm}^{-1})$		4.6 <sup>d</sup>

<sup>a</sup>Reference 39.

<sup>b</sup>Reference 40.

<sup>c</sup>Reference 26.

<sup>d</sup>Reference 24.

$$\eta(\nu) = \frac{\mathcal{F}_t[\frac{1}{45} F_{11}(t) + \frac{4}{105} F_{33}(t)]}{\mathcal{F}_t[\frac{1}{5} F_{11}(t) + \frac{2}{35} F_{33}(t)]} = \frac{107}{633} = 0.169. \quad (19)$$

Since our spectrum results only from one light scattering mechanism the frequency dependent depolarization ratio is reduced to a constant. We note quite different value of this constant from the depolarization ratio equal to  $\frac{2}{3}$  for one-molecule HR scattering by molecules of tetrahedral symmetry (e.g.,  $\text{CCl}_4$ ).

It is interesting to note that in the case of octahedral molecules, another first order (in  $\mathbf{T}_N$ ) hyper-Rayleigh light scattering mechanism, due to second hyperpolarizability  $\gamma$  and permanent  $\text{SF}_6$  hexadecapole ( $\mathbf{Q}_4$ ) moment is possible:<sup>31</sup>

$$\begin{aligned} \Delta\beta_{LM}[(11)a1] &= -(1 + \mathcal{P}^{AB}) \sum_{\text{all but } L, M, a} (-1)^{j_A + L + N} \\ &\times \left( \frac{2^N}{(2L_A)!(2L_B)!} \right)^{1/2} \frac{X_{j_A N}}{X_{L L_A}} \\ &\times \{ \gamma_{j_A} [((11)a1) L L_A] \otimes [\mathbf{T}_N(\mathbf{R}_{AB})] \\ &\otimes \mathbf{Q}_{L_B}^{(L_A)} \}_{LM}. \end{aligned} \quad (20)$$

From the formula Eq. (20), however, it results that this  $\gamma\mathbf{T}_5\mathbf{Q}_4$  light scattering mechanism and the pair induced hyperpolarizability varies as  $R_{AB}^{-6}$  being therefore smaller by  $R_{AB}^{-2}$  than the now discussed  $\alpha\mathbf{T}_3\mathbf{B}$  hyper-Rayleigh light scattering mechanism in  $R_{AB}^{-4}$ . Consult the figure for estimated  $\gamma\mathbf{T}_5\mathbf{Q}_4$  contributions to HR  $\text{SF}_6$  spectrum.

### IV. COLLISION-INDUCED HYPER-RAYLEIGH SPECTRUM OF $\text{SF}_6$

Now using Eqs. (14)–(17) and the sulphur-hexafluoride ( $\text{SF}_6$ ) polarizability and hyperpolarizability values<sup>39</sup> as well as the  $\text{SF}_6$  potential data<sup>40</sup> we are in a position to compute the collision-induced spectrum for gaseous  $\text{SF}_6$ . The data used in our computations are collected in a Table I. Again the right-angle light scattering geometry is used. We compute the polarized component ( $\mathbf{n} \parallel \mathbf{e}$ )  $I_{VV}^{(2\omega_L)}(\Delta\omega)$  of the CI HR scattered spectrum:

$$I_{VV}^{(2\omega_L)}(\Delta\omega) = A^{2\omega} \frac{n}{2} \mathcal{F}_t \left[ \frac{1}{5} F_{11}(t) + \frac{2}{35} F_{33}(t) \right] \quad (21)$$

of SF<sub>6</sub> fluid at the molecular number density  $n = 25$  Amagat and at  $T = 294$  K.

When using spherical top wave functions for the evaluation of transition matrix elements, the Fourier transform of  $R_{j_1}(t)R_{j_2}(t)$  has the form:<sup>35</sup>

$$\begin{aligned} \mathcal{F}_t[R_{j_1}(t)R_{j_2}(t)] \\ = \frac{(2J_1+1)(2J_2+1)(2J'_1+1)(2J'_2+1)}{Z_1 Z_2} \\ \times \exp \left[ -\frac{(E_{J_1} + E_{J_2})}{k_B T} \right] \delta(\omega - \omega_{J_1 J_2 J'_1 J'_2}), \end{aligned} \quad (22)$$

where:

$$\begin{aligned} \omega_{J_1 J_2 J'_1 J'_2} = & -[J'_1(J'_1+1) + J'_2(J'_2+1) - J_1(J_1+1) \\ & - J_2(J_2+1)]B. \end{aligned} \quad (23)$$

$B$  is the rotational constant and  $Z_i$  denotes the rotational partition function. The selection rules have the following form:

$$\Delta J_1 = 0, \pm 1, \pm 2 \dots \pm j_1 \quad J_1 + J'_1 \geq j_1, \quad (24)$$

$$\Delta J_2 = 0, \pm 1, \pm 2 \dots \pm j_2 \quad J_2 + J'_2 \geq j_2. \quad (25)$$

We calculate the rotational part of our spectrum using Eqs. (22)–(25). To deal with the translational part  $S_N(t)$  of our spectrum we compute the zeroth, second and fourth translational spectral moments for the  $\alpha\mathbf{T}_3\mathbf{B}$  and  $\gamma\mathbf{T}_5\Phi$  HR light scattering mechanisms using the SF<sub>6</sub>–SF<sub>6</sub> intermolecular potentials discussed here. Then, we compute the Birnbaum–Cohen model profiles<sup>41</sup> for each HR light scattering mechanism involved and in turn convolute the rotational transitions with their corresponding translational ones. As a next step, we normalize our SF<sub>6</sub> collision-induced HR spectrum to the Lorentzian monomer HR spectrum of CCl<sub>4</sub>:<sup>24</sup>

$$I_{\parallel}^{(2\omega_L)}(\Delta\omega) = A^{2\omega} \frac{12}{35} \beta^2 \frac{1}{\pi} \frac{\Gamma}{(\Delta\omega)^2 + \Gamma^2} \quad (26)$$

with  $\Gamma$  denoting its half width at half maximum (HWHM). For normalization we take the spectrum Eq. (26) at  $\Delta\omega = 40$  cm<sup>−1</sup>. We note that our reference CCl<sub>4</sub> spectrum should be rather considered as a *model* spectrum resulting only from the permanent hyperpolarizability  $\beta$  of CCl<sub>4</sub> molecule. Moreover, in our considerations we assume that: (1) both CCl<sub>4</sub> and SF<sub>6</sub> spectra are calculated *per one molecule*; (2) local field corrections give the same contributions to both spectra considered.

Also we imply the same laser intensity for the SF<sub>6</sub> as well as for the CCl<sub>4</sub> HR light scattering experiments. In other words when calculating the normalized intensity factors,  $A^{2\omega}$  in Eqs. (21) and (26) mutually cancel. We then plot our normalized Stokes wing of the hyper-Rayleigh collision-induced spectrum

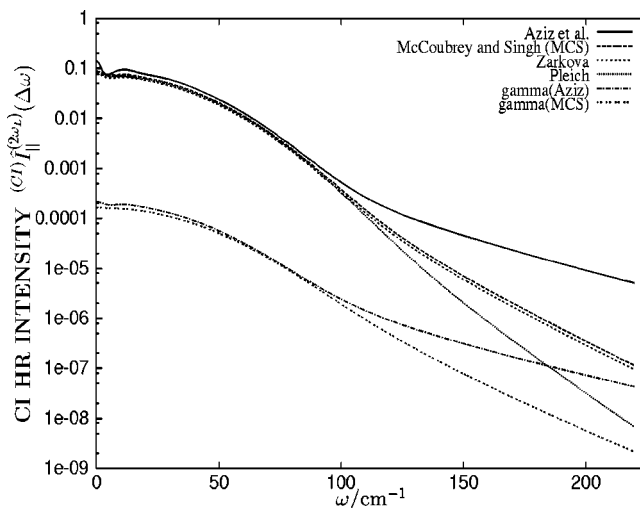


FIG. 1. Normalized collision-induced  $\alpha\mathbf{T}_3\mathbf{B}$  hyper-Rayleigh spectra  $(CI) I_{\parallel}^{(2\omega_L)}(\Delta\omega)$  of SF<sub>6</sub> for different intermolecular potentials. From top at 200 cm<sup>−1</sup> we plot the SF<sub>6</sub> spectra for the respective potentials, Aziz *et al.* (Ref. 43), McCoubrey and Singh (Ref. 44), Zarkova (Ref. 45), and Pleich (Ref. 46). Estimated normalized HR spectra due to  $\gamma\mathbf{T}_5\Phi$  light scattering mechanism are plotted as well, respectively, for Aziz *et al.* and McCoubrey and Singh potentials.

$$(CI) \hat{I}_{\parallel}^{(2\omega_L)}(\Delta\omega) = \frac{(CI) I_{\parallel}^{(2\omega_L)}(\Delta\omega)}{(CCl_4) I_{\parallel}^{(2\omega_L)}(40 \text{ cm}^{-1})} \quad (27)$$

in dimensionless units. Figure 1 shows the results of our computations. We note that for Aziz *et al.*<sup>42</sup> potential the computed HR spectral shape is quite different than for the other SF<sub>6</sub> potentials. When calculated per one molecule the HR collision-induced SF<sub>6</sub> spectrum at *zero* frequency is one order of magnitude smaller than our model the monomer HR spectrum (due to permanent hyperpolarizability of CCl<sub>4</sub>) at  $\Delta\omega = 40$  cm<sup>−1</sup>. Moreover we estimated the CI HR spectral contributions due to  $\gamma\mathbf{T}_5\Phi(Q_4 = \Phi)$  light scattering mechanism. For the same potential the  $\gamma\mathbf{T}_5\Phi$  contribution is more than 100 times smaller than  $\alpha\mathbf{T}_3\mathbf{B}$  HR light scattering spectrum. However when we consider the potential leading to a very steep spectrum (e.g., Pleich one) and the very flat spectrum given by the potential of Aziz *et al.* (Ref. 43) potential the  $\alpha\mathbf{T}_3\mathbf{B}$  contribution and the  $\gamma\mathbf{T}_5\Phi$  contribution cross at high frequency (about 180 cm<sup>−1</sup>) (see Fig. 1).

We computed as well the integrated normalized CI HR intensities. For Aziz *et al.*<sup>42</sup> potential the CI HR integrated intensity normalized to integrated CCl<sub>4</sub> intensity of Eq. (26) amounts to 0.0060, for McCoubrey and Singh potential<sup>43</sup> to 0.0054, for Zarkova potential to 0.0045 and for Pleich potential to 0.0048. The normalized CI HR integrated intensity due to  $\gamma\mathbf{T}_5\Phi$  light scattering mechanism for Aziz *et al.* potential equals 0.000 013 whereas the McCoubrey and Singh potential equals 0.000 011. We note that the integrated  $\gamma\mathbf{T}_5\Phi$  HR intensity amounts less than 0.2 percent of the intensity due to  $\alpha\mathbf{T}_3\mathbf{B}$  HR light scattering mechanism considered in this work.



## V. CONCLUSION

This paper presents a spectral theory for the pair collision-induced hyper-Rayleigh spectrum of centrosymmetric octahedral molecules. The long-range contribution to the pair hyperpolarizability, the dipole<sup>2</sup>-quadrupole  $\mathbf{B}^{(1+1+2)}$  term in  $R_{AB}^{-4}$  is discussed in detail and attributed to CI HR spectrum. We apply the results of our theoretical considerations to the case of SF<sub>6</sub>. Using our spectral hyper-Rayleigh light scattering formulas and the sulphur-hexafluoride polarizability and hyperpolarizability values as well as the SF<sub>6</sub> potential data, the sulphur-hexafluoride CI HR spectrum is computed. For the hyper-Rayleigh light scattering mechanism  $\alpha\mathbf{T}_3\mathbf{B}$  discussed, the frequency dependent depolarization ratio  $\eta(\nu)$  is reduced to a constant 107/633. We normalize our computed CI hyper-Rayleigh spectrum to the monomer HR spectrum of CCl<sub>4</sub> at 40 cm<sup>-1</sup>. Figure 1 shows an important potential's dependence of the collision-induced hyper-Rayleigh spectrum. The spectral contribution due to  $\gamma\mathbf{T}_3\mathbf{D}$  HR light scattering mechanism is estimated as well and showed to be negligible. Contemporary success in detecting very weak spectral signals (see e.g., Refs. 42 and 47) as well as the results of our computations throws a promising light on gaseous collision-induced experimental spectroscopy.

<sup>1</sup>P. A. M. Dirac, Proc. R. Soc. London, Ser. A **114**, 242,710 (1927).

<sup>2</sup>M. Goepfert-Mayer, Annalen der Physik **9**, 273 (1931).

<sup>3</sup>S. Kielich, Bull. Acad. Pol. Sci., Ser. Sci., Math., Astron. Phys. **12**, 53 (1964).

<sup>4</sup>S. Kielich, Acta Phys. Pol. **24**, 135 (1964).

<sup>5</sup>Y. Y. Li, Acta Phys. Sin. **20**, 164 (1964).

<sup>6</sup>S. J. Cyvin, J. E. Rauch, and J. C. Decius, J. Chem. Phys. **43**, 4083 (1965).

<sup>7</sup>R. W. Terhune, P. D. Maker, and C. M. Savage, Phys. Rev. Lett. **14**, 681 (1965).

<sup>8</sup>R. Bersohn, Y. H. Pao, and H. L. Frisch, J. Chem. Phys. **45**, 3184 (1966).

<sup>9</sup>P. D. Maker, Phys. Rev. A **1**, 923 (1970).

<sup>10</sup>W. Alexiewicz, T. Bancewicz, S. Kielich, and Z. Ożgo, J. Raman Spectrosc. **2**, 529 (1974).

<sup>11</sup>S. Kielich and M. Kozierowski, Acta Phys. Pol. A **45**, 231 (1974).

<sup>12</sup>K. Altman and G. Strey, J. Raman Spectrosc. **12**, 1 (1982).

<sup>13</sup>S. Kielich, Prog. Opt. **20**, 155 (1983).

<sup>14</sup>S. Kielich and T. Bancewicz, J. Raman Spectrosc. **21**, 791 (1990).

<sup>15</sup>T. Bancewicz and Z. Ożgo, in *Modern Nonlinear Optics*, Vol. 85 of *Advances in Chemical Physics*, edited by M. Evans and S. Kielich (Wiley, New York, 1993), pp. 89–126.

<sup>16</sup>K. Clays, A. Persoons, and L. DeMayer, in *Modern Nonlinear Optics*, Vol. 85 of *Advances in Chemical Physics*, edited by M. Evans and S. Kielich (Wiley, New York, 1993).

<sup>17</sup>S. Kielich, Physica (Amsterdam) **30**, 1717 (1964).

<sup>18</sup>S. N. Yaliraki and R. J. Silbey, J. Chem. Phys. **111**, 1561 (1999).

<sup>19</sup>D. P. Shelton and J. E. Rice, Chem. Rev. **94**, 3 (1994).

<sup>20</sup>J. Zyss and I. Ledoux, Chem. Rev. **94**, 77 (1994).

<sup>21</sup>K. Clays and A. Persoons, Phys. Rev. Lett. **66**, 2980 (1991).

<sup>22</sup>G. J. T. Hessink, A. G. T. Ruiter, N. F. van Hulst, and B. Bolger, Phys. Rev. Lett. **71**, 999 (1993).

<sup>23</sup>V. Ostroverkhov, R. G. Petschek, K. D. Singer, L. Sukhomlinova, R. J. Tweig, S.-X. Wang, and L. C. Chien, J. Opt. Soc. Am. B **17**, 1531 (2000).

<sup>24</sup>P. Kaatz and D. P. Shelton, Mol. Phys. **88**, 683 (1996).

<sup>25</sup>P. Kaatz and E. A. Donley, and D. P. Shelton, J. Chem. Phys. **108**, 849 (1998).

<sup>26</sup>R. D. Pyatt and D. P. Shelton, J. Chem. Phys. **114**, 9938 (2001).

<sup>27</sup>S. Kielich, J. R. Lalanne, and F. B. Martin, Phys. Rev. Lett. **26**, 1295 (1971).

<sup>28</sup>W. J. Schmid and H. W. Schrotter, Chem. Phys. Lett. **45**, 502 (1977).

<sup>29</sup>R. Samson and A. Ben-Reuven, J. Chem. Phys. **65**, 3586 (1976).

<sup>30</sup>A. D. Buckingham and G. C. Tabisz, Mol. Phys. **36**, 583 (1978).

<sup>31</sup>T. Bancewicz, J. Chem. Phys. **111**, 7440 (1999).

<sup>32</sup>D. A. Kleinman, Phys. Rev. **126**, 1977 (1962).

<sup>33</sup>A. D. Buckingham, Adv. Chem. Phys. **12**, 107 (1967).

<sup>34</sup>X. Li, K. L. C. Hunt, J. Pipin, and D. M. Bishop, J. Chem. Phys. **105**, 10954 (1996).

<sup>35</sup>H. Posch, Mol. Phys. **46**, 1213 (1982).

<sup>36</sup>A. Elliasmine, J.-L. Godet, Y. Le Duff, and T. Bancewicz, Mol. Phys. **90**, 147 (1997).

<sup>37</sup>D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Kvantovaya Teoriya Uglovogo Momenta* (Nauka, 1975).

<sup>38</sup>R. Zawodny, Ph.D. thesis, Poznań University, 1977.

<sup>39</sup>J. M. St-Arnaud and T. K. Bose, J. Chem. Phys. **71**, 4951 (1979).

<sup>40</sup>G. Maroulis, Chem. Phys. Lett. **312**, 255 (1999).

<sup>41</sup>N. Meinander, J. Chem. Phys. **99**, 8654 (1993).

<sup>42</sup>T. Bancewicz, Y. Le Duff, and J. L. Godet, in *Modern Nonlinear Optics, Part 1, 2nd ed.*, Vol. 119 of *Advances in Chemical Physics*, edited by M. Evans (Wiley, New York, 2002), Chap. Multipolar Polarizabilities from Interaction-Induced Raman Scattering, (in press).

<sup>43</sup>R. A. Aziz, M. J. Slaman, W. L. Taylor, and J. J. Hurly, J. Chem. Phys. **94**, 1034 (1991).

<sup>44</sup>J. C. McCoubrey and N. M. Singh, Trans. Faraday Soc. **55**, 1826 (1959).

<sup>45</sup>L. Zarkova, Mol. Phys. **88**, 489 (1996).

<sup>46</sup>R. Pleich, thesis, University of Vienna (Vienna, 1983).

<sup>47</sup>F. Rachet, M. Chrysos, C. Guillot-Noel, and Y. Le Duff, Phys. Rev. Lett. **84**, 2120 (2000).