

Symmetric and Non-Symmetric Hyper-Raman Scattering: Its Polarization States and Angular Dependences*

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A theory of three-photon (hyper-Raman and hyper-Rayleigh) scattering is proposed using the approach of irreducible Cartesian and spherical tensors. A general expression for the intensity-time correlation function of symmetric, non-symmetric and symmetric-non-symmetric three-photon scattering is derived in terms of separated, irreducible field- and molecular-rotational invariants. The occurrence of the various types of scattering is dependent on the physical conditions, i.e. on the molecular symmetry and the ratio of the light frequency and molecular frequency. The (general) number of five irreducible molecular-rotation and field invariants can undergo a reduction under appropriately chosen experimental and model conditions. The expressions for the intensity function hold for arbitrary (e.g. elliptical) states of light polarization and angular distributions. In particular, they are applied to linear and circular polarization. On their basis, equations are derived for the depolarization ratio and reversal coefficient of hyper-Raman and hyper-Rayleigh scattering.

INTRODUCTION

When a molecule is in the electric field of a light beam with a high density of photons, there is a by no means negligible probability for the occurrence of three-photon scattering: the molecule 'absorbs' simultaneously two photons (of circular frequency ω) and 'emits' a photon with doubled frequency $\omega_3 = 2\omega$ in a process of spontaneous elastic three-photon scattering, referred to as hyper-Rayleigh scattering. If, in the process, the molecule undergoes a transition from its initial quantum state $|i\rangle$ to a final state $\langle f|$ with the transition frequency ω_{fi} , we have inelastic three-photon scattering at the vibration frequency $\omega_s = 2\omega \mp \omega_{fi}$, referred to as hyper-Raman scattering.

The earliest experiment ensuring non-linear three-photon light scattering from molecular liquids is due to Terhune *et al.*,¹ who used the beam of a ruby laser. In addition to elastic non-linear (hyper-Rayleigh) scattering, they observed inelastic three-photon (hyper-Raman) scattering. Cyvin *et al.*² showed that the selection rules for vibrational hyper-Raman scattering differ from those for infrared and the usual Raman scattering, the polarizability theory of which is due to Placzek.³ The foundations of the quantum-mechanical theory of hyper-Raman scattering⁴⁻⁷ were established and various theoretical⁸⁻¹⁷ and experimental¹⁸⁻²⁵ aspects of this novel type of scattering were studied. The achievements in this new branch of non-linear molecular spectroscopy have been discussed in several reviews.²⁶⁻³⁰

In this paper it is our aim to give a complete mathematical description of three-photon scattering on the basis of irreducible tensors, both Cartesian and spherical (Racah algebra). The formalism applied will permit

the expression of the intensity components of three-photon scattering in terms of the respective irreducible molecular-rotational and geometrical-field invariants. This will enable us to separate the symmetric, non-symmetric and mixed symmetric-non-symmetric parts. Our results are generalizations of the partial results obtained hitherto.^{9,10,12,17,28-31}

FOUNDATIONS OF THE THEORY

Consider a system of N molecules in a volume V on which is incident a light wave with electric vector

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{e}E_0 \exp \{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} \quad (1)$$

at the space-time point (\mathbf{r}, t) and of frequency ω , propagation vector \mathbf{k} and polarization vector \mathbf{e} .

We define as follows the intensity-time correlation function of scattered light analysed at the point $\mathbf{R} = \mathbf{k}_s R$ (of the wave zone $R \gg \lambda_0$) with an analyser transmitting waves with polarization $\mathbf{n}(\mathbf{n} \perp \mathbf{k}_s)$:

$$I_{\mathbf{n}}(t) = \frac{1}{2c^4} \left\langle \sum_{p,q}^N [\mathbf{n}^* \cdot \mathbf{m}_p(t_0) \mathbf{m}_q(t_0 + t)^* \cdot \mathbf{n}] \right\rangle \quad (2)$$

where $\mathbf{m}_p(t)$ is the electric dipole moment induced in a molecule p at the moment of time t_0 , and the symbol $\langle \rangle$ represents appropriate statistical averaging over the positions and orientations of the molecules.

If the field strength $\mathbf{E}(t)$ is sufficiently great (although still unable to cause optical breakdown), the dipole moment induced can be expressed by the series

$$\mathbf{m}_p(t) = \mathbf{m}_p^{(1)}(t) + \mathbf{m}_p^{(2)}(t) + \mathbf{m}_p^{(3)}(t) + \dots \quad (3)$$

where the first component of the sum describes normal (linear) light scattering and the other components describe non-linear scattering.

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Here, we are interested in non-linear scattering of the second order given by the expression

$$\mathbf{m}_p^{(2)}(t) = \frac{1}{2} \beta_p : \mathbf{E}(t)\mathbf{E}(t) \quad (4)$$

where $\beta_p = \beta_{IJK}^{(p)}$ is a tensor of the third rank describing the non-linear polarizability of the second order (the hyperpolarizability) of molecule p .

Placzek³ has shown that the polarizability of a molecule is not constant in time but is subject to different changes caused by vibrations of its nuclei. Thus, molecular polarizabilities are functions of the normal vibrations

$$Q_v(t) = Q_{0v} \cos(\omega_v t + \phi_v) \quad (5)$$

where Q_{0v} and ω_v are the amplitude and frequency, respectively, of the v th normal vibration.

For small harmonic vibrations we can write, in Placzek's approximation, the following expansion:⁴

$$\beta_p(Q) = \beta_p(0) + \sum_v \left(\frac{\partial \beta_p}{\partial Q_v} \right)_0 Q_v + \dots \quad (6)$$

where the tensor $\beta_p(0)$ is the hyperpolarizability when the normal vibrations are in their equilibrium positions.

From Eqns (2) and (4), we have for the intensity correlation function (2) of second-order (second-harmonic) scattering

$$I_n^{(2)}(t) = A^{2\omega} \left\langle \sum_{p,q}^N [\mathbf{W} : \beta_p(t_0)] \times [\mathbf{W} : \beta_q(t_0 + t)]^* \exp[i\mathbf{k} \cdot \mathbf{R}(t)] \right\rangle \quad (7)$$

where $\mathbf{k} = \mathbf{k}_s - 2\mathbf{k}$, $\mathbf{R}(t) = \mathbf{R}_p(0) - \mathbf{R}_q(t)$ and we have introduced the tensor (triad)

$$\mathbf{W} = \mathbf{n}^* \mathbf{e} \mathbf{e} \quad (8)$$

constructed with the unit polarization vectors of the incident and scattered fields. The factor $A^{2\omega}$ contains ω_s^4 and $\langle |E(0)E(t)|^2 \rangle$ in addition to other quantities.²⁹

Making use of the Rayleigh expansion³² of the interference factor

$$\exp[i\mathbf{k} \cdot \mathbf{R}(t)] = 4\pi \sum_{l=0}^{\infty} i^l j_l[\kappa R(t)] \times (\mathbf{Y}^{(l)}(\hat{\mathbf{k}}) \odot \mathbf{Y}^{(l)}[\hat{\mathbf{R}}(t)]) \quad (9)$$

and expressing the internal product $\mathbf{W} : \beta$ in terms of the sum of scalar products of the irreducible parts^{13,33,34} of \mathbf{W} and β :

$$\mathbf{W} : \beta = W_{IJK} \beta_{IJK} = \sum_{s,J} (\mathbf{W}^{(s,J)} \odot \beta^{(s,J)}) \quad (10)$$

where J is the rank of the irreducible tensor and s is an index describing its permutational symmetry, we transform Eqn (7) to

$$I_n^{(2)}(t) = A^{2\omega} 4\pi \left\langle \sum_{\substack{p,q,s_1,s_2 \\ J_1,J_2,l}} i^l j_l[\kappa R(t)] (\mathbf{W}^{(s_1,J_1)} \odot \beta_{p,0}^{(s_1,J_1)})(\mathbf{W}^{(s_2,J_2)} \odot \beta_{q,t}^{(s_2,J_2)})^* \times (\mathbf{Y}^{(l)}(\hat{\mathbf{k}}) \odot \mathbf{Y}^{(l)}[\hat{\mathbf{R}}(t)]) \right\rangle \quad (11)$$

Equation (11) gives the autocorrelation function of the scattered light which, for $t = 0$, expresses its integral intensity. Here, we propose equations for hyper-Rayleigh scattering. For hyper-Raman scattering due to very weak correlations of the normal vibrations of different molecules, the coherent part (when $p \neq q$) of the intensity Eqns (7) and (11) is negligible.³⁵ Moreover, for hyper-Raman scattering, the hyperpolarizability tensors of Eqn (7) denote the derivative of β over the appropriate normal vibration Q_v [Eqn (6)].

On applying the rules governing changes in the coupling scheme of irreducible spherical tensors,³² it is readily found that, in particular,³⁶

$$(\mathbf{A}^{(a)} \odot \mathbf{B}^{(a)})(\mathbf{C}^{(c)} \odot \mathbf{D}^{(c)})(\mathbf{E}^{(e)} \odot \mathbf{F}^{(e)}) = \sum_{g,h} \{[(\mathbf{A}^{(a)} \otimes \mathbf{C}^{(c)})^{(g)} \otimes \mathbf{E}^{(e)}]^{(h)} \odot [(\mathbf{B}^{(a)} \otimes \mathbf{D}^{(c)})^{(g)} \otimes \mathbf{F}^{(e)}]^{(h)}\} \quad (12)$$

where \odot represents a scalar product and \otimes an irreducible tensorial product.

The transformation (12) enables us to separate, in Eqn (11), the factors which are dependent on the geometry of the experimental set-up from those which originate in the properties of the molecular system. Obviously, the expression accounting for the geometry requires no averaging. We thus write

$$I_n^{(2)}(t) = A^{2\omega} 4\pi \sum_{\substack{s_1,s_2,J_1 \\ J_2,J_3,J,l}} i^l \left\{ [(\mathbf{W}^{(s_1,J_1)} \otimes \mathbf{W}^{(s_2,J_2)})^{(J_3)} \otimes \mathbf{Y}^{(l)}(\hat{\mathbf{k}})]^{(J)} \odot \left\langle \sum_{p,q} j_l[\kappa R(t)] [(\beta_{p,0}^{(s_1,J_1)} \otimes \beta_{q,t}^{(s_2,J_2)})^{(J_3)} \otimes \mathbf{Y}^{(l)}[\hat{\mathbf{R}}(t)]]^{(J)} \right\rangle \right\} \quad (13)$$

For an isotropic fluid the mean value occurring in Eqn (13) has to be a rotational invariant.³⁶ Hence, in Eqn (13), only the terms with $J = 0$ differ from zero. This greatly simplifies our further considerations. Each of the terms of the expansion for the scattered light intensity can now be written as the product of a geometrical-field factor dependent on the experimental set-up:

$$\phi_{s_1 J_1 s_2 J_2}^{(l)} = i^l \sqrt{\frac{4\pi}{(2l+1)(2J_1+1)}} [(\mathbf{W}^{(s_1,J_1)} \otimes \mathbf{W}^{(s_2,J_2)})^{(l)} \odot \mathbf{Y}^{(l)}(\hat{\mathbf{k}})] \quad (14a)$$

and a molecular factor dependent on the properties of the individual scatterers and the medium as a whole:

$$F_{s_1 J_1 s_2 J_2}^l(t) = \sqrt{\frac{4\pi(2J_1+1)}{2l+1}} \times \left\langle \sum_{p,q} j_l[\kappa R(t)] \{ [\beta_{p,0}^{(s_1,J_1)} \otimes \beta_{q,t}^{(s_2,J_2)}]^{(l)} \odot \mathbf{Y}^{(l)}[\hat{\mathbf{R}}(t)] \} \right\rangle \quad (14b)$$

The scattered light intensity is the sum (13) of the respective components. The number of the latter depends on the range of variability of s_1, J_1, s_2, J_2 and l . The hyperpolarizability tensor β_{IJK} responsible for second-harmonic scattering, like the tensor W_{IJK} constructed with the polarization vectors (Eqn (8)), is sym-

metric in its last two indices: $\beta_{IJK} = \beta_{IKJ}$. In the irreducible representation such tensors have components of the first, second and third rank. Hence, J_1 and J_2 of Eqn (14) can assume the values 1, 2 or 3. The range of variability of l is limited by the triangular relationship, whence $l \leq 6$. The terms with $l = 0$ describe the scattering due to fluctuations in molecular orientations only. If $l \neq 0$, fluctuations in molecular positions are also active in the scattering process, and the respective expressions describe coupling between the rotational and translational motions of the molecules of the liquid. It follows from Eqn (14b) that fluctuations in positions alone, which lead to Rayleigh-Brillouin scattering in the linear case, cannot be a source of second-harmonic scattering (for the lack of a term with $J_1 = J_2 = 0$).

Second-harmonic scattering is predominantly the result of fluctuations in molecular orientation. The terms accounting for coupling between rotational and translational motion are considerably smaller and are responsible for the fine structure of the spectral line of hyper-scattering. Here, we shall restrict our considerations to second-harmonic scattering due to fluctuations in orientation alone, i.e. to the case when $l = 0$. The geometrical-field factor now reduces to

$$\phi_{s_1 J_1 s_2 J_2}^0 = \frac{1}{2J_1 + 1} (\mathbf{W}^{(s_1, J_1)} \odot \mathbf{W}^{(s_2, J_2)})^* \delta_{J_1 J_2} \quad (15a)$$

whereas the molecular factor takes the form

$$F_{s_1 J_1 s_2 J_2}^0(t) = \left\langle \sum_{p, q} j_0[\kappa R(t)] (\beta_{p, 0}^{(s_1, J_1)} \odot \beta_{q, t}^{(s_2, J_2)})^* \right\rangle \delta_{J_1 J_2} \quad (15b)$$

In Eqn (15b) and henceforth, the hyperpolarizability tensors should be expressed in the molecular frame. We accordingly denote this by small lower-case indices as β_{ijk} .

THE POLARIZATION STATE AND ANGULAR DISTRIBUTION OF SCATTERED LIGHT

Although in our further calculations we could make use of methods of the algebra of spherical tensors, the analysis, particularly that of the field-geometrical factor, simplifies considerably if one notes that the scalar products of irreducible spherical tensors occurring in Eqn (15) can be represented in terms of internal products of the irreducible Cartesian tensors²⁸ W_{IJK} and β_{ijk} , respectively:

$$(\mathbf{W}^{(s, J)} \odot \mathbf{W}^{(s, J)})^* = W_{IJK}^{(s, J)} W_{IJK}^{(s, J)*} \quad (16a)$$

$$(\beta^{(s, J)} \odot \beta^{(s, J)})^* = \beta_{ijk}^{(s, J)} \beta_{ijk}^{(s, J)*} \quad (16b)$$

When decomposing a Cartesian tensor T_{ijk} , symmetric in its last two indices, into its irreducible terms $T_{ijk}^{(s, J)}$, one readily finds¹¹ that one has two linearly independent terms of the first rank ($J = 1$), a single term of the second rank ($J = 2$) and a single term of the third rank ($J = 3$). Obviously, the third-rank term $T_{ijk}^{(3, 3)}$, equal in

rank to the tensor T_{ijk} itself, is completely symmetric. Separation of two linearly independent first-rank terms is not unique. Here, we shall separate the completely symmetric part:

$$T_{ijk}^{(s, 1)} = \frac{1}{15} [\delta_{ij}(2T_{nnk} + T_{knn}) + \delta_{ik}(2T_{nnj} + T_{jnn}) + \delta_{jk}(2T_{nni} + T_{inn})] \quad (17)$$

and the non-symmetric 'remainder':

$$T_{ijk}^{(N, 1)} = \frac{1}{6} [\delta_{ij}(T_{nnk} - T_{knn}) + \delta_{ik}(T_{nnj} - T_{jnn}) - 2\delta_{jk}(T_{nni} - T_{inn})] \quad (18)$$

Clearly, the tensor $T_{ijk}^{(N, 1)}$ is still symmetric in its last two indices, and so is the irreducible second rank tensor $T_{ijk}^{(s, 2)}$. Thus, among the irreducible Cartesian tensors we are confronted with two possibilities with regard to their permutational symmetry:

(1) complete permutational symmetry—we denote this case by $s = 1$;

(2) symmetry in the last two indices—to be denoted as $s = 2$.

Equations (16) are valid in the case of the scalar product of two irreducible tensors of the same rank possessing the same permutational symmetry s . The occurrence of two linearly independent first-rank irreducible tensors differing as to their permutational symmetry leads to the emergence of mixed products of the type

$$(\mathbf{T}^{(1, 1)} \odot \mathbf{T}^{(2, 1)}) \quad (19)$$

As stated above, in calculating this scalar product we are unable to make use of Eqn (16). If, however, the form of the irreducible components of the spherical tensors $T_{\alpha}^{(1, 1)}$ and $T_{\alpha}^{(2, 1)}$ is known^{28, 37} as a function of T_{ijk} , the required scalar products can be calculated directly from the definition of the scalar product in spherical coordinates:

$$(\mathbf{T}^{(1, 1)} \odot \mathbf{T}^{(2, 1)}) = \sum_{\alpha} T_{\alpha}^{(1, 1)} (T_{\alpha}^{(2, 1)})^* \quad (20)$$

The autocorrelation function of the scattered radiation can now be written in the following form:

$$I_{\mathbf{n}}^{(2)}(t) = A^{2\omega} \sum_{\substack{J_1 = J_2 = 1; s_1, s_2 = 1, 2 \\ J_1 = J_2 = 2; s_1 = s_2 = 2 \\ J_1 = J_2 = 3; s_1 = s_2 = 1}} \phi_{s_1 J_1 s_2 J_2} F_{s_1 J_1 s_2 J_2}^0(t) \quad (21)$$

as the sum of six terms, four of which are 'quadratic', $J_1 = J_2 = 1, s_1 = s_2 = 1$; $J_1 = J_2 = 1, s_1 = s_2 = 2$; $J_1 = J_2 = 2, s_1 = s_2 = 2$; $J_1 = J_2 = 3, s_1 = s_2 = 1$, and two mixed, $J_1 = J_2 = 1, s_1 = 1, s_2 = 2$ and $J_1 = J_2 = 1, s_1 = 2, s_2 = 1$. We shall calculate the geometrical factors $\phi_{s_1 J_1 s_2 J_2}^0$ determining the angular dependence of each of the above terms, in addition to the molecular factors $F_{s_1 J_1 s_2 J_2}^0(t)$ corresponding thereto. For brevity, we shall henceforth omit the subscripts $p, 0$ on the tensors β_{ijk} related to the p th molecule at the moment of time $t = 0$. The fact that a tensor β_{ijk} refers to a molecule q at a moment of time t will be denoted by a bar over β ; thus $\bar{\beta}_{ijk} = \beta_{ijk}^*(q, t)$. Moreover, we shall assume that the range of the intermolecular correlations is much shorter than the wavelength of the scattered radiation:

$j_0[\kappa R(t)] \approx 1$. We thus have $((\mathbf{n} \cdot \mathbf{n}^*) = (\mathbf{e} \cdot \mathbf{e}^*) = 1)$:

$$\begin{aligned} \phi_{1111}^0 &= \frac{1}{45} \{4(\mathbf{n}^* \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e}^*) + (\mathbf{e} \cdot \mathbf{e})(\mathbf{e}^* \cdot \mathbf{e}^*) \\ &\quad + 2(\mathbf{n}^* \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e})(\mathbf{e}^* \cdot \mathbf{e}^*) \\ &\quad + 2(\mathbf{n}^* \cdot \mathbf{e}^*)(\mathbf{n} \cdot \mathbf{e}^*)(\mathbf{e} \cdot \mathbf{e})\} \end{aligned} \quad (22a)$$

$$\begin{aligned} F_{1111}^0(t) &= \frac{1}{15} \langle 4\beta_{ij}\bar{\beta}_{kkj} + 2\beta_{ij}\bar{\beta}_{jkk} \\ &\quad + 2\beta_{ij}\bar{\beta}_{kki} + \beta_{ij}\bar{\beta}_{ikk} \rangle \end{aligned} \quad (22b)$$

$$\begin{aligned} \phi_{2121}^0 &= \frac{1}{9} \{(\mathbf{e} \cdot \mathbf{e})(\mathbf{e}^* \cdot \mathbf{e}^*) + (\mathbf{n}^* \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e}^*) \\ &\quad - (\mathbf{n}^* \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e})(\mathbf{e}^* \cdot \mathbf{e}^*) \\ &\quad - (\mathbf{n} \cdot \mathbf{e}^*)(\mathbf{n}^* \cdot \mathbf{e}^*)(\mathbf{e} \cdot \mathbf{e})\} \end{aligned} \quad (23a)$$

$$\begin{aligned} F_{2121}^0(t) &= \frac{1}{3} \langle \beta_{ij}\bar{\beta}_{kkj} - \beta_{ij}\bar{\beta}_{jkk} \\ &\quad - \beta_{ij}\bar{\beta}_{kki} + \beta_{ij}\bar{\beta}_{ikk} \rangle \end{aligned} \quad (23b)$$

$$\begin{aligned} \phi_{2111}^0 &= \frac{(5)^{1/2}}{45} \{(\mathbf{e} \cdot \mathbf{e})(\mathbf{e}^* \cdot \mathbf{e}^*) - 2(\mathbf{n}^* \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e}^*) \\ &\quad + 2(\mathbf{n}^* \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e})(\mathbf{e}^* \cdot \mathbf{e}^*) \\ &\quad - (\mathbf{n}^* \cdot \mathbf{e}^*)(\mathbf{n} \cdot \mathbf{e}^*)(\mathbf{e} \cdot \mathbf{e})\} \end{aligned} \quad (24a)$$

$$\begin{aligned} F_{2111}^0(t) &= \frac{(5)^{1/2}}{15} \langle \beta_{ij}\bar{\beta}_{ikk} - \beta_{ij}\bar{\beta}_{jkk} \\ &\quad + 2\beta_{ij}\bar{\beta}_{kki} - 2\beta_{ij}\bar{\beta}_{kkj} \rangle \end{aligned} \quad (24b)$$

$$\begin{aligned} \phi_{1121}^0 &= \frac{(5)^{1/2}}{45} \{(\mathbf{e} \cdot \mathbf{e})(\mathbf{e}^* \cdot \mathbf{e}^*) - 2(\mathbf{n}^* \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e}^*) \\ &\quad - (\mathbf{n}^* \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e})(\mathbf{e}^* \cdot \mathbf{e}^*) \\ &\quad + 2(\mathbf{n}^* \cdot \mathbf{e}^*)(\mathbf{n} \cdot \mathbf{e}^*)(\mathbf{e} \cdot \mathbf{e})\} \end{aligned} \quad (25a)$$

$$\begin{aligned} F_{1121}^0(t) &= \frac{(5)^{1/2}}{15} \langle \beta_{ij}\bar{\beta}_{ikk} - \beta_{ij}\bar{\beta}_{kki} \\ &\quad + 2\beta_{ij}\bar{\beta}_{jkk} - 2\beta_{ij}\bar{\beta}_{kkj} \rangle \end{aligned} \quad (25b)$$

We note that

$$\phi_{2111}^0 = (\phi_{1121}^0)^* \quad \text{and} \quad F_{2111}^0(0) = (F_{1121}^0(0))^* \quad (25c)$$

Moreover,

$$\begin{aligned} \phi_{2222}^0 &= \frac{1}{15} \{2 - (\mathbf{e} \cdot \mathbf{e})(\mathbf{e}^* \cdot \mathbf{e}^*) - (\mathbf{n}^* \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e}^*) \\ &\quad - 2(\mathbf{n}^* \cdot \mathbf{e}^*)(\mathbf{n} \cdot \mathbf{e}) + (\mathbf{n}^* \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e})(\mathbf{e}^* \cdot \mathbf{e}^*) \\ &\quad + (\mathbf{n}^* \cdot \mathbf{e}^*)(\mathbf{n} \cdot \mathbf{e}^*)(\mathbf{e} \cdot \mathbf{e})\} \end{aligned} \quad (26a)$$

$$\begin{aligned} F_{2222}^0(t) &= \frac{1}{3} \langle 2\beta_{ijk}\bar{\beta}_{ijk} + \beta_{ij}\bar{\beta}_{kki} + \beta_{ij}\bar{\beta}_{jkk} \\ &\quad - 2\beta_{ijk}\bar{\beta}_{jik} - \beta_{ij}\bar{\beta}_{ikk} - \beta_{ij}\bar{\beta}_{kkj} \rangle \end{aligned} \quad (26b)$$

$$\begin{aligned} \phi_{1313}^0 &= \frac{1}{105} \{5 - (\mathbf{e} \cdot \mathbf{e})(\mathbf{e}^* \cdot \mathbf{e}^*) \\ &\quad + 10(\mathbf{n}^* \cdot \mathbf{e}^*)(\mathbf{n} \cdot \mathbf{e}) - 4(\mathbf{n}^* \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e}^*) \\ &\quad - 2(\mathbf{n}^* \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{e})(\mathbf{e}^* \cdot \mathbf{e}^*) \\ &\quad - 2(\mathbf{n}^* \cdot \mathbf{e}^*)(\mathbf{n} \cdot \mathbf{e}^*)(\mathbf{e} \cdot \mathbf{e})\} \end{aligned} \quad (27a)$$

$$\begin{aligned} F_{1313}^0(t) &= \frac{1}{15} \langle 5\beta_{ijk}\bar{\beta}_{ijk} + 10\beta_{ijk}\bar{\beta}_{jik} - 4\beta_{ij}\bar{\beta}_{kkj} \\ &\quad - 2\beta_{ij}\bar{\beta}_{jkk} - 2\beta_{ij}\bar{\beta}_{kki} - \beta_{ij}\bar{\beta}_{ikk} \rangle \end{aligned} \quad (27b)$$

On the assumption that the hyperpolarizability tensor β_{ijk} is completely symmetric, the only non-zero molecular parameters will be $F_{1111}^0(t)$ and $F_{1313}^0(t)$. For the integral intensity ($t = 0$) of the incoherent part ($p = q$) of the scattered radiation, they take the form

$$F_{1111}^0(0) = \frac{3}{5} \beta_{ij}\beta_{jkk} \quad (28a)$$

$$F_{1313}^0(0) = \beta_{ijk}\beta_{ijk} - \frac{3}{5} \beta_{ij}\beta_{jkk} \quad (28b)$$

One readily finds that for arbitrary symmetry of scatterers the parameters $F_{s_1 J_1 s_2 J_2}^0(t = 0)$ are related directly to the molecular parameters $|B_M^J|^2$ previously introduced by us:^{14,15,17,34}

$$F_{1111}^0(0) = \sum_M |B_M^1|^2 \quad (29a)$$

$$F_{1313}^0(0) = \sum_M |B_M^3|^2 \quad (29b)$$

In particular, for molecules of the symmetry groups $C_4 \dots C_\infty$ and $C_{4v} \dots C_{\infty v}$, the totally symmetric tensor β_{ijk} has the form $b_{333} = a$, $b_{311} = b_{131} = b_{113} = b_{322} = b_{232} = b_{223} = b$. From Eqn (28) we now obtain

$$F_{1111}^0(0) = \frac{3}{5} (a + 2b)^2 = |B_0^1|^2 \quad (30a)$$

$$F_{1313}^0(0) = \frac{2}{5} (a - 3b)^2 = |B_0^3|^2 \quad (30b)$$

DEPOLARIZATION RATIO

Let us assume the following set-up: the linearly polarized (vertically along the X -axis or horizontally along the Y -axis) light beam propagates along the Z -axis of the laboratory system of coordinates XYZ . The scattered radiation is observed in the YZ plane at an angle θ (subtended by the propagation vectors \mathbf{k} and \mathbf{k}_0). The respective intensities with vertical vibrations, I_V , or horizontal vibrations, I_H , are calculated with Eqns (21) and (22)–(27). If the incident beam is polarized vertically, the depolarization ratio will be defined as $D_V = I_{HV}/I_{VV}$ and, by Eqns (21)–(27) and introducing $F^{1SN} = F_{2111}^0 + F_{1121}^0$, we obtain

$$D_V^{2\omega} = \frac{7F_{1111}^0 + 12F_{1313}^0 + 7(5F_{2121}^0 + 3F_{2222}^0 + \sqrt{5}F^{1SN})}{63F_{1111}^0 + 18F_{1313}^0} \quad (31)$$

Similarly, for the depolarization ratio of horizontally polarized incident light $D_H = I_{VH}/I_{HH}$ we obtain

$$\begin{aligned} D_H^{2\omega} &= \frac{7F_{1111}^0 + 12F_{1313}^0 + 7(5F_{2121}^0 + 3F_{2222}^0 + \sqrt{5}F^{1SN})}{7F_{1111}^0(1 + 8\cos^2\theta) + 6F_{1313}^0} \\ &\quad (2 + \cos^2\theta) + 7(5F_{2121}^0 + 3F_{2222}^0 + \sqrt{5}F^{1SN})\sin^2\theta \end{aligned} \quad (32)$$

On neglecting the non-symmetric and symmetric–non-symmetric parts, Eqns (31) and (32) take the form of our earlier results.²⁹

REVERSAL COEFFICIENT

In the case of incident circularly polarized light, the unit field polarization vectors are

$$\mathbf{e}_{\pm} = \frac{1}{\sqrt{2}}(\mathbf{x} \pm i\mathbf{y}) \quad (33)$$

where \mathbf{e}_+ and \mathbf{e}_- refer, respectively, to the right- and left-polarized waves with unit vectors \mathbf{x} and \mathbf{y} in the direction of X and Y .

On assuming the incident light wave to be right-polarized circularly, we calculate with Eqns (21)–(27) the scattered intensity components I_{++} and I_{--} . Defining the reversal coefficient as $R_+ = I_{--}/I_{++}$, we obtain generally

$$\begin{aligned} R_+^{2\omega}(\theta) = & \{7(4F_{1111}^0 + 5F_{2121}^0 - 2\sqrt{5}F^{1SN}) \\ & \times (1 - \cos\theta)^2 + 21F_{2222}^0 \\ & \times (5 - 2\cos\theta - 3\cos^2\theta) + 6F_{1313}^0 \\ & \times (13 + 14\cos\theta + 3\cos^2\theta)\} / \\ & \{7(4F_{1111}^0 + 5F_{2121}^0 - 2\sqrt{5}F^{1SN}) \\ & \times (1 + \cos\theta)^2 + 21F_{2222}^0 \\ & \times (5 + 2\cos\theta - 3\cos^2\theta) + 6F_{1313}^0 \\ & \times (13 - 14\cos\theta + 3\cos^2\theta)\} \quad (34) \end{aligned}$$

In the case of forward scattering ($\theta = 0$), Eqn (34) gives

$$R_+^{2\omega}(0) = \frac{45F_{1313}^0}{7(4F_{1111}^0 + 5F_{2121}^0 - 2\sqrt{5}F^{1SN}) + 21F_{2222}^0 + 3F_{1313}^0} \quad (35)$$

On restricting ourselves to symmetric scattering, we find that Eqns (34) and (35) lead to our earlier results.²⁹

Equations (21)–(27) moreover enable us to calculate other quantities measured in studies on light scattering,^{29,35} including studies involving elliptically polarized light.³¹

CONCLUSIONS

Rejecting Kleinmann's assumption of complete symmetry of the hyperpolarizability tensor β_{ijk} , we have obtained, in addition to symmetric three-photon scattering, non-symmetric and symmetric–non-symmetric scattered components. The occurrence of these types of scattering hinges on the physical conditions, namely the symmetry of the molecules and the relationship between their characteristic frequencies and the frequency of the incident light beam. In general, the number of irreducible rotational invariants is five; however, under certain well defined conditions, their number reduces to four, three, two or one, permitting the determination of the numerical values of the molecular invariants for well defined conditions of observation of hyper-Raman and hyper-Rayleigh scattering. The experimental studies of Long *et al.*²² have shown with a high degree of accuracy that the hyperpolarizability tensor β_{ijk} can be dealt with as completely symmetric, reducing to two the number of molecular and field invariants in Eqns (21)–(27) and thus simplifying the Eqns (31), (32), (34) and (35). There are, nonetheless, cases when β_{ijk} is not completely symmetric^{23,24,30} and its non-symmetry has to be taken into account in order to describe the spectra observed. Measurements can be extended as well beyond the depolarization ratio and reversal coefficient to deal with other quantities for other states of polarization^{10,12,35,38} and the respective structural models of the incident light beam.^{10,28,29,39–41}

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