

Molecular-quantum-electrodynamics calculation of multipolar optical harmonics generation from isotropic media in the presence of a surface

G. X. Cao and X. D. Zhu

Department of Physics, University of California at Davis, Davis, California 95616-8677

(Received 8 September 1994)

Using the method of molecular quantum electrodynamics, we investigate the polarization dependence of multipolar optical second-harmonic and third-harmonic generation including up to two multipolar interactions from an isotropic medium with a surface.

I. INTRODUCTION

It is widely known that optical second-harmonic generation (SHG) is a surface-specific process.¹⁻⁴ This is due to the lack of inversion symmetry in a surface region separating two dissimilar bulk media. When irradiated with an intense optical field, the surface region produces electric-dipole-allowed optical second harmonics. If the bulk media are centrosymmetric (i.e., with a center of inversion) or isotropic, there will be no electric-dipole-allowed optical second harmonics generated from the bulk. It is also known, however, that when the electric quadrupole ($E2$) and magnetic dipole ($M1$) responses are taken into consideration, the bulk can generate comparable SHG in the presence of a surface.⁵⁻¹² It has been shown that the multipolar SHG involving one multipolar interaction is often indistinguishable from the surface SHG.⁷⁻¹⁰ In cases where electron orbitals are much larger than the Bohr radius, multipolar SHG with two or more multipolar interactions may have to be considered as well. Fullerene and fullerene-based materials are examples of such systems.¹³ Recently, Koopmans and co-workers reported a study of optical SHG from C_{60} films.¹³ They showed that most SHG signals were from the magnetic dipole response of the C_{60} in the bulk rather than the electric dipole response in the surface region. The purpose of this paper is to investigate the polarization properties of multipolar harmonic generation from isotropic fluids and solids involving up to two multipolar interactions.¹⁴

There are many papers which have dealt with multipolar effects in optical harmonic generation.^{5-12,14,15} Most authors start from macroscopic constitutive relations of polarization fields to macroscopic electric fields and their spatial derivatives.^{5-11,14,15} The coherent radiation from the polarization fields is obtained by solving inhomogeneous Maxwell equations with appropriate boundary conditions.¹⁶ The order of a nonlinear optical process is defined by the number of electric fields on the source side of a constitutive relation, while the order of a multipolar process is determined by the number of derivatives of electric fields in the constitutive relation. The latter is more transparent in the molecular-quantum-electrodynamics formalism.^{12,17} In a recent paper, Zhu and Wong showed that the molecular-quantum-

electrodynamics calculation of multipolar SHG from isotropic fluids produces the same results as the macroscopic polarization field formalism.¹² The advantages of the molecular-quantum-electrodynamics formalism are that (1) it offers a convenient bookkeeping method to distinguish nonlinear optical processes by how photons are being annihilated and created; and (2) it separates the effect of microscopic properties of individual molecules from that of the macroscopic symmetries of the molecule ensemble. These advantages facilitate the analysis of the polarization properties of a nonlinear optical generation process. In this paper, we apply the scheme of Zhu and Wong to higher-order multipolar harmonic generation. We also incorporate proper macroscopic local-field factors and two additional factors which are necessary for multipolar harmonic generation processes.^{2,3,7}

II. MOLECULAR-QUANTUM-ELECTRODYNAMICS FORMALISM OF MULTIPOLAR OPTICAL HARMONIC GENERATION FROM ISOTROPIC FLUIDS AND SOLIDS

In the framework of molecular quantum electrodynamics, an optical harmonic generation is a process in which two or more fundamental photons are annihilated and one harmonic photon is created, while the mediating molecular system remains unchanged.¹⁷ The photon annihilation and creation are achieved through a combination of electric dipole, magnetic dipole, and electric quadrupole interactions between the molecular system and the electromagnetic fields. A multipolar harmonic generation is a process where at least one of the photons is created or destroyed by a multipolar interaction. Various multipolar processes are distinguished by both the combination of the involved multipolar interaction and the time ordering with which these interactions are applied.

We consider coherent optical harmonic generation from isotropic molecular fluids or solids in the presence of an interface.¹² To simplify the matter, we assume that only one of the two adjoining bulk media has nonvanishing multipolar optical nonlinearities. Typical situations can be a molecular liquid or solid in contact with air or vacuum. As shown in Fig. 1, we assume that a plane-wave electromagnetic field $\mathbf{E}_{\text{inc}}(\mathbf{x}, t) = \mathbf{E}_{\text{inc}}(\omega) \exp[i\mathbf{k}_{\omega, a} \cdot \mathbf{x} - i\omega t]$ is incident at an angle θ_{inc}

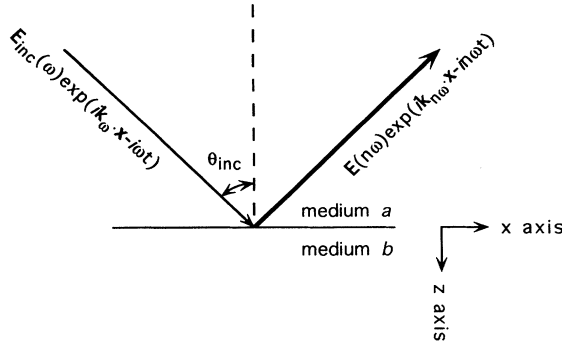


FIG. 1. Geometry of multipolar optical harmonic generation in the reflection direction from a molecular fluid or an isotropic molecular solid (labeled by b). The fundamental electromagnetic field is incident from medium a . The latter is assumed to have no optical nonlinearities.

from the medium (denoted by a) with no optical nonlinearity. The incidence plane coincides with the x - z plane. We denote the adjoining medium by b which possesses finite multipolar nonlinearities. It is easy to extend the results to more general cases. In this section we further assume that the two media have same linear dielectric constants, $\epsilon_{\Omega,a} = \epsilon_{\Omega,b}$. In Sec. IV, we will generalize our results to cases when $\epsilon_{\Omega,a} \neq \epsilon_{\Omega,b}$. Under these assumptions, Zhu and Wong have worked out details of the rotation average and the integration over the half-space where the multipolar responses are nonzero.¹² Here we briefly outline the key results.

The interaction Hamiltonian H_{int} between radiation fields and a molecular fluid is partitioned into an electric dipole, an electric quadrupole, and a magnetic dipole term:¹⁴

$$H_{\text{int}} = - \sum_{\xi, \Omega} \left\{ \mathbf{p}_{\xi} \cdot \mathbf{E}(\Omega) - i \mathbf{k}_{\Omega} \cdot \vec{Q}_{\xi} \cdot \mathbf{E}(\Omega) + \frac{c}{\Omega} [\mathbf{k}_{\Omega} \times \mathbf{E}(\Omega)] \cdot \mathbf{m}_{\xi} \right\} \exp(i \mathbf{k}_{\Omega} \cdot \mathbf{r}_{\xi} - i \Omega t). \quad (1)$$

The summation over ξ includes those molecules enveloped in the radiation field $\mathbf{E}(\Omega)$ of frequency Ω . The summation over Ω includes the fundamental and its harmonics. \mathbf{p}_{ξ} , \vec{Q}_{ξ} , and \mathbf{m}_{ξ} are the electric dipole, electric quadrupole, and magnetic dipole operators of the ξ th molecule, respectively. \mathbf{r}_{ξ} labels its center of mass. In Eq. (1), $c/\Omega[\mathbf{k}_{\Omega} \times \mathbf{E}(\Omega)]$ is the magnetic field $\mathbf{B}(\Omega)$. We denote the three terms in the curly brackets by $E1$, $E2$, and $M1$, respectively.

The radiated power of optical n th harmonics is calculated by the Fermi golden rule:¹⁷

$$S(n\omega) = (n\hbar\omega) \int_{\Omega=4\pi} d\Omega \frac{2\pi}{\hbar} \langle |M_{\hat{n}}(n\omega)|^2 \rangle \frac{d\rho(n\omega)}{d\Omega}. \quad (2)$$

$d\rho(n\omega)/d\Omega$ is the density of states of the radiation field at $n\omega$ into a unit solid angle. The matrix element $M_{\hat{n}}(n\omega)$ is calculated through a $(n+1)$ th-order perturbation.¹⁷ Following the same procedure as used by Zhu and

Wong, we define an effective nonlinear polarizability $\alpha_{\text{eff}}^{(n)}$ for each multipolar process, and express the radiated power at n th harmonics by¹²

$$S(n\omega) = \frac{8\pi^3(n\omega)^2 \sec^2 \theta_{\text{inc}}}{c^3 \epsilon_{n\omega,a}^{1/2} \epsilon_{\omega,a}} |N_{s,\text{eff}}^{(n)} \alpha_{\text{eff}}^{(n)}|^2 I_{\omega,a}^n A. \quad (3)$$

Here θ_{inc} is the angle of incidence. $\epsilon_{\omega,a}$ and $\epsilon_{n\omega,a}$ are the linear dielectric constants of medium a . I_{ω} and A are the intensity and cross section of the fundamental field, respectively. The effective surface density of the molecules in medium b for optical n th harmonics is given by¹²

$$N_{s,\text{eff}}^{(n)} \equiv \frac{n_b}{nk_{\omega,a;z} - k_{n\omega,a;z}}, \quad (4)$$

where $k_{\omega,a;z} = +(\omega/c)\sqrt{\epsilon_{\omega,a}} \cos \theta_{\text{inc}}$, $k_{n\omega,a;z} = - (n\omega/c)\sqrt{\epsilon_{n\omega,a} - \epsilon_{\omega,a}(\sin \theta_{\text{inc}})^2}$, and $k_{n\omega,a;x} = nk_{\omega,a;x} = + (n\omega/c)\sqrt{\epsilon_{\omega,a}} \sin \theta_{\text{inc}}$. n_b is the bulk density of the molecules. The relative strength and the polarization dependence of a given multipolar process are described by the corresponding effective nonlinear polarizability $\alpha_{\text{eff}}^{(n)}$ on which we will focus our attention in Sec. III.

III. POLARIZATION DEPENDENCE OF MULTIPOLAR OPTICAL SECOND-HARMONIC GENERATION

To distinguish various multipolar processes, we use the following notation: $E1+M1 \rightarrow E2$ represents an optical second-harmonic generation process in which two fundamental photons are annihilated in succession by an electric dipole interaction $E1$ and a magnetic dipole interaction $M1$, and a second-harmonic photon is created by an electric quadrupole interaction $E2$. The time ordering of the annihilation of two fundamental photons is significant, and thus $E1+M1 \rightarrow E2$ is to be distinguished from $M1+E1 \rightarrow E2$. Other multipolar SHG processes will be represented by similar notation without further clarification. An example of how the polarization dependence of a multipolar harmonic generation process is represented in the effective nonlinear polarizability has been given by Zhu and Wong for the $E1+E1 \rightarrow E2$ process.¹² In this case, $\alpha_{\text{eff}}^{E2E1E1}$ in the laboratory frame (denoted by coordinates $ijkl$) is expressed as

$$\alpha_{\text{eff}}^{E2E1E1} \equiv \langle \beta_{ijkl}^{E2E1E1} \rangle_{\text{rotation average}} \times k_{2\omega,a;i} e_{2\omega,a;j} e_{\omega,a;k} e_{\omega,a;l}, \quad (5)$$

$$\beta_{ijkl}^{E2E1E1} \equiv \sum_{u,v,g} \left[\frac{Q_{ij}^{gu}(p_k^{uv} p_l^{vg} + p_l^{uv} p_k^{vg})}{(E_{ug} - 2\hbar\omega)(E_{vg} - \hbar\omega)} + \frac{Q_{ij}^{uv}(p_k^{vg} p_l^{gu} + p_l^{vg} p_k^{gu})}{(E_{ug} + \hbar\omega)(E_{vg} - \hbar\omega)} + \frac{Q_{ij}^{vg}(p_k^{gu} p_l^{uv} + p_l^{gu} p_k^{uv})}{(E_{ug} + \hbar\omega)(E_{vg} + 2\hbar\omega)} \right]. \quad (6)$$

After performing the rotational average (see the Appen-

dix), we arrive at

$$\alpha_{\text{eff}}^{E2E1E1} = \frac{1}{15} (-\beta_{\zeta\zeta\eta\eta}^{E2E1E1} + 3\beta_{\zeta\eta\zeta\eta}^{E2E1E1}) \times (\mathbf{k}_{2\omega,a} \cdot \mathbf{e}_{\omega,a})(\mathbf{e}_{2\omega,a} \cdot \mathbf{e}_{\omega,a}). \quad (7)$$

$\beta_{\zeta\zeta\eta\eta}^{E2E1E1}$ and $\beta_{\zeta\eta\zeta\eta}^{E2E1E1}$ are defined in a molecular frame. The summation over repeated indices is implied. From Eq. (7), one finds that the $E1 + E1 \rightarrow E2$ process contributes to the reflected optical second-harmonic generation only when both the fundamental field and the second-harmonic field are p polarized. In other words, $E1 + E1 \rightarrow E2$ yields only P -in/ P -out SHG. We now apply this procedure to other multipolar second-harmonic generation processes. The summary of the results is listed in Table I. As a general rule, an electric quadrupole polarizability is less than that of an electric dipole polarizability by a factor of $k_{\omega} a_B \sim 10^{-3}$; a magnetic dipole polarizability is less than that of an electric dipole polarizability by a factor of the fine-structure constant $\alpha = \frac{1}{137}$.^{14,18} This factor of 10 has also been observed experimentally by Koopmans and co-workers.¹³

There is a general result for second-harmonic generation involving only electric and magnetic dipole interactions. In these cases, the corresponding nonlinear susceptibilities χ_{ijk} are proportional to the unit antisymmetric tensor ε_{ijk} (the Levi-Civita epsilon). Consequently, those processes in which two fundamental photons are annihilated by the same dipole interaction produce no second harmonics. These processes are $E1 + E1 \rightarrow E1$, $E1 + E1 \rightarrow M1$, and $M1 + M1 \rightarrow E1$. This result is valid regardless whether any individual molecule possesses optical nonlinearities. It is also valid without requiring the

presence of time-reversal symmetry.^{8,14}

The leading multipolar processes which produce non-vanishing optical second harmonics are single-magnetic dipole processes.^{5-12,14} In the notation of Guyot-Sionnest and Shen, these magnetic dipole responses are contained in $\vec{\chi}^p : \mathbf{E}(\omega) \nabla \mathbf{E}(\omega)$.⁸ The effective nonlinear polarizabilities are given by

$$\alpha_{\text{eff}}^{E1E1M1} + \alpha_{\text{eff}}^{E1M1E1} = \frac{1}{6} [\varepsilon_{\xi\eta\zeta} (\beta_{\xi\eta\zeta}^{E1E1M1} - \beta_{\xi\eta\zeta}^{E1M1E1})] \times (\mathbf{k}_{\omega,a} \cdot \mathbf{e}_{2\omega,a})(\mathbf{e}_{\omega,a} \cdot \mathbf{e}_{\omega,a}), \quad (8)$$

$$\beta_{\xi\eta\zeta}^{E1M1E1} \equiv \sum_{u,v,g} \left[\frac{p_{\xi}^{gu} m_{\eta}^{uv} p_{\zeta}^{vg}}{(E_{ug} - 2\hbar\omega)(E_{vg} - \hbar\omega)} + \frac{m_{\eta}^{gu} p_{\xi}^{uv} p_{\zeta}^{vg}}{(E_{ug} + \hbar\omega)(E_{vg} - \hbar\omega)} + \frac{m_{\eta}^{gu} p_{\xi}^{uv} p_{\zeta}^{vg}}{(E_{ug} + \hbar\omega)(E_{vg} + 2\hbar\omega)} \right], \quad (9)$$

$$\beta_{\xi\eta\zeta}^{E1E1M1} \equiv \sum_{u,v,g} \left[\frac{p_{\xi}^{gu} p_{\eta}^{uv} m_{\zeta}^{vg}}{(E_{ug} - 2\hbar\omega)(E_{vg} - \hbar\omega)} + \frac{p_{\eta}^{gu} p_{\xi}^{uv} m_{\zeta}^{vg}}{(E_{ug} + \hbar\omega)(E_{vg} - \hbar\omega)} + \frac{p_{\eta}^{gu} m_{\zeta}^{uv} p_{\xi}^{vg}}{(E_{ug} + \hbar\omega)(E_{vg} + 2\hbar\omega)} \right]. \quad (10)$$

From Eq. (8), we see that these two processes yield P -in/ P -out and S -in/ P -out SHG.

The next group consists of three electric quadrupole

TABLE I. Rotational symmetry-allowed polarization combinations for multipolar optical second-harmonic generation from a molecular fluid or an isotropic solid involving up to two multipolar interactions.

Multipolar processes	Multipolar polarization density	Relative strength	P -in, P -out (P - P)	P -in, S -out (P - S)	S -in, P -out (S - P)	S -in, S -out (S - S)
$E1 + E1 \rightarrow E1$	$\mathbf{P}^{(2)} = \chi_{pp}^{(P)} \mathbf{E}\mathbf{E}$	1				
$E1 + E1 \rightarrow M1$	$\mathbf{M}^{(2)} = \chi_{pp}^{(M)} \mathbf{E}\mathbf{E}$	10^{-2}				
$E1 + M1 \rightarrow E1$	$\mathbf{P}^{(2)} = \chi_{pm}^{(P)} \mathbf{E}\mathbf{B}$	10^{-2}	×		×	
$M1 + E1 \rightarrow E1$	$\mathbf{P}^{(2)} = \chi_{mp}^{(P)} \mathbf{B}\mathbf{E}$	10^{-2}	×		×	
$E1 + E1 \rightarrow E2$	$\mathbf{Q}^{(2)} = \chi_{pp}^{(Q)} \mathbf{E}\mathbf{E}$	10^{-3}	×		×	
$E1 + E2 \rightarrow E1$	$\mathbf{P}^{(2)} = \chi_{pq}^{(P)} \mathbf{E}\mathbf{V}\mathbf{E}$	10^{-3}	×		×	
$E2 + E1 \rightarrow E1$	$\mathbf{P}^{(2)} = \chi_{qp}^{(P)} (\nabla \mathbf{E})\mathbf{E}$	10^{-3}	×		×	
$E1 + M1 \rightarrow M1$	$\mathbf{M}^{(2)} = \chi_{pm}^{(M)} \mathbf{E}\mathbf{B}$	10^{-4}		×		×
$M1 + E1 \rightarrow M1$	$\mathbf{M}^{(2)} = \chi_{mp}^{(M)} \mathbf{B}\mathbf{E}$	10^{-4}		×		×
$M1 + M1 \rightarrow E1$	$\mathbf{P}^{(2)} = \chi_{mm}^{(P)} \mathbf{B}\mathbf{B}$	10^{-4}				
$E1 + M1 \rightarrow E2$	$\mathbf{Q}^{(2)} = \chi_{pm}^{(Q)} \mathbf{E}\mathbf{B}$	10^{-5}		×		×
$M1 + E1 \rightarrow E2$	$\mathbf{Q}^{(2)} = \chi_{mp}^{(Q)} \mathbf{B}\mathbf{E}$	10^{-5}		×		×
$E1 + E2 \rightarrow M1$	$\mathbf{M}^{(2)} = \chi_{pq}^{(M)} \mathbf{E}\mathbf{V}\mathbf{E}$	10^{-5}		×		×
$E2 + E1 \rightarrow M1$	$\mathbf{M}^{(2)} = \chi_{qp}^{(M)} (\nabla \mathbf{E})\mathbf{E}$	10^{-5}		×		×
$E2 + M1 \rightarrow E1$	$\mathbf{P}^{(2)} = \chi_{pm}^{(P)} (\nabla \mathbf{E})\mathbf{B}$	10^{-5}				
$M1 + E2 \rightarrow E1$	$\mathbf{P}^{(2)} = \chi_{mq}^{(P)} \mathbf{B}(\nabla \mathbf{E})$	10^{-5}				
$E1 + E2 \rightarrow E2$	$\mathbf{Q}^{(2)} = \chi_{pq}^{(Q)} \mathbf{E}\mathbf{V}\mathbf{E}$	10^{-6}		×		×
$E2 + E1 \rightarrow E2$	$\mathbf{Q}^{(2)} = \chi_{qp}^{(Q)} (\nabla \mathbf{E})\mathbf{E}$	10^{-6}		×		×
$E2 + E2 \rightarrow E1$	$\mathbf{P}^{(2)} = \chi_{qq}^{(P)} (\nabla \mathbf{E})(\nabla \mathbf{E})$	10^{-6}				

processes which involve one electric quadrupole interaction. We consider molecular systems which have no intrinsic electric dipole nonlinearity, so that the quadrupolar response comes only from individual molecules. The effective nonlinear polarizability for the $E1+E1 \rightarrow E2$ process has been given in Eq. (7). The joint effective nonlinear polarizability for the $E1+E2 \rightarrow E1$ and $E2+E1 \rightarrow E1$ processes is given by

$$\alpha_{\text{eff}}^{E1E1E2} + \alpha_{\text{eff}}^{E1E2E1} = \frac{1}{15} [(-\beta_{\xi\xi\eta\eta}^{E1E1E2} + 3\beta_{\xi\eta\eta\xi}^{E1E1E2}) + (-\beta_{\xi\eta\eta\xi}^{E1E2E1} + 3\beta_{\xi\xi\eta\eta}^{E1E2E1})] \times (\mathbf{k}_{\omega,a} \cdot \mathbf{e}_{2\omega,a})(\mathbf{e}_{\omega,a} \cdot \mathbf{e}_{\omega,a}). \quad (11)$$

These two processes yield both P -in/ P -out and S -in/ P -out SHG. The nonlinear polarizabilities in the molecular frame have a similar form to Eq. (10), and from now on we will not give them explicitly.

The third group consists of two magnetic dipole processes involving two magnetic interactions: $E1+M1 \rightarrow M1$ and $M1+E1 \rightarrow M1$. This group gives the leading correction to the standard multipolar optical second harmonics. The joint effective nonlinear polarizability is given by

$$\alpha_{\text{eff}}^{M1E1M1} + \alpha_{\text{eff}}^{M1M1E1} = \frac{1}{6} [\epsilon_{\xi\xi\eta} (\beta_{\xi\xi\eta}^{M1E1M1} - \beta_{\xi\xi\eta}^{M1M1E1})] \times [(\mathbf{k}_{2\omega,a} \times \mathbf{k}_{\omega,a}) \cdot \mathbf{e}_{2\omega,a}](\mathbf{e}_{\omega,a} \cdot \mathbf{e}_{\omega,a}). \quad (12)$$

These two processes produce S -in/ S -out and P -in/ S -out SHG. It is noteworthy that even though the effective nonlinear polarizabilities for $E1+M1 \rightarrow M1$ and $M1+E1 \rightarrow M1$ are usually less than that for $E1+E1 \rightarrow E2$ by a factor of 10, they can become comparable when the electron orbitals are significantly larger than the Bohr radius a_B . The latter is certainly the case for fullerene-based molecules. However, the intrinsic molecular polarizability $\epsilon_{\xi\xi\eta} (\beta_{\xi\xi\eta}^{M1E1M1} - \beta_{\xi\xi\eta}^{M1M1E1})$ vanishes if the molecule possesses an inversion center. Therefore, to observe the contribution from $E1+M1 \rightarrow M1$ and $M1+E1 \rightarrow M1$ processes, the molecular system must not have inversion symmetry. The latter is not the case for fullerene molecules or their weakly modified derivatives.

For completeness, we also consider the next two groups. The fourth group consists of multipolar processes involving one electric quadrupole interaction and one magnetic dipole interaction. The joint effective nonlinear polarizability for the $E1+M1 \rightarrow E2$ and $M1+E1 \rightarrow E2$ processes is given by

$$\alpha_{\text{eff}}^{E2E1M1} + \alpha_{\text{eff}}^{E2M1E1} = \frac{1}{30} [(-\beta_{\xi\xi\eta\eta}^{E2E1M1} + 3\beta_{\xi\eta\xi\eta}^{E2E1M1}) + (-\beta_{\xi\xi\eta\eta}^{E2M1E1} + 3\beta_{\xi\eta\xi\eta}^{E2M1E1})] \times \{(\mathbf{k}_{2\omega,a} \cdot \mathbf{e}_{\omega,a})(\mathbf{e}_{2\omega,a} \cdot (\mathbf{k}_{\omega,a} \times \mathbf{e}_{\omega,a})) + (\mathbf{e}_{2\omega,a} \cdot \mathbf{e}_{\omega,a})(\mathbf{e}_{\omega,a} \cdot (\mathbf{k}_{2\omega,a} \times \mathbf{k}_{\omega,a}))\}. \quad (13)$$

The first term in the curly brackets gives P -in/ S -out SHG while the second term yields S -in/ S -out SHG. The joint effective nonlinear polarizability for the $E1+E2 \rightarrow M1$ and $E2+E1 \rightarrow M1$ processes is given by

$$\alpha_{\text{eff}}^{M1E1E2} + \alpha_{\text{eff}}^{M1E2E1} = \frac{1}{30} [(-\beta_{\xi\xi\eta\eta}^{M1E1E2} + 3\beta_{\xi\eta\xi\eta}^{M1E1E2}) + (-\beta_{\xi\eta\eta\xi}^{M1E2E1} + 3\beta_{\xi\xi\eta\eta}^{M1E2E1})] [(\mathbf{e}_{2\omega,a} \cdot (\mathbf{k}_{2\omega,a} \times \mathbf{k}_{\omega,a}))(\mathbf{e}_{\omega,a} \cdot \mathbf{e}_{\omega,a})], \quad (14)$$

which produces both S -in/ S -out and P -in/ S -out SHG. The effective nonlinear polarizabilities for $E2+M1 \rightarrow E1$ and $M1+E2 \rightarrow E1$ vanish as a result of rotational average.

The fifth group consists of three processes. The $E2+E2 \rightarrow E1$ process has a vanishing effective nonlinear polarizability after the rotational average. For the $E1+E2 \rightarrow E2$ and $E2+E1 \rightarrow E2$ processes, we can write a joint effective nonlinear polarizability

$$\alpha_{\text{eff}}^{E2E1E2} + \alpha_{\text{eff}}^{E2E2E1} = \frac{1}{30} [\epsilon_{\xi\xi\eta} (\beta_{\xi\gamma\zeta\eta}^{E2E1E2} - \beta_{\xi\gamma\zeta\eta}^{E2E2E1})] \{[\mathbf{e}_{2\omega,a} \cdot (\mathbf{k}_{2\omega,a} \times \mathbf{k}_{\omega,a})](\mathbf{e}_{\omega,a} \cdot \mathbf{e}_{\omega,a}) + (\mathbf{e}_{2\omega,a} \cdot \mathbf{e}_{\omega,a})[\mathbf{e}_{\omega,a} \cdot (\mathbf{k}_{2\omega,a} \times \mathbf{k}_{\omega,a})]\}, \quad (15)$$

which yields P -in/ S -out from the first term and S -in/ S -out from both the first and second terms.

We summarize these results in Table I. In the first column, we display processes which are listed by their order of relative strength. The latter is displayed in the third column. These processes are distinguished by both the combination of involved multipolar interactions and the time ordering with which these interactions are applied. In the second column, we show the corresponding macroscopic multipolar polarization densities. The nonlinear susceptibility is given by $\chi^{(2)} \approx N_{s,\text{eff}}^{(2)} \alpha_{\text{eff}}^{(2)}$. On the

left-hand sides of the expressions, we use $P^{(2)}$, $M^{(2)}$, and $Q^{(2)}$ to represent the densities of nonlinear electric dipole, magnetic dipole, and electric quadrupole moments. On the right-hand sides, the superscript indicates the multipolar interaction with which the harmonic photon is created. The subscript indicates the combination of the multipolar interactions with which the fundamental photons are annihilated. The remaining four columns are four fundamental second-harmonic polarization combinations, and the crosses indicate the symmetry-allowed ones.

IV. MACROSCOPIC LOCAL-FIELD FACTORS

The expressions for the effective nonlinear polarizabilities in Sec. III have to be modified when the linear dielectric constants of the two adjoining isotropic media are different. In a description of surface optical second-harmonic generation, Heinz and Shen introduced macroscopic local-field factors which properly incorporate the effect of different linear dielectric constants for the two bulk media and the surface region.^{2,3,7} The local-field factors were shown to form a second-rank tensor

$$\vec{L} = \begin{bmatrix} L_{xx} & 0 & 0 \\ 0 & L_{yy} & 0 \\ 0 & 0 & L_{zz} \end{bmatrix}. \quad (16)$$

By rewriting $|N_{s,\text{eff}}^{(2)}\alpha_{\text{eff}}^{(2)}|^2$ in Eq. (3) as $|N_{s,\text{eff}}^{(2)}\alpha_{\text{eff}}^{(2)}|^2 = |\mathbf{e}_{2\omega,a} \cdot \vec{\chi}_{\text{eff}}^{(2)} \cdot \mathbf{e}_{\omega,a} \mathbf{e}_{\omega,a}|^2$ in the case of surface second-harmonic generation, they showed that the modification is achieved by simply replacing $|\mathbf{e}_{2\omega,a} \cdot \vec{\chi}_{\text{eff}}^{(2)} \cdot \mathbf{e}_{\omega,a} \mathbf{e}_{\omega,a}|^2$ with

$$|(\vec{L}_{2\omega} \cdot \mathbf{e}_{2\omega,a}) \cdot \vec{\chi}_{\text{eff}}^{(2)} \cdot (\vec{L}_{\omega} \cdot \mathbf{e}_{\omega,a})(\vec{L}_{\omega} \cdot \mathbf{e}_{\omega,a})|^2$$

(Refs. 2,3,7). We can modify the results of Sec. III by using similar local-field factors. For multipolar optical harmonic generation in the bulk, the proper macroscopic local-field factors also form a second-rank tensor as shown in Eq. (16) with

$$L_{\Omega,xx} = \frac{2\varepsilon_{\Omega,a}k_{\Omega,b;z}}{\varepsilon_{\Omega,b}k_{\Omega,a;z} + \varepsilon_{\Omega,a}k_{\Omega,b;z}}, \quad (17)$$

$$L_{\Omega,yy} = \frac{2k_{\Omega,a;z}}{k_{\Omega,a;z} + k_{\Omega,b;z}}, \quad (18)$$

$$L_{\Omega,zz} = \frac{2\varepsilon_{\Omega,a}k_{\Omega,a;z}}{\varepsilon_{\Omega,b}k_{\Omega,a;z} + \varepsilon_{\Omega,a}k_{\Omega,b;z}}, \quad (19)$$

where

$$\begin{aligned} k_{\omega,a;z} &= +(\omega/c)\sqrt{\varepsilon_{\omega,a}\cos\theta_{\text{inc}}}, \\ k_{\omega,b;z} &= +(\omega/c)\sqrt{\varepsilon_{\omega,b} - \varepsilon_{\omega,a}(\sin\theta_{\text{inc}})^2}, \\ k_{n\omega,a;z} &= -(n\omega/c)\sqrt{\varepsilon_{n\omega,a} - \varepsilon_{\omega,a}(\sin\theta_{\text{inc}})^2}, \\ k_{n\omega,b;z} &= -(n\omega/c)\sqrt{\varepsilon_{n\omega,b} - \varepsilon_{\omega,a}(\sin\theta_{\text{inc}})^2}. \end{aligned} \quad (20)$$

$$S(2\omega) = \frac{8\pi^3(2\omega)^2(\sec\theta_{\text{inc}})^2 I_{\omega,a}^2 A}{c^3 \varepsilon_{2\omega,a} \varepsilon_{\omega,a}} |N_{s,\text{eff}}^{(2)} N_{ab}^{(2)} [\frac{1}{6}(\varepsilon_{\xi\xi\eta} \beta_{\xi\xi\eta}^{E1M1E1})]|^2 [(\vec{M}_{\Omega} \cdot \mathbf{k}_{\Omega}) \cdot (\vec{L}_{2\omega} \cdot \mathbf{e}_{2\omega,a})][(\vec{L}_{\omega} \cdot \mathbf{e}_{\omega,a}) \cdot (\vec{L}_{\omega} \cdot \mathbf{e}_{\omega,a})]^2. \quad (24)$$

It is easily seen that the polarization properties of optical second-harmonic generation for all multipolar processes remain valid after the local-field correction factors are included.

At this point, we note that for three-layer systems, the local-field corrections are conceptually just as simple but are algebraically much more involved.¹⁹ This is due to the fact that there are two counterpropagating electric fields in the intermediate layer as a result of reflection.¹⁶

We note that $L_{\Omega,zz}$ is different from that for the surface optical harmonic generation by a factor of $\varepsilon_{\Omega,b}/\varepsilon_{\Omega,\text{surf}}$. $\varepsilon_{\Omega,\text{surf}}$ is the dielectric constant of the surface region.^{2,3,7} We also note that Snell's law requires $k_{n\omega,b;x} = k_{n\omega,a;x} = nk_{\omega,b;x} = nk_{\omega,a;x} = n(\omega/c)\sqrt{\varepsilon_{\omega,a}\sin\theta_{\text{inc}}}$. Since the components of L_{ω} are merely the transmission Fresnel coefficients for the fundamental field, we may replace $\mathbf{e}_{\omega,a}$ in Eqs. (3), (5), (7), (8), (9), (11), (12), (13), (14), and (15) by $(\vec{L}_{\omega} \cdot \mathbf{e}_{\omega,a})$. Furthermore, because the deduction of $\vec{L}_{2\omega}$ for the outgoing optical second harmonics is independent of which nonlinear current source is operative, we may replace $\mathbf{e}_{2\omega,a}$ in these equations by $(\vec{L}_{2\omega} \cdot \mathbf{e}_{2\omega,a})$. These two changes are not yet complete. Unlike the surface second-harmonic generation, the effective surface densities $N_{s,\text{eff}}^{(2)}$ for multipolar optical SHG processes depend on the dielectric constants of the medium b . Therefore, to be symmetric, we define a surface density correction factor for n th harmonics

$$N_{ab}^{(n)} \equiv \frac{nk_{\omega,a;z} - k_{n\omega,a;z}}{nk_{\omega,b;z} - k_{n\omega,b;z}}, \quad (21)$$

so that we may replace $N_{s,\text{eff}}^{(2)}$ in Eq. (3) with $N_{s,\text{eff}}^{(2)} N_{ab}^{(2)}$. Another distinct feature of a multipolar SHG process is that the effective nonlinear polarizability $\alpha_{\text{eff}}^{(2)}$ involves wave vectors \mathbf{k}_{Ω} which are contained in the nonlinear source current in medium b . We define a second-rank tensor \vec{M} :

$$\vec{M} = \begin{bmatrix} M_{xx} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & M_{zz} \end{bmatrix}, \quad (22)$$

so that we only need to replace \mathbf{k}_{Ω} with $(\vec{M}_{\Omega} \cdot \mathbf{k}_{\Omega})$ in Eqs. (7), (8), (11), (12), (13), (14), and (15). From the boundary condition, we find

$$\begin{aligned} M_{\Omega,xx} &= 1, \\ M_{\Omega,zz} &= \frac{k_{\Omega,a;z}}{k_{\Omega,b;z}}. \end{aligned} \quad (23)$$

As an example, a complete expression of the reflected optical second harmonics from the $E1+M1 \rightarrow E1$ process from an isotropic medium is given by

For a multipolar optical second-harmonic generation in the intermediate layer, the two fundamental photons do not have to be annihilated by the upward-going field alone or by the downward-going field alone. Consequently, some of the terms which do not survive in deriving Eqs. (7), (8), and (11)–(15) as required by the transversality relation will contribute. Furthermore, the finite width of the intermediate layer complicates the forms of the local-field factors even for the processes where the two

fundamental photons are annihilated by the same upward-going or downward-going fields. This aspect has been discussed fairly thoroughly in the work of Bloembergen and Pershan, and we will not pursue this matter further.¹⁶

V. POLARIZATION DEPENDENCE OF MULTIPOLAR OPTICAL THIRD-HARMONIC GENERATION (THG)

Optical third-harmonic generation (THG) from isotropic media can be obtained similarly. Since the electric dipole process $E1 + E1 + E1 \rightarrow E1$ is allowed, we only consider multipolar processes containing one multipolar interaction. The results are summarized in Table II. Because there is one more photon to be annihilated in a

third-harmonic generation process, there are more possible time orderings with which three fundamental photons are annihilated and one third-harmonic photon is created. The radiated third-harmonic power in reflection is given by

$$S(3\omega) = \frac{8\pi^3(3\omega)^2 \sec^2 \theta_{\text{inc}}}{c^3 \epsilon_{3\omega,a}^{1/2} \epsilon_{\omega,a}} |N_{s,\text{eff}}^{(3)} N_{ab}^{(3)} \alpha_{\text{eff}}^{(3)}|^2 I_{\omega,a}^3 A, \quad (25)$$

where the effective surface density $N_{s,\text{eff}}^{(3)}$ is given by Eq. (4), and $N_{ab}^{(3)}$ by Eq. (20). Again the polarization dependence is completely determined by the corresponding effective nonlinear polarizability $\alpha_{\text{eff}}^{(3)}$.

For the $E1 + E1 + E1 \rightarrow E1$ process, we find that

$$\alpha_{\text{eff}}^{E1E1E1E1} = \frac{1}{15} (\beta_{\xi\xi\eta\eta}^{E1E1E1E1} + \beta_{\xi\eta\xi\eta}^{E1E1E1E1} + \beta_{\xi\eta\eta\xi}^{E1E1E1E1}) [(\vec{L}_{3\omega} \cdot \mathbf{e}_{3\omega,a}) \cdot (\vec{L}_{\omega} \cdot \mathbf{e}_{\omega,a})] [(\vec{L}_{\omega} \cdot \mathbf{e}_{\omega,a}) \cdot (\vec{L}_{\omega} \cdot \mathbf{e}_{\omega,a})], \quad (26)$$

$$\beta_{ijkl}^{E1E1E1E1} \equiv \sum_{u,v,w,g} \left[\frac{p_i^{gu} (p_j^{uv} p_k^{vw} p_l^{wg} + p_j^{uv} p_l^{vw} p_k^{wg} + p_k^{uv} p_j^{vw} p_l^{wg} + p_k^{uv} p_l^{vw} p_j^{wg} + p_l^{uv} p_j^{vw} p_k^{wg} + p_l^{uv} p_k^{vw} p_j^{wg})}{(E_{ug} - 3\hbar\omega)(E_{vg} - 2\hbar\omega)(E_{wg} - \hbar\omega)} \right. \\ \left. + \text{three other terms with different time ordering} \right]. \quad (27)$$

It produces *P*-in/*P*-out and *S*-in/*S*-out third harmonics (THG).

If the molecular systems of the fluid or solid have no intrinsic inversion centers, the four multipolar processes containing one magnetic dipole interaction give the leading corrections to the third harmonics. For the $E1 + E1 + E1 \rightarrow M1$ process, we have

$$\alpha_{\text{eff}}^{M1E1E1E1} = \frac{1}{15} (\beta_{\xi\xi\eta\eta}^{M1E1E1E1} + \beta_{\xi\eta\xi\eta}^{M1E1E1E1} + \beta_{\xi\eta\eta\xi}^{M1E1E1E1}) \{ [(\vec{M}_{3\omega} \cdot \mathbf{k}_{3\omega,a}) \times (\vec{L}_{3\omega} \cdot \mathbf{e}_{3\omega,a})] \cdot (\vec{L}_{\omega} \cdot \mathbf{e}_{\omega,a}) \} \cdot [(\vec{L}_{\omega} \cdot \mathbf{e}_{\omega,a}) \cdot (\vec{L}_{\omega} \cdot \mathbf{e}_{\omega,a})], \quad (28)$$

$$\beta_{ijkl}^{M1E1E1E1} \equiv \sum_{u,v,w,g} \left[\frac{m_i^{gu} (p_j^{uv} p_k^{vw} p_l^{wg} + p_j^{uv} p_l^{vw} p_k^{wg} + p_k^{uv} p_j^{vw} p_l^{wg} + p_k^{uv} p_l^{vw} p_j^{wg} + p_l^{uv} p_j^{vw} p_k^{wg} + p_l^{uv} p_k^{vw} p_j^{wg})}{(E_{ug} - 3\hbar\omega)(E_{vg} - 2\hbar\omega)(E_{wg} - \hbar\omega)} \right. \\ \left. + \text{three other terms with different time ordering} \right]. \quad (29)$$

It produces *S*-in/*P*-out and *P*-in/*S*-out THG. The effective nonlinear polarizabilities of the other three processes have

TABLE II. Rotational symmetry-allowed polarization combinations for multipolar optical third-harmonic generation (THG) from a molecular fluid or an isotropic solid involving one multipolar interaction.

Multipolar processes	Multipolar polarization density	Relative strength	<i>P</i> -in, <i>P</i> -out (<i>P</i> - <i>P</i>)	<i>P</i> -in, <i>S</i> -out (<i>P</i> - <i>S</i>)	<i>S</i> -in, <i>P</i> -out (<i>S</i> - <i>P</i>)	<i>S</i> -in, <i>S</i> -out (<i>S</i> - <i>S</i>)
$E1 + E1 + E1 \rightarrow E1$	$\mathbf{P}^{(3)} = \chi_{ppp}^{(P)} \mathbf{EEE}$	1	×			×
$E1 + E1 + E1 \rightarrow M1$	$\mathbf{M}^{(3)} = \chi_{ppp}^{(M)} \mathbf{EEE}$	10^{-2}		×	×	
$E1 + E1 + M1 \rightarrow E1$	$\mathbf{P}^{(3)} = \chi_{ppm}^{(P)} \mathbf{EEB}$	10^{-2}		×	×	
$E1 + M1 + E1 \rightarrow E1$	$\mathbf{P}^{(3)} = \chi_{pmp}^{(P)} \mathbf{EBE}$	10^{-2}		×	×	
$M1 + E1 + E1 \rightarrow E1$	$\mathbf{P}^{(3)} = \chi_{mpp}^{(P)} \mathbf{BEE}$	10^{-2}		×	×	
$E1 + E1 + E1 \rightarrow E2$	$\mathbf{Q}^{(3)} = \chi_{ppp}^{(Q)} \mathbf{EEE}$	10^{-3}				
$E1 + E1 + E2 \rightarrow E1$	$\mathbf{P}^{(3)} = \chi_{ppq}^{(P)} \mathbf{EE}(\nabla\mathbf{E})$	10^{-3}		×	×	
$E1 + E2 + E1 \rightarrow E1$	$\mathbf{P}^{(3)} = \chi_{ppq}^{(P)} \mathbf{E}(\nabla\mathbf{E})\mathbf{E}$	10^{-3}		×	×	
$E2 + E1 + E1 \rightarrow E1$	$\mathbf{P}^{(3)} = \chi_{qpq}^{(P)} \mathbf{E}(\nabla\mathbf{E})\mathbf{EE}$	10^{-3}		×	×	

the same form except for the molecular polarizabilities. Their joint polarizability can be expressed as

$$\begin{aligned} & \alpha_{\text{eff}}^{E1E1E1M1} + \alpha_{\text{eff}}^{E1E1M1E1} + \alpha_{\text{eff}}^{E1M1E1E1} \\ &= \frac{1}{15} [(\beta_{\xi\xi\eta\eta}^{E1E1E1M1} + \beta_{\xi\eta\xi\eta}^{E1E1E1M1} + \beta_{\xi\eta\eta\xi}^{E1E1E1M1}) \\ & \quad + (\beta_{\xi\xi\eta\eta}^{E1E1M1E1} + \beta_{\xi\eta\xi\eta}^{E1E1M1E1} + \beta_{\xi\eta\eta\xi}^{E1E1M1E1}) + (\beta_{\xi\xi\eta\eta}^{E1M1E1E1} + \beta_{\xi\eta\xi\eta}^{E1M1E1E1} + \beta_{\xi\eta\eta\xi}^{E1M1E1E1})] \\ & \quad \times [(\vec{L}_\omega \cdot \mathbf{e}_{\omega,a}) \cdot (\vec{L}_\omega \cdot \mathbf{e}_{\omega,a})] \{ [\vec{M}_\omega \cdot \mathbf{k}_{\omega,a}] \times (\vec{L}_\omega \cdot \mathbf{e}_{\omega,a}) \} \cdot (\vec{L}_{3\omega} \cdot \mathbf{e}_{3\omega,a}) \}, \quad (30) \end{aligned}$$

which also produces only *S*-in/*P*-out and *P*-in/*S*-out THG. The molecular polarizabilities are given by expressions similar to Eq. (29).

The processes containing one electric quadrupole interaction give rise to the next-order correction. These processes also require the molecular systems to be noncentrosymmetric. The effective nonlinear polarizability for $E1+E1+E1 \rightarrow E2$ vanishes as a result of the rotational average. The effective polarizabilities for the $E1+E1+E2 \rightarrow E1$, $E1+E2+E1 \rightarrow E1$, and $E2+E1+E1 \rightarrow E1$ processes have the same form except for the molecular polarizabilities. Their joint nonlinear polarizability is given by

$$\begin{aligned} & \alpha_{\text{eff}}^{E1E1E1E2} + \alpha_{\text{eff}}^{E1E1E2E1} + \alpha_{\text{eff}}^{E1E2E1E1} \\ &= \frac{1}{30} [-\varepsilon_{\xi\eta\zeta} (\beta_{\xi\eta\gamma\zeta}^{E1E1E1E2} + \beta_{\xi\gamma\eta\zeta}^{E1E1E1E2}) - \varepsilon_{\xi\eta\zeta} (\beta_{\xi\gamma\eta\zeta}^{E1E1E2E1} - \beta_{\xi\eta\gamma\zeta}^{E1E1E2E1}) + \varepsilon_{\xi\eta\zeta} (\beta_{\xi\eta\gamma\zeta}^{E1E2E1E1} + \beta_{\xi\eta\gamma\zeta}^{E1E2E1E1})] \\ & \quad \times [(\vec{L}_\omega \cdot \mathbf{e}_{\omega,a}) \cdot (\vec{L}_\omega \cdot \mathbf{e}_{\omega,a})] \{ [(\vec{M}_\omega \cdot \mathbf{k}_{\omega,a}) \times (\vec{L}_\omega \cdot \mathbf{e}_{\omega,a})] \cdot (\vec{L}_{3\omega} \cdot \mathbf{e}_{3\omega,a}) \}, \quad (31) \end{aligned}$$

which yields *S*-in/*P*-out and *P*-in/*S*-out THG as well.

VI. CONCLUSIONS

In the framework of molecular quantum electrodynamics, the polarization properties of optical harmonic generation can be analyzed in a unified way by defining effective nonlinear polarizabilities $\alpha_{\text{eff}}^{(n)}$.¹² The macroscopic local-field factors can also be included in a unified way. For multipolar harmonics generation processes, we have introduced two additional local-field factors (\vec{M} and $N_{ab}^{(n)}$), so that the effects of different linear dielectric constants of the two bulk media are incorporated fully and symmetrically in the expression of the radiated power [for example, Eq. (24)].^{2,3,7} These bookkeeping procedures are convenient in an analysis of optical harmonic generation under suitable experimental situations. We have investigated the polarization properties of multipolar optical second harmonics and third harmonics generated from the bulk of isotropic molecular fluids or solids up to two multipolar interactions. In the geometry shown in Fig. 1, and when the nonlinearity of the medium *a* can be neglected, each multipolar optical harmonics has a distinct polarization dependence as displayed in Tables I and II. This result facilitates the identification and characterization of higher-order multipolar harmonic generation from isotropic fluids and solids. From the magnitudes of multipolar harmonics, one may be able to deduce information on the sizes of electron orbitals of the molecular systems.¹³

ACKNOWLEDGMENT

Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, under Grant PRF No. 27240-AC5, for the support of this research.

APPENDIX: ROTATIONAL AVERAGE OF TENSORS

A tensor $\beta_{ijk\dots}^{(n)}$ in a laboratory frame is related to that in the molecular frame $\beta_{\xi\eta\zeta\dots}^{(n)}$ by a direction cosine $I_{ijk\dots,\xi\eta\zeta\dots}^{(n)}$.^{12,17} A rotational average of $\beta_{ijk\dots}^{(n)}$ is then expressed as

$$\langle \beta_{ijk\dots}^{(n)} \rangle = \langle I_{ijk\dots,\xi\eta\zeta\dots}^{(n)} \rangle \beta_{\xi\eta\zeta\dots}^{(n)}. \quad (A1)$$

The full rotational average of direction cosine $\langle I_{ijk\dots,\xi\eta\zeta\dots}^{(n)} \rangle$ has been worked out by Andrews and Thirunamachandran.¹⁷

We consider situations which are relevant to the main text. The effective nonlinear polarizability can be written in the following form:

$$\alpha_{\text{eff}}^{(n)} = \langle I_{ijk\dots,\xi\eta\zeta\dots}^{(n)} \rangle \beta_{\xi\eta\zeta\dots}^{(n)} A_{1,i} A_{2,j} A_{3,k} \dots \quad (A2)$$

Using the results of Andrews and Thirunamachandran, we find that, for third-rank tensors,

$$\alpha_{\text{eff}}^{(3)} = \frac{1}{6} \varepsilon_{\xi\eta\zeta} \beta_{\xi\eta\zeta}^{(3)} [(\mathbf{A}_1 \times \mathbf{A}_2) \cdot \mathbf{A}_3]. \quad (A3)$$

For fourth-rank tensors,

$$\begin{aligned} \alpha_{\text{eff}}^{(4)} = \frac{1}{30} [& (4\beta_{\xi\xi\eta\eta}^{(4)} - \beta_{\xi\eta\xi\eta}^{(4)} - \beta_{\xi\eta\eta\xi}^{(4)}) (\mathbf{A}_1 \cdot \mathbf{A}_2) (\mathbf{A}_3 \cdot \mathbf{A}_4) \\ & + (4\beta_{\xi\eta\xi\eta}^{(4)} - \beta_{\xi\xi\eta\eta}^{(4)} - \beta_{\xi\eta\eta\xi}^{(4)}) (\mathbf{A}_1 \cdot \mathbf{A}_3) (\mathbf{A}_2 \cdot \mathbf{A}_4) \\ & + (4\beta_{\xi\eta\eta\xi}^{(4)} - \beta_{\xi\xi\eta\eta}^{(4)} - \beta_{\xi\eta\xi\eta}^{(4)}) (\mathbf{A}_1 \cdot \mathbf{A}_4) (\mathbf{A}_2 \cdot \mathbf{A}_3)]. \quad (A4) \end{aligned}$$

For fifth-rank tensors,

$$\begin{aligned}
\alpha_{\text{eff}}^{(5)} = & \frac{1}{30} [(3W_1^{(5)} - W_2^{(5)} - W_3^{(5)} + W_4^{(5)} + W_5^{(5)}) [\mathbf{A}_1 \cdot (\mathbf{A}_2 \times \mathbf{A}_3)] (\mathbf{A}_4 \cdot \mathbf{A}_5) \\
& + (-W_1^{(5)} + 3W_2^{(5)} - W_3^{(5)} - W_4^{(5)} + W_6^{(5)}) [\mathbf{A}_1 \cdot (\mathbf{A}_2 \times \mathbf{A}_4)] (\mathbf{A}_3 \cdot \mathbf{A}_5) \\
& + (-W_1^{(5)} - W_2^{(5)} + 3W_3^{(5)} - W_5^{(5)} - W_6^{(5)}) [\mathbf{A}_1 \cdot (\mathbf{A}_2 \times \mathbf{A}_5)] (\mathbf{A}_3 \cdot \mathbf{A}_4) \\
& + (W_1^{(5)} - W_2^{(5)} + 3W_4^{(5)} - W_5^{(5)} + W_6^{(5)}) [\mathbf{A}_1 \cdot (\mathbf{A}_3 \times \mathbf{A}_4)] (\mathbf{A}_2 \cdot \mathbf{A}_5) \\
& + (W_1^{(5)} - W_3^{(5)} - W_4^{(5)} + 3W_5^{(5)} - W_6^{(5)}) [\mathbf{A}_1 \cdot (\mathbf{A}_3 \times \mathbf{A}_5)] (\mathbf{A}_2 \cdot \mathbf{A}_4) \\
& + (W_2^{(5)} - W_3^{(5)} + W_4^{(5)} - W_5^{(5)} + 3W_6^{(5)}) [\mathbf{A}_1 \cdot (\mathbf{A}_4 \times \mathbf{A}_5)] (\mathbf{A}_2 \cdot \mathbf{A}_3)] ,
\end{aligned} \tag{A5}$$

where

$$\begin{aligned}
W_1^{(5)} & \equiv \epsilon_{\xi\eta\zeta} \beta_{\xi\eta\xi\gamma\gamma}^{(5)} , \\
W_2^{(5)} & \equiv \epsilon_{\xi\eta\zeta} \beta_{\xi\eta\gamma\xi\gamma}^{(5)} , \\
W_3^{(5)} & \equiv \epsilon_{\xi\eta\zeta} \beta_{\xi\eta\gamma\gamma\xi}^{(5)} , \\
W_4^{(5)} & \equiv \epsilon_{\xi\eta\zeta} \beta_{\xi\gamma\eta\xi\gamma}^{(5)} , \\
W_5^{(5)} & \equiv \epsilon_{\xi\eta\zeta} \beta_{\xi\gamma\eta\gamma\xi}^{(5)} , \\
W_6^{(5)} & \equiv \epsilon_{\xi\eta\zeta} \beta_{\xi\gamma\gamma\eta\xi}^{(5)} .
\end{aligned} \tag{A6}$$

For processes involving electric quadrupole interaction terms, Eq. (A5) may be simplified further, as the corresponding $\beta_{\xi\eta\xi\gamma\tau}^{(5)}$ have permutation symmetry with respect to the exchange of some of the subindices.

For sixth-rank tensors,

$$\begin{aligned}
\alpha_{\text{eff}}^{(6)} = & \frac{1}{210} [W_1^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_2) (\mathbf{A}_3 \cdot \mathbf{A}_4) (\mathbf{A}_5 \cdot \mathbf{A}_6) + W_2^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_2) (\mathbf{A}_3 \cdot \mathbf{A}_5) (\mathbf{A}_4 \cdot \mathbf{A}_6) \\
& + W_3^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_2) (\mathbf{A}_3 \cdot \mathbf{A}_6) (\mathbf{A}_4 \cdot \mathbf{A}_5) + W_4^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_3) (\mathbf{A}_2 \cdot \mathbf{A}_4) (\mathbf{A}_5 \cdot \mathbf{A}_6) \\
& + W_5^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_3) (\mathbf{A}_2 \cdot \mathbf{A}_5) (\mathbf{A}_4 \cdot \mathbf{A}_6) + W_6^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_3) (\mathbf{A}_2 \cdot \mathbf{A}_6) (\mathbf{A}_4 \cdot \mathbf{A}_5) \\
& + W_7^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_4) (\mathbf{A}_2 \cdot \mathbf{A}_3) (\mathbf{A}_5 \cdot \mathbf{A}_6) + W_8^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_4) (\mathbf{A}_2 \cdot \mathbf{A}_5) (\mathbf{A}_3 \cdot \mathbf{A}_6) \\
& + W_9^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_4) (\mathbf{A}_2 \cdot \mathbf{A}_6) (\mathbf{A}_3 \cdot \mathbf{A}_5) + W_{10}^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_5) (\mathbf{A}_2 \cdot \mathbf{A}_3) (\mathbf{A}_4 \cdot \mathbf{A}_6) \\
& + W_{11}^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_5) (\mathbf{A}_2 \cdot \mathbf{A}_4) (\mathbf{A}_3 \cdot \mathbf{A}_6) + W_{12}^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_5) (\mathbf{A}_2 \cdot \mathbf{A}_6) (\mathbf{A}_3 \cdot \mathbf{A}_4) \\
& + W_{13}^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_6) (\mathbf{A}_2 \cdot \mathbf{A}_3) (\mathbf{A}_4 \cdot \mathbf{A}_5) + W_{14}^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_6) (\mathbf{A}_2 \cdot \mathbf{A}_4) (\mathbf{A}_3 \cdot \mathbf{A}_5) \\
& + W_{15}^{(6)} (\mathbf{A}_1 \cdot \mathbf{A}_6) (\mathbf{A}_2 \cdot \mathbf{A}_5) (\mathbf{A}_3 \cdot \mathbf{A}_4)] ,
\end{aligned} \tag{A7}$$

with

$$W_n^{(6)} \equiv [M_{nm}^{(6)} f_{m,\xi\eta\xi\gamma\tau\nu}^{(6)}] \beta_{\xi\eta\xi\gamma\tau\nu}^{(6)} . \tag{A8}$$

Here $M_{nm}^{(6)}$ and $f_{m,\xi\eta\xi\gamma\tau\nu}^{(6)}$ are matrix elements defined by Andrews and Thirunamachandran in their Eq. (20), and Table II.¹⁷

¹Y. R. Shen, *Nature* **337**, 519 (1989); *Surf. Sci.* **299**, 551 (1994).

²Y. R. Shen, *Annu. Rev. Phys. Chem.* **40**, 327 (1989).

³T. F. Heinz, in *Nonlinear Surface Electromagnetic Phenomena*, edited by H.-E. Ponath and G. I. Stegeman (Elsevier, Amsterdam, 1991).

⁴C. K. Chen, T. F. Heinz, D. Richard, and Y. R. Shen, *Phys. Rev. Lett.* **46**, 1010 (1981); T. F. Heinz, H. W. K. Tom, and Y. R. Shen, *Laser Focus* **19**, 101 (1983).

⁵N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, *Phys. Rev.* **174**, 813 (1968).

⁶H. W. K. Tom, T. F. Heinz, and Y. R. Shen, *Phys. Rev. Lett.* **51**, 1983 (1983).

⁷T. F. Heinz, Ph.D. thesis, University of California at Berkeley,

1982; H. W. K. Tom, Ph.D. thesis, University of California at Berkeley, 1984.

⁸P. Guyot-Sionnest and Y. R. Shen, *Phys. Rev. B* **38**, 7985 (1988); P. Guyot-Sionnest, W. Chen, and Y. R. Shen, *ibid.* **33**, 8254 (1986).

⁹P. Guyot-Sionnest and Y. R. Shen, *Phys. Rev. B* **35**, 4420 (1987).

¹⁰J. E. Sipe, V. Mizrahi, and G. I. Stegeman, *Phys. Rev. B* **35**, 9091 (1987); J. E. Sipe, D. J. Moss, and H. M. van Driel, *ibid.* **35**, 1129 (1987).

¹¹T. F. Heinz and D. P. Divincenzo, *Phys. Rev. A* **42**, 6249 (1990).

¹²X. D. Zhu and A. Wong, *Phys. Rev. B* **46**, 2540 (1992).

- ¹³B. Koopmans, A. Anema, H. T. Jonkman, G. A. Sawatzky, and F. van der Woude, *Phys. Rev. B* **48**, 2759 (1993); B. Koopmans, Anna-Maria Janner, H. T. Jonkman, G. A. Sawatzky, and F. van der Woude, *Phys. Lett. B* **71**, 3569 (1993).
- ¹⁴E. Alder, *Phys. Rev.* **134**, A728 (1963); P. S. Pershan, *ibid.* **130**, 919 (1963).
- ¹⁵G. Lupke, D. J. Bottomley, and H. M. van Driel, *J. Opt. Soc. Am. B* **11**, 34 (1994).
- ¹⁶N. Bloembergen and P. S. Pershan, *Phys. Rev.* **128**, 606 (1962).
- ¹⁷D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Academic, London, 1984); D. L. Andrews and T. Thirunamachandran, *J. Chem. Phys.* **67**, 5026 (1977); D. L. Andrews and N. P. Blake, *Phys. Rev. A* **38**, 3113 (1988).
- ¹⁸Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).
- ¹⁹V. Mizrahi and J. E. Sipe, *J. Opt. Soc. Am. B* **5**, 660 (1988).