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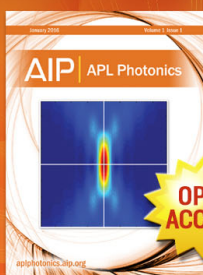
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# Hyper-Rayleigh scattering in centrosymmetric systems

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Hyper-Rayleigh scattering (HRS) is an incoherent mechanism for optical second harmonic generation. The frequency-doubled light that emerges from this mechanism is not emitted in a laser-like manner, in the forward direction; it is scattered in all directions. The underlying theory for this effect involves terms that are quadratic in the incident field and involves an even-order optical susceptibility (for a molecule, its associated hyperpolarizability). In consequence, HRS is often regarded as formally forbidden in centrosymmetric media. However, for the fundamental three-photon interaction, theory based on the standard electric dipole approximation, representable as  $E1^3$ , does not account for all experimental observations. The relevant results emerge upon extending the theory to include  $E1^2M1$  and  $E1^2E2$  contributions, incorporating one magnetic dipolar or electric quadrupolar interaction, respectively, to a consistent level of multipolar expansion. Both additional interactions require the deployment of higher orders in the multipole expansion, with the  $E1^2E2$  interaction analogous in rank and parity to a four-wave susceptibility. To elicit the correct form of response from fluid or disordered media invites a tensor representation which does not oversimplify the molecular components, yet which can produce results to facilitate the interpretation of experimental observations. The detailed derivation in this work leads to results which are summarized for the following: perpendicular detection of polarization components both parallel and perpendicular to the pump radiation, leading to distinct polarization ratio results, as well as a reversal ratio for forward scattered circular polarizations. The results provide a route to handling data with direct physical interpretation, to enable the more sophisticated design of molecules with sought nonlinear optical properties. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4931584>]

## I. INTRODUCTION

Light-matter interaction events are ubiquitous in nature. One familiar process, responsible for the azure color of the sky, is the Rayleigh scattering of light — a concerted process of single-photon annihilation and creation by atomic and molecular optical centers. Comprising of one input and one output photon per scattering event, there is a linear dependence on the intensity of light, and hence, this is the most probable form of non-resonant interaction that can occur in a given molecular volume. With two electric dipole ( $E1$ ) transitions, this form of scattering engages the finite polarizability  $\alpha$ , which is a property with a finite value in all systems. In the microscopic regime, these two dipole transitions are described as an  $E1^2$  optical response tensor, the even number of dipolar transitions signifying an optical susceptibility of even parity, and hence the universality of the phenomenon it mediates.

By increasing the intensity, and consequently the number of photons simultaneously traversing an optically nonlinear medium, mechanisms involving more instantaneous interaction events become more noticeable in the output signal, primarily through the involvement of a second photon annihilation: when the overall process returns molecules to their ground state, this case accommodates two possibilities — the generation of sum-frequency or second harmonic output. Both are primarily considered to involve  $E1^3$  mechanisms. The

latter form of interaction, widely employed in condensed phase media that support collective, coherent forward scattering of monochromatic light, is generally known as second harmonic generation (SHG).

Hyper-Rayleigh scattering (HRS)<sup>1</sup> is an incoherent variant of SHG: not subject to the rules of wave-vector matching, it leads to harmonic emission in all directions (i.e., over  $4\pi$  steradians). It offers unique technical applications in the optical characterization of minerals,<sup>2</sup> and recently, it has been exploited in the analysis of liquid suspensions — in particular with regard to nanoparticles and nanorods.<sup>3,4</sup> The fundamental interactions involved in both SHG and HRS depend on the same third-rank ( $E1^3$ ) optical response tensor<sup>5</sup> known as the first order hyperpolarizability,  $\beta$ , or in bulk media its counterpart bearing a Lorentz field factor, which represents a “second optical susceptibility.”<sup>6,7</sup> A commonly used simplification, in attempts to develop a materials science framework for describing optical nonlinearity, is the two-level approximation, which correlates the magnitude of the principal hyperpolarizability components with a linear charge shift for a specific prominent optical transition.<sup>8–11</sup> The limitations of such an approach and related “push-pull” models<sup>12–14</sup> have been addressed in several recent works,<sup>15–19</sup> whilst other quantum electrodynamical studies have established formal links to sum-frequency generation and its static electric field-induced analogue.<sup>20</sup>

In materials comprising optical centers of high symmetry, such as centrosymmetric media, the frequency conversion process that occurs in each center must terminate in a material

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electronic state of the same parity as it began, irrespective of the (virtual intermediate) states through which the process evolves. As such, and in view of the Laporte selection rule for each E1 transition, the hyperpolarizabilities associated with processes that involve an overall odd number of photons vanish for such materials. Nonetheless, second harmonic signals can still be detected in such media, and there are two prominent mechanisms to account for such observations. One, especially significant for forward coherent emission, relies on doubling the number of photon interaction events to satisfy the parity preservation and thus exhibit frequency doubling through a six-wave mixing mechanism.<sup>21,22</sup>

However, in the second permissible mechanism, incoherent HRS also delivers a second harmonic signal in centrosymmetric species, and this is the focus of our present paper. Historically, most theoretical work in this area has assumed all three of the light-matter interactions involved in the optical frequency conversion to be limited to E1 transition moments. Now, by considering the detailed form of the quantum interaction Hamiltonian, it becomes apparent that other mechanisms are capable of subverting the standard selection rules.<sup>23</sup> Here, we accommodate the next most significant multipolar contributions: the magnetic dipole (M1) and electric quadrupole (E2).<sup>24,25</sup> Both arise from the same order of expansion of a minimal coupling interaction, on conversion to the multipolar form through canonical transformation.<sup>26,27</sup> It may also be noted that in the present connection, the ensuing additional contributions to the quantum amplitudes for frequency conversion arise only for *incoherent* harmonic processes in fluid media. The more stringent symmetry principles associated with bulk isotropy, which come into play when rotational averages are effected, in fact preclude the coherent generation of even harmonics to all levels of multipole approximation.<sup>28,29</sup>

In materials for which E1<sup>3</sup> contributions to second harmonic emission are forbidden, terms such as E1<sup>2</sup>M1 and E1<sup>2</sup>E2 generally become significant in the quantum amplitude, and in the quadratic product of amplitudes that features in the eventual state equation, there also arises an interference between the two. In the following analysis, the molecular responses entailing E1<sup>2</sup>M1 and E1<sup>2</sup>E2 couplings are to be denoted by tensors  $\mathbf{J}^{(\prime)}$  and  $\mathbf{K}^{(\prime)}$ , respectively: the absence of a prime signifies that the M1 or E2 multipole is associated with an input pump photon annihilation; the presence of a prime denotes that it is the harmonic photon emission that is associated with the respective M1 or E2 multipole. Although  $\mathbf{J}^{(\prime)}$  is a third-rank tensor and  $\mathbf{K}^{(\prime)}$  is fourth-rank, each of them is of even spatial parity, with non-zero values for all molecules. It thus emerges that these forms of light-matter coupling may account for the occurrence of hyper-Rayleigh scattering in all molecules of all symmetry types, even those that are centrosymmetric, and for which second harmonic scattering would conventionally be regarded as forbidden.

The work to be reported now seeks to formalize the theory, establishing the quantum electrodynamical mechanism through a detailed derivation, and thereby delivering the corresponding rate equations for HRS. Our final results incorporate choice assumptions to provide relative magnitudes for a selection of commonly used experimental setups for measuring the scattered radiation.

## II. THEORETICAL CONTEXT

### A. Framework

The formulation begins by considering the evolution of electronic state in an optically nonlinear center during an interaction that produces a second harmonic signal. A key consideration is that for each interaction event, there is the full set of (multi)polar interaction Hamiltonians engaged. These are commonly developed from a starting point in the standard minimal coupling Hamiltonian<sup>26</sup> which, as commonly cast for microscopic (molecular-level) quantum interactions, is expressed as<sup>30</sup>

$$H_{\text{int}} = (e/m) \mathbf{p} \cdot \mathbf{a}^{\perp} + (e^2/2m) \mathbf{a}^{\perp 2}. \quad (1)$$

Here,  $e$  and  $m$  are the particle charge and mass;  $\mathbf{p}$  is the momentum and  $\mathbf{a}^{\perp}$  the microscopic vector potential. The “perpendicular” superscript designates the transverse part of the field, whilst the use of lowercase characters serves to highlight the distinction of local field operators from their conventional bulk field variables — see, for example, chapter 10 of Ref. 30. Utilizing a multipolar transformation delivers

$$H_{\text{int}} = -\varepsilon_0^{-1} (\mu_i d_i^{\perp} - Q_{ij} \nabla_j d_i^{\perp} + \dots) - (m_i b_i + \dots), \quad (2)$$

where  $d_i^{\perp}$  and  $b_i$  are the partial time derivative and curl of the vector potential,

$$\mathbf{d}^{\perp} = -\frac{1}{\varepsilon_0} \frac{\partial \mathbf{a}^{\perp}}{\partial t}, \quad (3)$$

$$\mathbf{b} = \nabla \times \mathbf{a}^{\perp}. \quad (4)$$

Also in Equation (2),  $\mu_i$  and  $Q_{ij}$  are the first two terms ( $n = 1, 2$ ) of the En (electric multipole) series and  $m_i$  is the corresponding first term ( $n = 1$ ) of the magnetic counterpart Mn.

As mentioned above, the electric quadrupole and magnetic dipole interaction terms both originate, through the multipolar transformation, from the gradient of the vector potential in Equation (2). Accordingly, they are of generally similar strength — both of the order of the fine structure constant ( $\alpha^{-1} \approx 137$ ) smaller than the leading electric dipole term. In this sense, it is helpful to recast Equation (2) as

$$H_{\text{int}} = \underbrace{-\varepsilon_0^{-1} \mu_i d_i^{\perp}}_{1^{\text{st}} \text{ order}} - \underbrace{\varepsilon_0^{-1} Q_{ij} \nabla_j d_i^{\perp}}_{2^{\text{nd}} \text{ order}} - m_i b_i + \dots, \quad (5)$$

in which “order” refers to the comparative degree  $n$  of intensity, which runs as  $\alpha^{n-1}$ . Here, we are extending the consideration from beyond the primary dipole approximation to include a single secondary contribution in either of the pair of photon annihilation events or in the photon creation. The Feynman diagram shown in Figure 1 offers one of three permutations for the interaction series, depicting two annihilation events preceding the creation of a second harmonic. (Since coherence is not an issue at this, single-particle level, the representation is identical to SHG.) However, there is one significant distinction from the conventional E1<sup>3</sup> mechanism: engaging another multipole moment now requires a subset of three extra diagrams to be taken into account, as a result of the annihilation events becoming distinguishable.

We now seek the overall rate for HRS, associated with the matrix element delivered as the leading (third-order) term in a

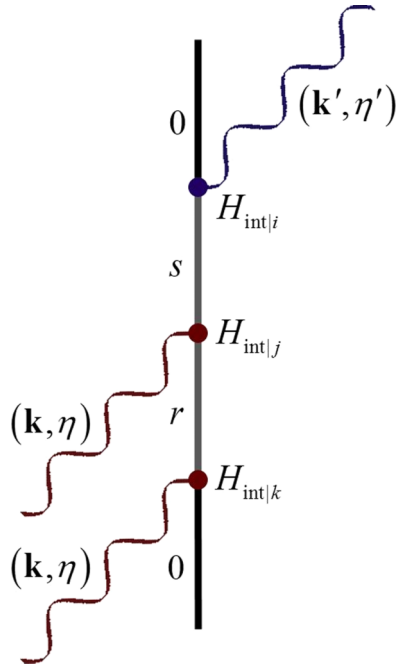


FIG. 1. One representative non-relativistic Feynman diagram, showing the time-ordering corresponding to the photon sequence “annihilation, annihilation, creation.” The Cartesian index  $i$  denotes the photon creation event;  $j$  and  $k$  each represent a photon annihilation. Each in principle engages the complete interaction Hamiltonian. The scatterer returns to its initial state 0 via two intermediary states,  $r$  followed by  $s$ . The emitted photon conveys the energy sum of the two annihilated photons:  $\hbar ck' = \hbar ck + \hbar ck$ .

time-dependent perturbation theory expansion,

$$M_{FI} = \sum_{R, S \neq I, F} \frac{\langle F | H_{int} | S \rangle \langle S | H_{int} | R \rangle \langle R | H_{int} | I \rangle}{(E_I - E_S)(E_I - E_R)}, \quad (6)$$

for which the interaction pathway shown in Fig. 1 and its two time-order permutations all need to be considered. It is at this stage that a distinction needs to be made between the multipole engagements on either an annihilation or a creation event. The full set of permutations to be accounted for are the following: (i) two E1 photon annihilations and an M1 creation ( $E1^2M1'$ ); (ii) one E1 annihilation, one M1 annihilation, and an E1 creation ( $E1M1E1'$ ); (iii) two E1 annihilations and an E2 creation ( $E1^2E2'$ ); (iv) one E1 annihilation, one E2 annihilation, and an E1 creation ( $E1E2E1'$ ). The “Fermi golden rule” rate equation, for the HRS of a collection of  $N$  static molecules given a density of final states  $\rho_F$ , then becomes

$$\Gamma_{FI} = \frac{2\pi\rho_F}{\hbar} \sum_{\text{Molecules}} \left| M_{FI}^{(E1^3)} + M_{FI}^{(E1^2M1')} + M_{FI}^{(E1M1E1')} + M_{FI}^{(E1^2E2')} + M_{FI}^{(E1E2E1')} \right|^2. \quad (7)$$

For the reason given earlier, the leading term will normally dominate, in any non-centrosymmetric material whose symmetry is such that it can support a finite hyperpolarizability. Even the leading correction terms, arising in the product of the  $E1^3$  term with the complex conjugate of each other term, are only significant in connection with relatively subtle circular differential effects in hyper-Raman spectroscopy.<sup>31</sup> However, the situation is very different if the material symmetry

precludes a finite hyperpolarizability; this is the case we shall now consider.

## B. Centrosymmetric systems

Attention now focuses upon a system in which the  $E1^3$  interaction pathway is *not* permitted, i.e.,  $M_{FI}^{(E1^3)} \equiv 0$ . As such, all terms resulting from a product of the first term in Eq. (7) will be neglected, and the expansion for each molecule produces ten rate terms, of which four arise directly from each of the allowed HRS mechanisms and six are quantum interferences between pairs thereof. The propensity of a bulk system to exhibit HRS is a colligative property, so the generalization from  $N$  static molecules (each in some specified orientation) to  $N$  stochastically rotating molecules (disorder typical of the condensed phase) is accomplished by applying an isotropic average of the molecular response tensors, here to be denoted by chevron brackets  $\langle \rangle$ , separately to each rate term.

By considering the intensity for a unit volume around a solid angle in the emission direction, a modified form for the rate can now be cast as

$$\Gamma_{FI} = \frac{k'^2 d\Omega' N V}{(2\pi)^2 \hbar^2 c} \langle \text{Re} [A^T G \bar{G}^T A] \rangle, \quad (8)$$

where  $d\Omega'$  is a solid angle element about the emission wave-vector  $\mathbf{k}'$ , and  $V$  signifies an arbitrary quantization volume, arising from the quantization of the electric displacement and magnetic induction field operators. It is assumed that this volume contains, on average,  $n$  photons of the input radiation (stochastic variation of the integer value is to be considered subsequently). Formally, the quantization volume also encapsulates all molecules within the interaction region for the HRS process. The two column matrices in Equation (8),  $G$  and  $A$ , are defined by

$$G = \begin{pmatrix} M_{FI}^{(E1^2M1')} \\ M_{FI}^{(E1M1E1')} \\ M_{FI}^{(E1^2E2')} \\ M_{FI}^{(E1E2E1')} \end{pmatrix}, \quad A = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}, \quad (9)$$

to allow a concise expression of the grand sum for the Gramian  $G\bar{G}^T$ . An overbar denotes complex conjugation. The explicit forms for the matrix elements of the two mechanisms involving M1 interactions are

$$M_{FI}^{(E1^2M1')} \propto \bar{b}'_i e_j e_k k'_l \mathbf{J}'_{i(jk)l}, \quad (10)$$

$$M_{FI}^{(E1M1E1')} \propto \bar{e}'_i e_j b_k \mathbf{J}_{ijk}. \quad (11)$$

And for those involving E2 interactions,

$$M_{FI}^{(E1^2E2')} \propto -i \bar{e}'_i e_j e_k k'_l \mathbf{K}'_{i(jk)l}, \quad (12)$$

$$M_{FI}^{(E1E2E1')} \propto i \bar{e}'_i e_j e_k k_l \mathbf{K}_{i(jk)l}. \quad (13)$$

Here,  $\mathbf{J}'$  and  $\mathbf{J}$  are readily defined by inspection of all nine permutations for the interaction series: the three variants in position of the creation event seen in Fig. 1, with each of those having a further three permutations for the choice of event

which engages as M1,

$$\mathbf{J}'_{i(jk)}(\omega) = \sum_{r,s} \left\{ \frac{m_i^{0s} \mu_j^{sr} \mu_k^{r0}}{[E_{r0} - 2\hbar\omega][E_{s0} - \hbar\omega]} + \frac{\mu_j^{0s} m_i^{sr} \mu_k^{r0}}{[E_{r0} + \hbar\omega][E_{s0} - \hbar\omega]} + \frac{\mu_j^{0s} \mu_k^{sr} m_i^{r0}}{[E_{r0} + \hbar\omega][E_{s0} + 2\hbar\omega]} \right\}, \quad (14)$$

$$\mathbf{J}_{ijk}(\omega) = \sum_{r,s} \left\{ \frac{\mu_i^{0s} m_j^{sr} \mu_k^{r0}}{[E_{r0} - 2\hbar\omega][E_{s0} - \hbar\omega]} + \frac{m_j^{0s} \mu_i^{sr} \mu_k^{r0}}{[E_{r0} + \hbar\omega][E_{s0} - \hbar\omega]} + \frac{m_j^{0s} \mu_k^{sr} \mu_i^{r0}}{[E_{r0} + \hbar\omega][E_{s0} + 2\hbar\omega]} \right\}. \quad (15)$$

By the same logic,  $\mathbf{K}'$  and  $\mathbf{K}$  are cast in terms that include one E2 interaction

$$\mathbf{K}'_{i(jk)l}(\omega) = \sum_{r,s} \left\{ \frac{Q_{il}^{0s} \mu_j^{sr} \mu_k^{r0}}{[E_{r0} - 2\hbar\omega][E_{s0} - \hbar\omega]} + \frac{\mu_j^{0s} Q_{il}^{sr} \mu_k^{r0}}{[E_{r0} + \hbar\omega][E_{s0} - \hbar\omega]} + \frac{\mu_j^{0s} \mu_k^{sr} Q_{il}^{r0}}{[E_{r0} + \hbar\omega][E_{s0} + 2\hbar\omega]} \right\}, \quad (16)$$

$$\mathbf{K}_{i(jk)l}(\omega) = \sum_{r,s} \left\{ \frac{\mu_i^{0s} Q_{jl}^{sr} \mu_k^{r0}}{[E_{r0} - 2\hbar\omega][E_{s0} - \hbar\omega]} + \frac{Q_{jl}^{0s} \mu_i^{sr} \mu_k^{r0}}{[E_{r0} + \hbar\omega][E_{s0} - \hbar\omega]} + \frac{Q_{jl}^{0s} \mu_k^{sr} \mu_i^{r0}}{[E_{r0} + \hbar\omega][E_{s0} + 2\hbar\omega]} \right\}. \quad (17)$$

In consequence, the rate contributions in Equation (8) require the evaluation of isotropic Cartesian tensor averages of rank  $(6 + j)$ , where  $j$  is the total number of E2 couplings involved. The seventh and eighth rank terms that in consequence arise demand the evaluation of  $105 \times 105$  matrix products.<sup>32–34</sup>

Every term in the overall matrix element from Equation (7) involves a “photon density” factor, included within the constants of proportionality for Equations (10)–(13), which has the form,

$$M_{FI} \sim \frac{\sqrt{n}\sqrt{n-1}}{V}, \quad (18)$$

where  $n$  is the number of photons in the quantization volume. Given that the process is optically nonlinear, the ensuing result displays a dependence not only on the input beam irradiance, through the formula

$$I = \frac{n\hbar c^2 k}{V}, \quad (19)$$

but also the associated degree of second order coherence, accounting for stochastic variations in photon number. For

a single beam, its standard definition is as follows:

$$g_{11}^{(2)} = \frac{\langle n(n-1) \rangle}{\langle n \rangle^2}. \quad (20)$$

Hence, the square of the right-hand side of Equation (18) emerges in the following form in the ensuing rate equations, which are thereby directly expressed in terms of physically meaningful (and experimentally determinable) parameters,

$$g_{11}^{(2)} \left( \frac{\bar{I}}{\hbar c^2 k} \right)^2. \quad (21)$$

### III. RESULTS

Each term in Eq. (8) can be evaluated in order to obtain the overall rate expression. Generally, the results of any specific experiment will depend on the nature of the specimen sample, the characteristics of the laser input, and the state of polarization as determined by selected optical elements. Moreover, the emergent hyper-Rayleigh signal can be resolved into any suitable pair of independent polarization components. Each of the material parameters is unique; they are in principle amenable to computational determination, and yet they are not separately determinable simply by varying experimental conditions. However, it is reasonable to consider that their collective effect will give results that are distinct for each given molecule. For the complete results, see Tables SI and SII.<sup>35</sup>

Often, the total HRS response is analyzed in terms of two distinct polarization contributions. For plane polarizations, this is commonly expressed through a ratio of the perpendicular and parallel light polarizations, called the depolarization ratio (DR). For circular polarizations, a comparable measurement, known as the reversal ratio (RR), can be made: it relates the relative intensities of emission that have reversed and preserved circularities:  $(c \rightarrow c^*)/(c \rightarrow c)$ . (In our analysis,  $c$  stands for L, but on interchanging throughout, it can equally represent R.) To automate this kind of characterization, many technologies exist to observe the process by rapidly switching between polarization states.<sup>36</sup>

In their most general form, the results are remarkably complex, cast in the form of lengthy equations that include a huge number of terms. Accordingly, to arrive at results more directly suited to experimental application, it is appropriate to entertain approximations that can still indicate the relative magnitudes of each term contributing to observations of HRS.

Incorporating the relative magnitudes of the transition moments — see Eq. (5) — we recall that the M1 and E2 transition moments are typically weaker, by a factor in the order of the fine structure constant, compared to the E1 moment of the same transition, when each is allowed. Assuming that all transition moments of the same electric or magnetic multipole type have a similar order of magnitude greatly simplifies the rate expressions for each of the observation setups displayed in Figure 2. The following much simplified equations then serve to describe the relative intensities of each term in Equation (7), in which an experimental pre-factor is written explicitly as

$$C_0 = \frac{k^4 \bar{I}^2 \epsilon_0 g_{11}^{(2)}}{5040 \pi^2 c}. \quad (22)$$

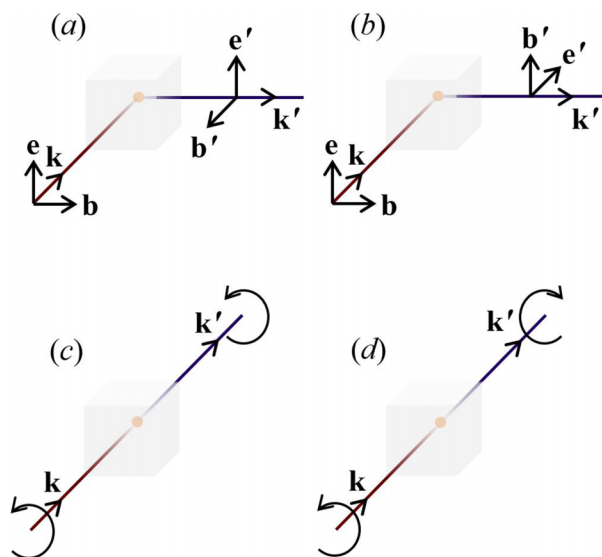


FIG. 2. Experimental setup: (a) parallel plane-polarized light is detected at right angles to the input laser; (b) perpendicularly plane-polarized light detected also detected at right angles; (c) forward scattered circular-polarized light with preserved circularity; (d) forward scattered circular-polarized light of reversed circularity.

Introducing further constants  $C_1 = i\varepsilon_0^{-4}$ ,  $C_2 = -i\varepsilon_0^{-2}ck$ ,  $C_3 = c^2k^2$ , we have these final results for the intensities of radiant emission in given directions:

- (a) Parallel plane-polarized light detected orthogonal to the input laser,

$$I' = C_0N [3C_1 \{3\bar{J}\bar{J} - 2\bar{J}'\bar{J}'\} + 9C_2 \{K\bar{J}' - K'\bar{J}\} + 5C_3 \{K\bar{K} + K'\bar{K}'\}]. \quad (23)$$

- (b) Perpendicular plane-polarized light detected orthogonal to the input laser,

$$I' = C_0N [3C_1 \{15\bar{J}'\bar{J}' + \bar{J}\bar{J}\} + 3C_2 \{K'\bar{J} - K\bar{J}'\} + C_3 \{3K\bar{K} + K'\bar{K}'\}]. \quad (24)$$

Note that, in the simplified construction of terms in the above equations, a parameter such as  $K'\bar{J}$  is a shorthand notation for a representative inner tensor product of the  $K'$  and  $\bar{J}$  tensors. A final result for the depolarization ratio, in which the prefactor  $C_0$  cancels, can now be directly derived from the ratio of Equations (23) and (24).

- (c) Forward scattered circular-polarized light with preserved left circularity,

$$I' = 2C_0N [9C_1 \{J'\bar{J}' - 2\bar{J}\bar{J} + \bar{J}\bar{J}\} + 9C_2 \{K\bar{J}' + K\bar{J} + K'\bar{J}' - K'\bar{J}\} + C_3 \{K\bar{K} + 2K'\bar{K} + K'\bar{K}'\}]. \quad (25)$$

- (d) Forward scattered circular-polarized light with reversed (left to right) circularity,

$$I' = 2C_0N [9C_1 \{J'\bar{J}' + 2\bar{J}\bar{J} + \bar{J}\bar{J}\} - 6C_2 \{7K\bar{J}' + 11K'\bar{J}\} + C_3 \{K\bar{K} + 2K'\bar{K} + K'\bar{K}'\}]. \quad (26)$$

Once again, taking the ratio of the above results gives a cancellation of the prefactor and delivers a final result

for the reversal ratio. In this case, it is notable that when the “ $K$ ” terms involving electric quadrupole interaction dominate over the magnetic dipole “ $J$ ” contributions, the reversal ratio delivers a value of precisely 1; there is a complete reversal of circularity in the forward second harmonic emission. Such observations are likely to become most noticeable at short wavelengths, as can be recognized from the  $k^{n-1}$  dependence of the  $C_1$ ,  $C_2$ , and  $C_3$ .

#### IV. DISCUSSION

The present analysis extends earlier, well-known developments of theory for non-centrosymmetric molecules.<sup>37</sup> The primary conclusion, contrasting with conventional wisdom, is that HRS should occur universally. Furthermore, the evaluation of depolarization and reversal ratios together represents a means of securing a unique fingerprint of parameters to characterize the wider sphere of molecules exhibiting HRS. In this connection, it is worth noting that although local field effects have in fact been accommodated (by quantizing the transverse electric displacement field rather than its vacuum field counterpart, as shown by Craig and Thirunamachandran<sup>30</sup>), such effects disappear in the polarization ratios.

Although the intensities produced by centrosymmetric molecules will typically be in the order of  $10^{-4}$  to  $10^{-5}$  smaller than the signals from the more often studied non-centrosymmetric materials, we note that this diminution can be offset by the use of input wavelengths approaching a single or double optical resonance (where  $\hbar ck$  or  $2\hbar ck$  is close to the energy gap between the ground state and some real electronic excited state). Pre-resonance will substantially enhance the  $J$  and  $K$  tensor components to a similar degree to those of the  $\beta$  tensor, for which the landmark work by Long and Stanton<sup>38</sup> reported a potential enhancement in the region of  $10^6$ . A capacity to generate HRS should thus be a weak but discernible and measurable optical property of every material.

#### ACKNOWLEDGMENTS

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