

# Hyper-Raman scattering by chiral molecules

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A theory of hyper-Raman scattering by optically active molecules is presented. It is shown that scattering intensities depend on the helicity of the incident light: Expressions for the differential scattering intensities are derived taking into account electric dipole and quadrupole and magnetic dipole interactions. A helical box model is used to estimate circular differential scattering intensity ratios and depolarization ratios.

## I. INTRODUCTION

In a recent paper,<sup>1</sup> we presented a detailed theoretical analysis of the hyper-Raman effect with special emphasis on the selection rules and vibrational mode classification. We showed how, by collecting the hyper-Raman spectra in five different experimental arrangements, the symmetry species of each active mode could be assigned. In this paper, we discuss a new feature of the hyper-Raman effect which should be observable in chiral systems. Raman scattering experiments have already shown that chiral molecules scatter left- and right-circularly polarized photons at different rates.<sup>2</sup> These experiments usually involve irradiation with circularly polarized light and measurement of plane polarized components of the scattered light. The difference in scattered intensity resulting from a change in the handedness of the incident light, plotted against scattered frequency, is known as the circular differential Raman spectrum. An analogous effect can be expected in hyper-Raman scattering, and in this paper we derive expressions for the differential scattering intensities using quantum electrodynamics.

## II. THEORY

We begin by writing down the Hamiltonian for the dynamical system, comprising both the molecules and the radiation field, as

$$H = H_{\text{mol}} + H_{\text{rad}} + H_{\text{int}}, \quad (1)$$

$$M_{fi}(\beta) = -i[8\pi^3 \hbar^3 \omega^2 \omega' n(n-1)/V^3]^{1/2} e_i^{L/R} e_j^{L/R} e_k \langle \chi_{0N} | \beta_{ijk} | \chi_{0M} \rangle, \quad (5)$$

where

$$\beta_{ijk} = \frac{1}{2} \sum_{r,s} \left[ \frac{\mu_i^{0s} \mu_j^{sr} \mu_k^{r0}}{(E_{0s} + 2\hbar\omega)(E_{0r} + \hbar\omega)} + \frac{\mu_j^{0s} \mu_i^{sr} \mu_k^{r0}}{(E_{0s} - \hbar\omega)(E_{0r} + \hbar\omega)} + \frac{\mu_j^{0s} \mu_k^{sr} \mu_i^{r0}}{(E_{0s} - \hbar\omega)(E_{0r} - 2\hbar\omega)} \right. \\ \left. + \frac{\mu_i^{0s} \mu_k^{sr} \mu_j^{r0}}{(E_{0s} + 2\hbar\omega)(E_{0r} + \hbar\omega)} + \frac{\mu_k^{0s} \mu_i^{sr} \mu_j^{r0}}{(E_{0s} - \hbar\omega)(E_{0r} + \hbar\omega)} + \frac{\mu_k^{0s} \mu_j^{sr} \mu_i^{r0}}{(E_{0s} - \hbar\omega)(E_{0r} - 2\hbar\omega)} \right]. \quad (6)$$

In Eq. (5),  $n$  is the number of photons in the incident radiation mode,  $^{L/R}\mathbf{e}$  is the polarization vector of the circularly polarized incident light, and  $\mathbf{e}'$  that of the scattered light; since the "polarization tensor"  $e_i^{L/R} e_j^{L/R} e_k$  is  $j, k$  symmetric, the  $j, k$  symmetric form of  $\beta_{ijk}$  has been adopted. We have used the Born-Oppenheimer approximation to separate electronic and vibrational motions; the  $\beta$  tensor (6) thus contains electronic transition energies and transition moments;  $\chi_{0M}$  and  $\chi_{0N}$  are the vibrational wavefunctions of the initial and final states, respectively.

The  $J$  contribution to Eq. (4) is made up of two parts, one having the magnetic dipole interaction for emission and the other for absorption; we have

$$M_{fi}(J) = -i[8\pi^3 \hbar^3 \omega^2 \omega' n(n-1)/V^3]^{1/2} \{ (\mathbf{k}' \times \mathbf{e}')_i^{L/R} e_j^{L/R} e_k \langle \chi_{0N} | \alpha_{Jijk} | \chi_{0M} \rangle \mp i e_i^{L/R} e_j^{L/R} e_k \langle \chi_{0N} | \beta_{Jijk} | \chi_{0M} \rangle \}. \quad (7)$$

where the molecular Hamiltonian is known and the radiation field is second quantized. For  $H_{\text{int}}$ , we employ

$$H_{\text{int}} = - \sum_{\xi} [ \mu(\xi) \cdot \mathbf{e}^t(\mathbf{R}_{\xi}) + \mathbf{m}(\xi) \cdot \mathbf{b}(\mathbf{R}_{\xi}) + \mathbf{Q}(\xi) : \nabla \mathbf{e}^t(\mathbf{R}_{\xi}) ], \quad (2)$$

where  $\mu(\xi)$ ,  $\mathbf{m}(\xi)$ , and  $\mathbf{Q}(\xi)$  are the electric dipole, magnetic dipole, and electric quadrupole moment operators of molecule  $\xi$  located at  $\mathbf{R}_{\xi}$ , respectively;  $\mathbf{e}^t(\mathbf{R}_{\xi})$  and  $\mathbf{b}(\mathbf{R}_{\xi})$  are the transverse electric and magnetic field operators, respectively. For molecules in the gas phase or in dilute solution, the hyper-Raman scattering intensity may be written as a sum of the contributions from individual molecules, and we have<sup>1</sup>

$$I = \sum_{\xi} \frac{k'^3 V}{4\pi^2 \hbar} \langle | M_{fi}^{\xi} |^2 \rangle. \quad (3)$$

In Eq. (3),  $k' = \omega'/c$ ,  $V$  is the quantization volume, and the angular brackets denote rotational averaging. The matrix element  $M_{fi}^{\xi}$  for the hyper-Raman process is given by Eq. (2.5) of Ref. 1. It can be written approximately as a sum of three terms

$$M_{fi} = M_{fi}(\beta) + M_{fi}(J) + M_{fi}(K), \quad (4)$$

where we have suppressed the  $\xi$  dependence. The first term in Eq. (4) is the dominant contribution and involves three electric dipole interactions; the second and third terms are the leading corrections to  $M_{fi}(\beta)$ , involving two electric dipole interactions and either a magnetic dipole interaction [in  $M_{fi}(J)$ ] or an electric quadrupole interaction [in  $M_{fi}(K)$ ].

The  $M_{fi}(\beta)$  term is given by

The upper sign goes with left-handed polarization of the incident beam. Both  $J$  tensors are  $j, k$  symmetric; the six-term tensor  ${}^{\alpha}J_{ijk}$  is obtained from Eq. (6) by replacing  $\mu_i$  by  $m_i$ ;  ${}^{\beta}J_{ijk}$  is a 12-term tensor, six terms of which are obtained by replacing  $\mu_j$  by  $m_j$ , and the other six by replacing  $\mu_k$  by  $m_k$ .

The  $K$  contribution to Eq. (4) is obtained in a similar manner, and we have

$$M_{fi}(K) = [8\pi^3 \hbar^3 \omega^2 \omega' n(n-1)/V^3] e_i^{L/R} e_j^{L/R} e_k \\ \times \{k_i \langle \chi_{0N} | {}^{\beta}K_{ijk} | \chi_{0M} \rangle - k'_i \langle \chi_{0N} | {}^{\alpha}K_{ijk} | \chi_{0M} \rangle\}, \quad (8)$$

where  ${}^{\alpha}K_{ijk}$  and  ${}^{\beta}K_{ijk}$  are obtained from Eq. (6) in the same manner as the  $J$  tensors, with the corresponding substitutions  $\mu_i \rightarrow Q_{ii}$  and  $\mu_j \rightarrow Q_{jj}$ ,  $\mu_k \rightarrow Q_{kk}$ . Again, both  $K$  tensors are  $j, k$  symmetric; in addition,  ${}^{\alpha}K_{ijk}$  is  $i, l$  symmetric. It is interesting to note that similar  $K$  tensors can be important in second harmonic generation in centrosymmetric crystals.<sup>3,4</sup>

The scattering intensities now follow from Eqs. (3) and (4):

$$I = \frac{k'^3 V \mathfrak{N}}{4\pi^2 \hbar} \langle |M_{fi}(\beta) + M_{fi}(J) + M_{fi}(K)|^2 \rangle \\ \approx I(\beta^2) + I(\beta J) + I(\beta K), \quad (9)$$

where  $\mathfrak{N}$  is the number of molecules taking part in the scattering process,  $I(\beta^2)$  is the contribution from  $|M_{fi}(\beta)|^2$ , and the terms  $I(\beta J)$  and  $I(\beta K)$  arise from the  $\beta$ - $J$  and  $\beta$ - $K$  cross terms, respectively. They are as follows;

$$I(\beta^2) = \mathfrak{D} e_i^{L/R} e_j^{L/R} e_k e'_i{}^{R/L} e_m{}^{R/L} e_n \beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\rho}^{\text{NM}} I_{ijkilmnp}^{(6)}; \lambda\mu\nu\sigma\tau\rho, \quad (10)$$

$$I(\beta J) = -2\mathfrak{D} e_i^{L/R} e_j^{L/R} e_k{}^{R/L} e_m{}^{R/L} e_n \\ \times [(\hat{\mathbf{k}}' \times \mathbf{e}')_i \beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\sigma\tau\rho}^{\text{JNM}} \pm i e'_i \beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\rho}^{\text{JNM}}] I_{ijkilmnp}^{(6)}; \lambda\mu\nu\sigma\tau\rho, \quad (11)$$

$$I(\beta K) = 2i\mathfrak{D} e_i^{L/R} e_j^{L/R} e_k e'_i{}^{R/L} e_m{}^{R/L} e_n \\ \times (k_p \beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\rho}^{\text{KNM}} - k'_p \beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\sigma\tau\rho}^{\text{KNM}}) I_{ijkilmnp}^{(7)}; \lambda\mu\nu\sigma\tau\rho, \quad (12)$$

where  $\mathfrak{D}$  is defined by

$$a = -4 \text{Im}(4\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\mu\nu\lambda}^{\text{JNM}} - 6\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\nu\mu\lambda}^{\text{JNM}} - 5\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\lambda\nu\mu}^{\text{JNM}} + 4\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\nu\lambda\mu}^{\text{JNM}} + 11\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\lambda\mu\nu}^{\text{JNM}} - 6\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\mu\lambda\nu}^{\text{JNM}}) \\ + 2k(-4\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\rho}^{\text{KNM}} \epsilon_{\lambda\mu\sigma} + 2\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\nu\sigma\tau}^{\text{KNM}} \epsilon_{\lambda\mu\tau} + 6\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\nu}^{\text{KNM}} \epsilon_{\lambda\mu\tau} + 4\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\nu}^{\text{KNM}} \epsilon_{\lambda\mu\tau} - 5\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\mu\tau}^{\text{KNM}} \epsilon_{\lambda\sigma\tau} - 2\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\nu}^{\text{KNM}} \epsilon_{\lambda\sigma\tau}), \quad (16)$$

$$b = -28 \text{Im}(\beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\nu\mu\lambda}^{\text{JNM}} - \beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\mu\lambda\nu}^{\text{JNM}}) + 4k'(2\beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\sigma\tau\rho}^{\text{KNM}} \epsilon_{\lambda\mu\sigma} - 3\beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\sigma\tau\rho}^{\text{KNM}} \epsilon_{\lambda\mu\sigma} \\ - 6\beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\nu\sigma\tau}^{\text{KNM}} \epsilon_{\lambda\mu\tau} - 3\beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\sigma\tau\nu}^{\text{KNM}} \epsilon_{\lambda\sigma\tau} + 2\beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\sigma\tau\nu}^{\text{KNM}} \epsilon_{\lambda\sigma\tau}), \quad (17)$$

$$c = -2 \text{Im}(-12\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\mu\nu\lambda}^{\text{JNM}} + 18\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\nu\mu\lambda}^{\text{JNM}} + 8\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\lambda\nu\mu}^{\text{JNM}} - 12\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\nu\lambda\mu}^{\text{JNM}} - 12\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\lambda\mu\nu}^{\text{JNM}} + 18\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\mu\lambda\nu}^{\text{JNM}}) \\ + k(-2\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\rho}^{\text{KNM}} \epsilon_{\lambda\mu\sigma} + 8\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\nu\sigma\tau}^{\text{KNM}} \epsilon_{\lambda\mu\tau} - 4\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\nu}^{\text{KNM}} \epsilon_{\lambda\mu\tau} - 26\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\nu}^{\text{KNM}} \epsilon_{\lambda\mu\tau} \\ + 14\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\nu}^{\text{KNM}} \epsilon_{\lambda\sigma\tau} + \beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\nu}^{\text{KNM}} \epsilon_{\lambda\sigma\tau} - 8\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\sigma\tau\nu}^{\text{KNM}} \epsilon_{\lambda\sigma\tau}), \quad (18)$$

$$d = 2k'(-5\beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\sigma\tau\rho}^{\text{KNM}} \epsilon_{\lambda\mu\sigma} - 3\beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\sigma\tau\rho}^{\text{KNM}} \epsilon_{\lambda\mu\sigma} + 15\beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\sigma\tau\rho}^{\text{KNM}} \epsilon_{\lambda\mu\tau} - 3\beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\sigma\tau\nu}^{\text{KNM}} \epsilon_{\lambda\sigma\tau} - 5\beta_{\lambda\mu\nu}^{\text{NM}} \alpha_{\sigma\tau\nu}^{\text{KNM}} \epsilon_{\lambda\sigma\tau}), \quad (19)$$

$$f = 2(8\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\mu\nu\lambda}^{\text{NM}} - 6\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\nu\mu\lambda}^{\text{NM}} - 5\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\lambda\nu\mu}^{\text{NM}} + 11\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\nu\lambda\mu}^{\text{NM}} - 6\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\mu\lambda\nu}^{\text{NM}}), \quad (20)$$

$$g = 2(-12\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\mu\nu\lambda}^{\text{NM}} + 9\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\nu\mu\lambda}^{\text{NM}} + 4\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\lambda\nu\mu}^{\text{NM}} - 6\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\nu\lambda\mu}^{\text{NM}} + 9\beta_{\lambda\mu\nu}^{\text{NM}} \beta_{\mu\lambda\nu}^{\text{NM}}). \quad (21)$$

$$\mathfrak{D} = \frac{2\pi}{c} \mathfrak{N} k'^4 g^{(2)} \bar{I}_0^2, \quad (13)$$

and  $g^{(2)}$  and  $\bar{I}_0$  are the degree of second order coherence and mean irradiance of the incident beam, respectively. In deriving the above expressions, we have used the fact that, for real wavefunctions, the  $\beta$  and  $K$  tensors are real while the  $J$  tensors are imaginary. Also,  $\langle \chi_{0N} | \beta_{\lambda\mu\nu} | \chi_{0M} \rangle$  has been written as  $\beta_{\lambda\mu\nu}^{\text{NM}}$  with a similar shorthand notation for the  $J$  and  $K$  tensors. Explicit expressions for the sixth and seventh rank tensor rotational averages, denoted by  $I^{(6)}$  and  $I^{(7)}$ , respectively, are given elsewhere.<sup>5</sup>

### III. CIRCULAR INTENSITY DIFFERENTIAL RATIOS

The differential intensity of scattering is usually expressed in terms of a circular intensity differential ratio defined by

$$\Delta_{\mu}(\theta) = \frac{I_{\theta}(R-\mu) - I_{\theta}(L-\mu)}{I_{\theta}(R-\mu) + I_{\theta}(L-\mu)}, \quad (14)$$

where  $I_{\theta}(L/R-\mu)$  refers to the intensity of scattered light with polarization  $\mu$ , and  $L/R$  refers to left/right circularly polarized incident light;  $\theta$  is the convergence angle defined by  $\cos\theta = -\hat{\mathbf{k}} \cdot \hat{\mathbf{k}}'$ . In practice, scattered light is resolved into plane polarized components with polarization vectors  $\mathbf{e}^{\perp}$  and  $\mathbf{e}^{\parallel}$  normal to and lying in the scattering plane, respectively, such that  $\mathbf{e}^{\perp}$ ,  $\mathbf{e}^{\parallel}$ , and  $\hat{\mathbf{k}}'$  form a right-handed set.

The contribution to the scattered intensity arising from only electric dipole interactions  $I(\beta^2)$  is independent of the helicity of the incident light; the leading contributions to the numerator of Eq. (14) come from  $I(\beta J)$  and  $I(\beta K)$ . The intensity sum in the denominator of Eq. (14) is, however, essentially  $2I(\beta^2)$ . Using expressions (10)-(12), the differential ratio  $\Delta_{\parallel}(\theta)$  can now be written as

$$\Delta_{\parallel}(\theta) = \frac{a + b \cos\theta + c \cos^2\theta + d \cos^3\theta}{f + g \cos^2\theta}, \quad (15)$$

with

The result for the differential ratio  $\Delta_1(\theta)$  has a much simpler  $\theta$  dependence and may be expressed as

$$\Delta_1(\theta) = \frac{a + c + (b + d) \cos \theta}{f + g} \quad (22)$$

It is interesting to note that the  $\theta$  dependence for  $\Delta_1$  is similar in form to the corresponding Raman result.<sup>6</sup> For right-angled scattering, the circular differential ratios  $\Delta_\mu$  ( $\mu = \parallel, \perp$ ) do not have contributions from the  ${}^\alpha J$  and  ${}^\alpha K$  tensors.

We remark that the hyper-Raman results obtained in this section are easily adapted for hyper-Rayleigh circular differential scattering. For the latter case, the initial and final molecular states are identical and  $2|\mathbf{k}| = |\mathbf{k}'|$ . Thus, the molecular tensors  $\beta^{NM}$ ,  $J^{NM}$ , and  $K^{NM}$  are replaced by their electronic counterparts  $\beta$ ,  $J$ ,  $K$ ; in particular, the  $\beta^{NM}$  tensor becomes the well-known hyperpolarizability.

#### IV. MODEL CALCULATIONS

In this section, we use a helical box model to obtain estimates of hyper-Rayleigh differential ratios. A right-circular helix is defined by

$$\left. \begin{aligned} x &= a \cos \theta \\ y &= a \sin \theta \\ z &= b(\theta - \pi k) \end{aligned} \right\} 0 \leq \theta \leq 2\pi k, \quad (23)$$

where  $a$  is the cylindrical radius of the helix,  $2\pi b$  is the pitch, and  $k$  is the number of turns. The length of the helix is

$$L = 2\pi k(a^2 + b^2)^{1/2}. \quad (24)$$

The wavefunctions for the energy levels of a particle in a helical box have been described previously.<sup>7</sup> They involve a new system of coordinates  $(s, \eta, \zeta)$  describing a point near the helix:

$$\left. \begin{aligned} x &= (a - \eta) \cos \theta + \frac{b}{(a^2 + b^2)^{1/2}} \zeta \sin \theta \\ y &= (a - \eta) \sin \theta - \frac{b}{(a^2 + b^2)^{1/2}} \zeta \cos \theta \\ z &= b(\theta - \pi k) + \frac{a}{(a^2 + b^2)^{1/2}} \zeta \\ \theta &= \frac{s}{(a^2 + b^2)^{1/2}} \end{aligned} \right\} \quad (25)$$

$$\theta = \frac{s}{(a^2 + b^2)^{1/2}} \quad (26)$$

Here,  $s$  measures the distance along the curve;  $\eta$  and  $\zeta$  measure the components along the normal and binormal, respectively. The corresponding momentum operators in terms of  $(s, \eta, \zeta)$  have been given by Craig, Power, and Thirunamachandran.<sup>8</sup>

For the potential box with cross section  $\epsilon^2$ , such that  $V=0$  for  $|\eta| < \frac{1}{2}\epsilon$ ,  $|\zeta| < \frac{1}{2}\epsilon$ , and  $s < L$ , and  $V=\infty$  elsewhere, wavefunctions correct to order  $\epsilon^{-2}$  are

$$\psi_{mm'n} = \frac{2}{\epsilon} \sqrt{\frac{2}{L}} \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} \frac{m\pi\eta}{\epsilon} \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} \frac{m'\pi\zeta}{\epsilon} \sin \frac{n\pi s}{L}, \quad (27)$$

where  $m$  and  $m'$  are the quantum numbers for the transverse  $(\eta, \zeta)$  motion and  $n$  for the longitudinal  $(s)$  motion. The corresponding energies are

$$E_{mm'n} = \frac{\hbar^2 \pi^2}{2m_e} \left( \frac{m^2}{\epsilon^2} + \frac{m'^2}{\epsilon^2} + \frac{n^2}{L^2} \right). \quad (28)$$

Since  $\epsilon \ll L$ , low-energy transitions involve changes in the  $n$  quantum number only. In studies of optical activity, the particle in a helical box model has been used to represent the  $\pi$ -electron energy levels of the chiral molecule phenanthrophenanthrene, also known as hexahelicene.<sup>8,9</sup> We have performed calculations on the same basis. Phenanthrophenanthrene has 26  $\pi$  electrons so that  $n=13$  corresponds to the highest occupied level in the ground state. Using the crystallographic results of Mackay, Robertson, and Sime,<sup>10</sup> we have  $2\pi b = 0.305$  nm. By fitting the absorption at  $31\,400$   $\text{cm}^{-1}$  to the 14–13 transition, the radius  $a$  is found to be 0.252 nm;  $k$  is taken to be unity. For our calculations of the hyperpolarizability and other tensor components, we have assumed a value of 700 nm for the wavelength of the incident light. The summations over the intermediate states were carried out with an increasing number of levels until convergence was ensured. The hyperpolarizability components are found to have values of about  $10^{-30}$   $\text{esu}^{-1} \text{cm}^5$ , as expected for real molecular systems. An increase by up to three orders of magnitude can be expected under near-resonant conditions.

For right-angled scattering, we find that the circular intensity differential ratios are  $\Delta_\parallel = 1.24 \times 10^{-2}$  and  $\Delta_\perp = 7.49 \times 10^{-3}$ , which are noticeably larger than the corresponding Rayleigh values  $\Delta_\parallel = 1.59 \times 10^{-4}$  and  $\Delta_\perp = -4.27 \times 10^{-4}$ . In addition to calculating these differential ratios, we have used this model to calculate hyper-Rayleigh depolarization ratios using the formulas given in our previous paper<sup>1</sup>  $\rho_\perp = 0.425$  and  $\rho_u(\pi/2) = 0.596$ . These may be compared with the values obtained from the formulas of Cyvin, Rauch, and Decius<sup>11</sup>  $\rho_\perp = 0.499$  and  $\rho_u(\pi/2) = 0.666$ . The difference between the  $\rho_\perp$  values arises from the assumption of full index symmetry for the  $\beta$  tensor in their formulas. On the other hand, their formula for  $\rho_u$  is based on the use of the conventional relation  $\rho_u(\pi/2) = 2\rho_\perp(1 + \rho_\perp)$  which, as we have shown elsewhere,<sup>12</sup> is inapplicable to nonlinear scattering processes. Hence, the two values for  $\rho_u$  are not strictly comparable.

#### V. CONCLUSION

Since the hyper-Raman effect is a nonlinear process, the scattering intensities are generally weak, and high intensity sources are required for recording spectra. However, with a judicious choice of incident frequency, it is possible to approach near-resonant conditions making the  $\beta$  tensor greater in magnitude, and thus lead to a substantial increase in the scattered intensity. With recent advances in laser technology, hyper-Raman spectroscopy should be a useful complement to the more conventional forms of vibrational spectroscopy. In particular, measurement of the circular differential scattering by large chiral molecules should provide valuable

new information on the chiral environment of their functional groups.

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