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Surface second-harmonic generation from chiral materials

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We present a theory of second-harmonic generation from thin films of chiral materials. The formalism makes distinct the contributions of electric- and magnetic-dipole transitions to the radiative process. Three susceptibility tensors form a minimal description of the optical nonlinearity, two for the nonlinear surface polarization and one for the nonlinear surface magnetization. The influence of optical interfaces is made explicit by using Fresnel coefficients to describe the reflection and transmission of the fundamental and second-harmonic radiation. Hence, the characterization and metrology of chiral materials by surface second-harmonic generation are given a firm theoretical foundation. In agreement with recent experimental observations, second-harmonic signals from chiral surfaces are predicted to depend sensitively upon whether the fundamental light is right- or left-hand circularly polarized. We show that this second-harmonic-generation circular-dichroism effect is a key signature of chirality and originates fundamentally from contributions of magnetic-dipole transitions to the nonlinear polarization and magnetization of the surface.

I. INTRODUCTION

Surface second-harmonic generation is an acknowledged method for the characterization and metrology of material systems.[1,2] The method has gained particular attention because a second-harmonic signal may originate from a surface of a material, whereas little or no signal comes from the bulk of the sample.[3] This behavior occurs owing to the surface having different physical properties than those of the bulk. In particular, assuming radiation from only electric dipoles, a centrosymmetric material system cannot radiate at the second-harmonic frequency of the fundamental wave that is driving the nonlinearity.[4] However, for a surface, the centrosymmetry is broken and second-harmonic radiation can occur.[5] The analysis of real material systems has been complicated by the fact that the source of the second-harmonic radiation may be other than electric dipoles, for instance, magnetic dipoles and electric quadrupoles. Theoretical formalisms have taken into account these other contributions by the use of an effective susceptibility for the second-order nonlinear response of the surface.[6,7] The result of comparing theory and experiment is a numerical value of this effective surface susceptibility. This approach is merited by the fact that in many cases distinguishing the particular source is extremely difficult, if not impossible.

Chiral materials possess a material structure that leads to optical activity, which includes such phenomena as optical rotation, optical rotary dispersion, and circular dichroism.[8,9] All of these effects demonstrate that optically active materials interact differently with right- and left-hand circularly-polarized light. Nonlinear optical processes in chiral media may also be sensitive to the handedness of the electromagnetic field driving the nonlinearity. Some specific examples have been worked out theoretically.[10–14] In recent experiments, sensitivity to the handedness of the fundamental light is observed in the process of second-harmonic generation from chiral molecules adsorbed on an air-water interface by Petralli-Mallow *et al.*,[15] from a Langmuir-Blodgett-deposited monolayer of a chiral polymer by Kauranen *et al.*,[16] and from bacteriorhodospin by Verbiest *et al.*[17] In all of these experiments, the phenomena may be said to be forms of nonlinear optical activity. We note that other experimental demonstrations of nonlinear-optical processes[18–20] have taken advantage of the specific properties of chiral materials, but they do not demonstrate nonlinear optical activity in the sense of the process depending differently upon whether the fundamental radiation is right- or left-hand circularly polarized.

Linear optical activity has been traced to contributions of magnetic dipoles,[21] which are substantial because of the helical structure that chiral molecules possess. Recent experimental results show that magnetic dipoles may also be responsible for nonlinear optical activity observed in second-harmonic generation[16,17] and for the occurrence of a second-harmonic signal.[20] All of this evidence makes it desirable to include explicitly in the formalism of surface second-harmonic generation the contributions of magnetic dipoles.

In this paper, we present a theory of second-harmonic generation from chiral surfaces. We make use of the formalism of Pershan,[22] which was used recently by Meijer *et al.*[20] in their description of second-harmonic generation from the bulk of a centrosymmetric crystal of chiral molecules. This formalism allows the contributions of electric- and magnetic-dipole transitions to the surface nonlinearity to be made distinct. In the limit in which the magnetic interaction is treated to first order, three different susceptibility tensors result. Two of them are for the nonlinear polarization and one is for the nonlinear magnetization. The influence of optical interfaces is made explicit by using Fresnel coefficients to describe the reflection and transmission of the fundamental and second-harmonic radiation. Hence, the characterization and metrology of chiral materials by surface second-harmonic generation are given a firm theoretical foundation. Furthermore, we use the theory to demonstrate the origin of the sensitivity of surface second-harmonic generation to the handedness of fundamental light and show that this sensitivity is a key signature of chirality.

The form of the nonlinearity leading to second-harmonic generation from a chiral surface is reviewed in Sec. II. In Sec. III, we summarize the general result of Ref. 23 for the electric field generated by a thin layer of both nonlinear polarization and magnetization. The specific form of the electromagnetic field that drives the nonlinearity is overviewed in Sec. IV. In Sec. V, we assemble the results of the previous three sections. Formulas for the reflected and transmitted second-harmonic waves as functions of the tensor components of the nonlinear susceptibilities are thus found for a chiral surface. We discuss the implications of the theory in Sec. VI. The main conclusions of this work are given in Sec. VII.

II. FORM OF THE SURFACE SECOND-ORDER NONLINEARITY

The helical structure of chiral molecules forces electrons displaced from their equilibrium position, by the application of an electric field, to follow a helical path. Thus, in addition to the usual electric-dipole moment that is present, a significant magnetic-dipole moment may also be present. For the same reason, chiral molecules also have a substantial response to the magnetic component of the driving field. For the process of second-harmonic generation, the magnetic-dipole interaction can result in the annihilation of a photon at the fundamental frequency ω or in the creation of a photon at the second-harmonic frequency 2ω.[11] The lowest-order contribution of magnetic dipoles is where only one of these transitions is due to a magnetic-dipole interaction.[14] For a magnetic-dipole interaction at ω, a contribution to the second-order nonlinear surface polarization,

$$\tilde{P}_i(2\omega)=\chi_{ijk}^{eee}E_j^F(\omega)E_k^F(\omega)+\chi_{ijk}^{eem}E_j^F(\omega)B_k^F(\omega) , \quad (1)$$

results, the strength of which scales with the surface-susceptibility-tensor element χ_{ijk}^{eem}. (Here, $\mathbf{E}^F$ and $\mathbf{B}^F$ are the fundamental electric field and magnetic-induction field, respectively, at the location of the nonlinear material.) For a magnetic-dipole interaction at 2ω, a second-order nonlinear surface magnetization,

$$\tilde{M}_i(2\omega)=\chi_{ijk}^{mee}E_j^F(\omega)E_k^F(\omega) , \quad (2)$$

occurs, the strength of which scales with the surface-susceptibility-tensor element χ_{ijk}^{mee}. Note that the first term of Eq. (1) is the nonlinear surface polarization resulting from response only to the electric field, the strength of which scales with the surface-susceptibility-tensor element χ_{ijk}^{eee}. In Eqs. (1) and (2), the subscripts i, j, or k refer to Cartesian coordinates and summation over repeated indices is implied. We see that three surface-susceptibility tensors form a minimal description of second-harmonic generation from a nonlinear surface when magnetic interactions, to first order, are made explicit.

We do not consider the detailed microscopic nature of chiral molecules, but do consider the general features that determine the nonvanishing elements of the macroscopic susceptibility tensors. The helicity of chiral molecules may be right or left handed. A consequence of this structure is that a chiral molecule cannot be superimposed upon its mirror image. There are no mirror planes for a single, chiral molecule. For an isotropic distribution of chiral molecules of a given handedness (i.e., one of the two possible enantiomers), the macroscopic structure of the material will also possess no mirror planes and hence is also chiral. The material may actually have a percentage of each enantiomer and still be chiral; however, for an equal percentage (i.e., a racemate), the macroscopic properties would possess mirror planes and the material system would be achiral and centrosymmetric. This achiral material would show no optical activity, which may be understood to be due to the magnetic-dipole transition moments of the two enantiomers being equal in magnitude but opposite in sign.[21]

The specific material system we shall consider is a thin layer of chiral molecules distributed isotropically upon a substrate. There continues to be no mirror planes, so the surface is chiral. Owing to the isotropic distribution of the molecules upon the surface, there is full rotational symmetry about any axis that is perpendicular to the plane of the surface (assumed to be in the x-y plane). These symmetry properties lead immediately to predictions of the nonvanishing elements of the susceptibility tensors. The nonvanishing elements of χ^{eee}, χ^{mee}, and χ^{eem} are summarized in Table I. We also give the nonvanishing elements for the case of an isotropic surface of achiral molecules. The presence of chirality is thus seen from Table I to lead to many more nonvanishing elements of the susceptibility tensors over those for the case of no chirality. For the case of a chiral surface, i.e., for only rotational symmetry, the same nonvanishing elements occur for each of the tensors χ^{eee}, χ^{mee}, and χ^{eem}. However, the tensor χ_{ijk}^{eem} does not obey intrinsic permutation symmetry in the indices j and k, because the components of the electric field and magnetic-induction field of the fundamental wave are distinguishable. Hence, the susceptibility χ^{eem} has seven independent elements, while χ^{eee} and χ^{mee} each have only four. We note that the electric-dipole-allowed susceptibility elements $\chi_{xyz}^{eee}=\chi_{xzy}^{eee}=-\chi_{yxz}^{eee}=-\chi_{yzx}^{eee}$ become nonvanishing for the chiral surface. These susceptibility elements do not involve magnetic dipoles; hence, magnetic dipoles are not responsible solely for the nonlinear optical response of the chiral surface being different from that of the achiral surface.

Second-harmonic generation (SHG) has been observed in a bulk sample of chiral molecules.[20] The material system was a centrosymmetric crystal made of an equal number of the two different enantiomers of the chiral molecule. Due to the centrosymmetry, second-harmonic generation is not allowed in the electric-dipole approximation, i.e., the bulk form of χ^{eee} must vanish.[4] The observed second-harmonic signal was found to confirm the presence of magnetic dipoles and hence makes χ^{eem} and χ^{mee} a compelling formalism. Furthermore, there is theoretical evidence that χ^{eee} for SHG in bulk should

TABLE I. Form of the second-order susceptibility tensors for an isotropic surface of an achiral material or a chiral material, where the surface is in the x-y plane. Each element is denoted by its Cartesian indices.

Susceptibility	Independent nonvanishing tensor elements: Isotropic and achiral (has mirror planes)	Isotropic and chiral (no mirror planes)
χ^{eee}	zzz	zzz
	$zxx = zyy$	$zxx = zyy$
	$xxz = xzx = yyz = yzy$	$xxz = xzx = yyz = yzy$
		$xyz = xzy = -yxz = -yzx$
χ^{mee}		zzz
		$zxx = zyy$
		$xxz = xzx = yyz = yzy$
	$xyz = xzy = -yxz = -yzx$	$xyz = xzy = -yxz = -yzx$
χ^{eem}		zzz
		$zxx = zyy$
		$xxz = yyz$
		$xzx = yzy$
	$xyz = -yxz$	$xyz = -yxz$
	$xzy = -yzx$	$xzy = -yzx$
	$zxy = -zyx$	$zxy = -zyx$

continue to vanish even for a noncentrosymmetric, chiral material providing that the material is isotropic.[24] For a thin sheet of chiral material, however, the surface-susceptibility tensor χ^{eee} will be nonvanishing because of the strong broken symmetry. In principle, electric-quadrupole effects, which occur together with magnetic-dipole effects in the multipole expansion of the matter-field interaction, may influence the measured values of the surface susceptibilities.[6,7] Many chiral molecules, though, have magnetic-dipole transitions that are much stronger than their electric-quadrupole transitions.[20,25] This fact makes it a well-justified assumption not to include the contributions of electric quadrupoles in the present theory.

For lossless materials (off-resonance excitation), the elements of χ^{eem} and χ^{mee} have been shown theoretically to be imaginary-valued quantities, while χ^{eee} is a real-valued quantity.[22,26] This 90° phase difference allows the effects of magnetic-dipole transitions to be distinguished from those of electric-dipole transitions. Magnetic dipoles will be seen as a dominant factor leading to the sensitivity of second-harmonic signals to whether right- or left-handed fundamental radiation drives the nonlinearity. This fact is completely consistent with the role of magnetic dipoles in linear optical activity.[21]

III. THE GENERATED ELECTRIC FIELD FROM A THIN LAYER OF NONLINEAR POLARIZATION AND MAGNETIZATION

The geometry of the material system we consider for surface second-harmonic generation is shown in Fig. 1. A thin sheet of nonlinear material at $z = z_0$ is assumed to be embedded in a layer of material possessing a linear-optical index of refraction n_3, where the material above this layer ($z > 0$) has the index n_1 and the material below ($z < -D$) has the index n_2. We take the thickness D, the position z_0, and the indices of refraction to be arbitrary in value at this stage. The fundamental wave $\mathbf{E}^I$ at frequency ω is incident from medium 1 upon the interface with medium 3 at an angle θ_1 with respect to the surface normal. The incident fundamental wave is transmitted into medium 3 and drives the nonlinearity. The nonlinearity will be seen below to generate an electric field at the

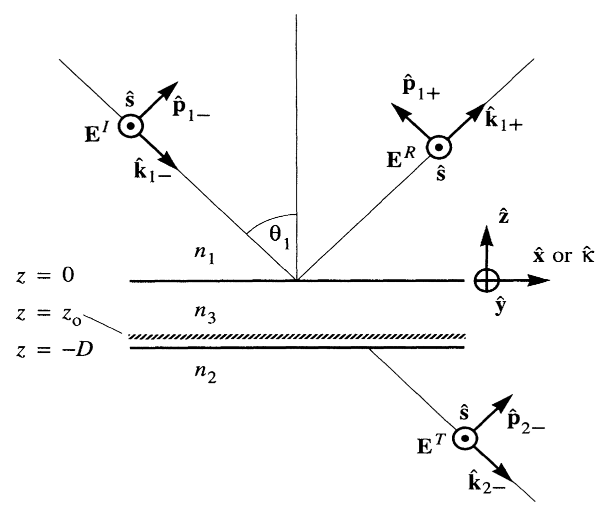

FIG. 1. Typical geometry of surface second-harmonic generation showing the unit vectors for the incident fundamental wave, and the reflected and transmitted second-harmonic waves. The dashed line indicates the thin, nonlinear layer. The circles with dots or crosses indicate vectors out of or into the drawing, respectively.

second-harmonic frequency 2ω, which forms a reflected wave $\mathbf{E}^R$ and a transmitted wave $\mathbf{E}^T$.

In the remainder of this section, we give a brief review of the result of Sipe[23] for the relation between the generated electric field and the nonlinear polarization and magnetization. We deal throughout with monochromatic fields of the form

$$\mathbf{F}(\mathbf{r},t)=\mathbf{F}(\mathbf{r},\omega)e^{-i\omega t}+\text{c.c.} \quad (3)$$

at the fundamental frequency and

$$\mathbf{F}(\mathbf{r},t)=\mathbf{F}(\mathbf{r},2\omega)e^{-i2\omega t}+\text{c.c.} \quad (4)$$

at the second-harmonic frequency.

Suppose that medium 3 is of infinite extent in the plus and minus z directions and that the sheet of nonlinear material at $z=z_0$ possesses a nonlinear polarization of the form

$$\mathbf{P}(\mathbf{r},2\omega)=\tilde{\mathbf{P}}(2\omega)\delta(z-z_0)\exp(i2\boldsymbol{\kappa}\cdot\mathbf{R}) \quad (5)$$

and a nonlinear magnetization of the form

$$\mathbf{M}(\mathbf{r},2\omega)=\tilde{\mathbf{M}}(2\omega)\delta(z-z_0)\exp(i2\boldsymbol{\kappa}\cdot\mathbf{R}) , \quad (6)$$

where $\delta(z)$ is the Dirac δ function, $\boldsymbol{\kappa}=\kappa\hat{\boldsymbol{\kappa}}$, $\mathbf{r}=z\hat{\mathbf{z}}+\mathbf{R}$, $\mathbf{R}=x\hat{\mathbf{x}}+y\hat{\mathbf{y}}$, and $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are the Cartesian unit vectors.

The nonlinear polarization and magnetization have been assumed to each have the same component $2\boldsymbol{\kappa}$ of their respective wave vectors that is in the plane of the surface (i.e., in the $\hat{\boldsymbol{\kappa}}$ direction). An electric field

$$\mathbf{E}(\mathbf{r},2\omega)=\mathbf{E}(z,2\omega)\exp(i2\boldsymbol{\kappa}\cdot\mathbf{R}) \quad (7)$$

will be generated by this sheet of nonlinear material that propagates with the same wave-vector component $2\kappa\boldsymbol{\kappa}$. The complete solution of the inhomogeneous, Maxwell equations for amplitude of the generated electric field is[27]

$$\begin{aligned}\mathbf{E}(z,2\omega)=&\,i\frac{8\pi\tilde{\omega}^2}{w_3^{2\omega}}[(\hat{\mathbf{s}}\hat{\mathbf{s}}+\hat{\mathbf{p}}_{3+}^{2\omega}\hat{\mathbf{p}}_{3+}^{2\omega})\cdot\tilde{\mathbf{P}}(2\omega)]\theta(z-z_0)\exp[iw_3^{2\omega}(z-z_0)]\\&+i\frac{8\pi\tilde{\omega}^2 n_3^{2\omega}}{w_3^{2\omega}}[(\hat{\mathbf{p}}_{3+}^{2\omega}\hat{\mathbf{s}}-\hat{\mathbf{s}}\hat{\mathbf{p}}_{3+}^{2\omega})\cdot\tilde{\mathbf{M}}(2\omega)]\theta(z-z_0)\exp[iw_3^{2\omega}(z-z_0)]\\&+i\frac{8\pi\tilde{\omega}^2}{w_3^{2\omega}}[(\hat{\mathbf{s}}\hat{\mathbf{s}}+\hat{\mathbf{p}}_{3-}^{2\omega}\hat{\mathbf{p}}_{3-}^{2\omega})\cdot\tilde{\mathbf{P}}(2\omega)]\theta(z_0-z)\exp[-iw_3^{2\omega}(z-z_0)]\\&+i\frac{8\pi\tilde{\omega}^2 n_3^{2\omega}}{w_3^{2\omega}}[(\hat{\mathbf{p}}_{3-}^{2\omega}\hat{\mathbf{s}}-\hat{\mathbf{s}}\hat{\mathbf{p}}_{3-}^{2\omega})\cdot\tilde{\mathbf{M}}(2\omega)]\theta(z_0-z)\exp[-iw_3^{2\omega}(z-z_0)]-\frac{4\pi}{\varepsilon_3^{2\omega}}[\hat{\mathbf{z}}\hat{\mathbf{z}}\cdot\tilde{\mathbf{P}}(2\omega)]\delta(z-z_0) ,\end{aligned} \quad (8)$$

where $\tilde{\omega}=\omega/c$ is the normalized angular frequency, and c is the speed of light in vacuum. The s-polarized components are given by $\hat{\mathbf{s}}\equiv\hat{\boldsymbol{\kappa}}\times\hat{\mathbf{z}}$ and the p-polarized components are given by

$$\hat{\mathbf{p}}_{i+}^{2\omega}=\frac{2\kappa\hat{\mathbf{z}}-w_i^{2\omega}\hat{\boldsymbol{\kappa}}}{2\tilde{\omega}n_i^{2\omega}} , \quad (9a)$$

$$\hat{\mathbf{p}}_{i-}^{2\omega}=\frac{2\kappa\hat{\mathbf{z}}+w_i^{2\omega}\hat{\boldsymbol{\kappa}}}{2\tilde{\omega}n_i^{2\omega}} . \quad (9b)$$

The quantity

$$w_i^{2\omega}=2(\tilde{\omega}^2\varepsilon_i^{2\omega}-\kappa^2)^{1/2} \quad (10)$$

is the component of the wave vector in the $\hat{\mathbf{z}}$ direction and $\varepsilon_i^{2\omega}=(n_i^{2\omega})^2$ is the linear dielectric constant. For use in Eq. (8), $i=3$ in Eqs. (9) and (10). The superscript 2ω indicates that a quantity is to be evaluated at the second-harmonic frequency. The unit-step function is given by

$$\begin{aligned}\theta(z)&=1 , \quad z>0\\&=0 , \quad z<0 .\end{aligned} \quad (11)$$

In Eq. (8), the first and second terms describe upward-propagating (increasing values of z) waves and the third and fourth terms describe downward-propagating (decreasing values of z) waves. The last term in Eq. (8) is not a propagating wave and hence is of no further interest.

We must now account for the finite extent of the material with index n_3 in which the nonlinear layer is embedded. The upward wave will reflect off of the interface between media 3 and 1, while the downward wave will reflect off of the interface between media 3 and 2. Multiple reflections of the generated light thus occur similar to that for light propagating through a Fabry-Perot etalon, but in this case the source of the light is within the etalon.

The calculation of the electric field that is transmitted upward into medium 1 and downward into medium 2 is also given in Ref. 23, but the contributions of nonlinear magnetization had been set to zero in favor of using an effective nonlinear polarization to include implicitly the contributions of nonlinear magnetization. We have reintroduced explicitly the nonlinear magnetization into the formalism. The results in the present notation are as follows. The generated electric field that is transmitted into medium 1 or the *reflected* second-harmonic wave is

$$\mathbf{E}^R(\mathbf{r},2\omega)=[\hat{\mathbf{s}}E_s^R(2\omega)+\hat{\mathbf{p}}_{1+}^{2\omega}E_p^R(2\omega)]\exp(i\mathbf{k}_{1+}^{2\omega}\cdot\mathbf{r}) , \quad (12)$$

where

$$E_s^R(2\omega)=t_{s31}^{2\omega}\frac{\nu_+^s\exp(-iw_3^{2\omega}z_0)+\nu_-^s r_{s32}^{2\omega}\exp[iw_3^{2\omega}(2D+z_0)]}{1-r_{s31}^{2\omega}r_{s32}^{2\omega}\exp(i2w_3^{2\omega}D)}, \tag{13a}$$

$$E_p^R(2\omega)=t_{p31}^{2\omega}\frac{\nu_+^p\exp(-iw_3^{2\omega}z_0)+\nu_-^p r_{p32}^{2\omega}\exp[iw_3^{2\omega}(2D+z_0)]}{1-r_{p31}^{2\omega}r_{p32}^{2\omega}\exp(i2w_3^{2\omega}D)}, \tag{13b}$$

and $\mathbf{k}_{1+}^{2\omega}=w_1^{2\omega}\hat{\mathbf{z}}+2\kappa\hat{\boldsymbol{\kappa}}$ is the wave vector [see Eq. (10) for the definition of $w_1^{2\omega}$]. The generated electric field that is transmitted into medium 2 or the *transmitted* second-harmonic wave is

$$\mathbf{E}^T(\mathbf{r},2\omega)=[\hat{\mathbf{s}}E_s^T(2\omega)+\hat{\mathbf{p}}_{2-}^{2\omega}E_p^T(2\omega)]\exp(i\mathbf{k}_{2-}^{2\omega}\cdot\mathbf{r}), \tag{14}$$

where

$$E_s^T(2\omega)=t_{s32}^{2\omega}\frac{\nu_-^s\exp(iw_3^{2\omega}z_0)+\nu_+^s r_{s31}^{2\omega}\exp(-iw_3^{2\omega}z_0)}{1-r_{s31}^{2\omega}r_{s32}^{2\omega}\exp(i2w_3^{2\omega}D)}, \tag{15a}$$

$$E_p^T(2\omega)=t_{p32}^{2\omega}\frac{\nu_-^p\exp(iw_3^{2\omega}z_0)+\nu_+^p r_{p31}^{2\omega}\exp(-iw_3^{2\omega}z_0)}{1-r_{p31}^{2\omega}r_{p32}^{2\omega}\exp(i2w_3^{2\omega}D)}, \tag{15b}$$

and $\mathbf{k}_{2-}^{2\omega}=-w_2^{2\omega}\hat{\mathbf{z}}+2\kappa\hat{\boldsymbol{\kappa}}$ is the wave vector. The field amplitudes at the second-harmonic frequency are

$$\nu_\pm^s=\frac{i8\pi\tilde{\omega}^2}{w_3^{2\omega}}[\hat{\mathbf{s}}\cdot\tilde{\mathbf{P}}(2\omega)-n_3^{2\omega}\hat{\mathbf{p}}_{3\pm}^{2\omega}\cdot\tilde{\mathbf{M}}(2\omega)], \tag{16a}$$

$$\nu_\pm^p=\frac{i8\pi\tilde{\omega}^2}{w_3^{2\omega}}[\hat{\mathbf{p}}_{3\pm}^{2\omega}\cdot\tilde{\mathbf{P}}(2\omega)+n_3^{2\omega}\hat{\mathbf{s}}\cdot\tilde{\mathbf{M}}(2\omega)]. \tag{16b}$$

The amplitude reflectivity coefficient r_{sij} and transmission coefficient t_{sij} for an s-polarized electric field as well as the amplitude reflectivity coefficient r_{pij} and transmission coefficient t_{pij} for a p-polarized electric field are calculated using the standard Fresnel formulas.[28] For completeness, we give the formulas

$$t_{sij}=\frac{2n_i\cos\theta_i}{n_i\cos\theta_i+n_j\cos\theta_j}, \tag{17a}$$

$$t_{pij}=\frac{2n_i\cos\theta_i}{n_i\cos\theta_j+n_j\cos\theta_i}, \tag{17b}$$

from which the other coefficients may be calculated using

$$r_{sij}=t_{sij}-1, \tag{17c}$$

$$r_{pij}=\frac{n_j}{n_i}t_{pij}-1, \tag{17d}$$

where for both s- and p-polarized light $r_{ij}=-r_{ji}$. The quantity $\cos\theta_i^{2\omega}$ may be calculated using the relation

$$w_i^{2\omega}=2\tilde{\omega}n_i^{2\omega}\cos\theta_i^{2\omega} \tag{18}$$

for the magnitude of the component of the second-harmonic wave vector in the $\hat{\mathbf{z}}$ direction, where $w_i^{2\omega}$ is given by Eq. (10). We take κ to be fixed in value at this stage, but note that

$$\kappa=\tilde{\omega}n_i^{2\omega}\sin\theta_i^{2\omega}. \tag{19}$$

We now consider the simplified case that medium 3 is thin such that $2Dw_3^{2\omega}\ll1$, which also implies that $z_0w_3^{2\omega}\ll1$. In addition, we use Eqs. (18) and (19) to write the amplitudes of the second-harmonic fields in terms of the Cartesian components of the nonlinear polarization and magnetization. The expressions for the amplitudes are

$$E_s^R(2\omega)=\frac{i4\pi\tilde{\omega}}{n_3^{2\omega}\cos\theta_3^{2\omega}}\frac{t_{s31}^{2\omega}}{1-r_{s31}^{2\omega}r_{s32}^{2\omega}}\times\{\tilde{M}_x(2\omega)[1-r_{s32}^{2\omega}]n_3^{2\omega}\cos\theta_3^{2\omega}-\tilde{P}_y(2\omega)[1+r_{s32}^{2\omega}]-\tilde{M}_z(2\omega)[1+r_{s32}^{2\omega}]n_3^{2\omega}\sin\theta_3^{2\omega}\}, \tag{20a}$$

$$E_p^R(2\omega)=\frac{i4\pi\tilde{\omega}}{n_3^{2\omega}\cos\theta_3^{2\omega}}\frac{t_{p31}^{2\omega}}{1-r_{p31}^{2\omega}r_{p32}^{2\omega}}\times\{-\tilde{P}_x(2\omega)[1-r_{p32}^{2\omega}]\cos\theta_3^{2\omega}-\tilde{M}_y(2\omega)[1+r_{p32}^{2\omega}]n_3^{2\omega}+\tilde{P}_z(2\omega)[1+r_{p32}^{2\omega}]\sin\theta_3^{2\omega}\}, \tag{20b}$$

$$E_s^T(2\omega)=\frac{i4\pi\tilde{\omega}}{n_3^{2\omega}\cos\theta_3^{2\omega}}\frac{t_{s32}^{2\omega}}{1-r_{s31}^{2\omega}r_{s32}^{2\omega}}\times\{-\tilde{M}_x(2\omega)[1-r_{s31}^{2\omega}]n_3^{2\omega}\cos\theta_3^{2\omega}-\tilde{P}_y(2\omega)[1+r_{s31}^{2\omega}]-\tilde{M}_z(2\omega)[1+r_{s31}^{2\omega}]n_3^{2\omega}\sin\theta_3^{2\omega}\}, \tag{20c}$$

$$E_p^T(2\omega)=\frac{i4\pi\tilde{\omega}}{n_3^{2\omega}\cos\theta_3^{2\omega}}\frac{t_{p32}^{2\omega}}{1-r_{p31}^{2\omega}r_{p32}^{2\omega}}\times\{\tilde{P}_x(2\omega)[1-r_{p31}^{2\omega}]\cos\theta_3^{2\omega}-\tilde{M}_y(2\omega)[1+r_{p31}^{2\omega}]n_3^{2\omega}+\tilde{P}_z(2\omega)[1+r_{p31}^{2\omega}]\sin\theta_3^{2\omega}\}. \tag{20d}$$

For comparison with other formalisms, we insert the explicit expressions for the Fresnel reflectivity and transmission coefficients [Eqs. (17)] into Eqs. (20), which yields the expressions

$$E_s^R(2\omega)=\frac{i8\pi\tilde{\omega}}{n_1^{2\omega}\cos\theta_1^{2\omega}+n_2^{2\omega}\cos\theta_2^{2\omega}}\{\tilde{M}_x(2\omega)n_2^{2\omega}\cos\theta_2^{2\omega}-\tilde{P}_y(2\omega)-\tilde{M}_z(2\omega)n_2^{2\omega}\sin\theta_2^{2\omega}\}\ , \tag{21a}$$

$$E_p^R(2\omega)=\frac{i8\pi\tilde{\omega}}{n_1^{2\omega}\cos\theta_2^{2\omega}+n_2^{2\omega}\cos\theta_1^{2\omega}}\left\{-\tilde{P}_x(2\omega)\cos\theta_2^{2\omega}-\tilde{M}_y(2\omega)n_2^{2\omega}+\tilde{P}_z(2\omega)\left[\frac{n_2^{2\omega}}{n_3^{2\omega}}\right]^2\sin\theta_2^{2\omega}\right\}\ , \tag{21b}$$

$$E_s^T(2\omega)=\frac{i8\pi\tilde{\omega}}{n_1^{2\omega}\cos\theta_1^{2\omega}+n_2^{2\omega}\cos\theta_2^{2\omega}}\{-\tilde{M}_x(2\omega)n_1^{2\omega}\cos\theta_1^{2\omega}-\tilde{P}_y(2\omega)-\tilde{M}_z(2\omega)n_1^{2\omega}\sin\theta_1^{2\omega}\}\ , \tag{21c}$$

$$E_p^T(2\omega)=\frac{i8\pi\tilde{\omega}}{n_1^{2\omega}\cos\theta_2^{2\omega}+n_2^{2\omega}\cos\theta_1^{2\omega}}\left\{\tilde{P}_x(2\omega)\cos\theta_1^{2\omega}-\tilde{M}_y(2\omega)n_1^{2\omega}+\tilde{P}_z(2\omega)\left[\frac{n_1^{2\omega}}{n_3^{2\omega}}\right]^2\sin\theta_1^{2\omega}\right\}\ . \tag{21d}$$

Note that in the limit of negligible nonlinear magnetization ($\mathbf{M}=0$), the expressions resulting from Eqs. (21) agree exactly with the results of Ref. 29. The results of this section have been presented explicitly for second-harmonic generation at a surface, but they are equally valid for many other nonlinear processes such as sum or difference-frequency generation.

IV. FORM OF THE FUNDAMENTAL ELECTROMAGNETIC FIELD

In preparation for calculating the detailed form of the nonlinear polarization and magnetization, we must find the form of the electromagnetic field in medium 3 at the fundamental frequency ω. We assume that the incident electric field (see Fig. 1) is

$$\mathbf{E}^I(\mathbf{r})=[\hat{\mathbf{s}}E_s^I(\omega)+\hat{\mathbf{p}}_{1-}^{\omega}E_p^I(\omega)]\exp(i\mathbf{k}_{1-}^{\omega}\cdot\mathbf{r})\ , \tag{22}$$

where $\mathbf{k}_{1-}^{\omega}=-w_1^{\omega}\hat{\mathbf{z}}+\kappa\hat{\boldsymbol{\kappa}}$. The form of the electromagnetic field within an etalon is a basic result of optics; hence, we do not derive it again, but refer the reader to Refs. 23 or 30 for guidance. Thus in the present notation the electric field in medium 3 is

$$\mathbf{E}^F(\mathbf{r})=[\hat{\mathbf{s}}E_s^{3+}(\omega)+\hat{\mathbf{p}}_{3+}^{\omega}E_p^{3+}(\omega)]\exp(i\mathbf{k}_{3+}^{\omega}\cdot\mathbf{r})+[\hat{\mathbf{s}}E_s^{3-}(\omega)+\hat{\mathbf{p}}_{3-}^{\omega}E_p^{3-}(\omega)]\exp(i\mathbf{k}_{3-}^{\omega}\cdot\mathbf{r}) \tag{23}$$

and the magnetic-induction field in medium 3 is

$$\mathbf{B}^F(\mathbf{r})=n_3^{\omega}\hat{\mathbf{k}}_{3+}^{\omega}\times[\hat{\mathbf{s}}E_s^{3+}(\omega)+\hat{\mathbf{p}}_{3+}^{\omega}E_p^{3+}(\omega)]\exp(i\mathbf{k}_{3+}^{\omega}\cdot\mathbf{r})+n_3^{\omega}\hat{\mathbf{k}}_{3-}^{\omega}\times[\hat{\mathbf{s}}E_s^{3-}(\omega)+\hat{\mathbf{p}}_{3-}^{\omega}E_p^{3-}(\omega)]\exp(i\mathbf{k}_{3-}^{\omega}\cdot\mathbf{r})\ , \tag{24}$$

where the various amplitudes are

$$E_s^{3+}(\omega)=E_s^I(\omega)\frac{t_{s13}^{\omega}r_{s32}^{\omega}\exp(i2w_3^{\omega}D)}{1-r_{s31}^{\omega}r_{s32}^{\omega}\exp(i2w_3^{\omega}D)}\ , \tag{25a}$$

$$E_p^{3+}(\omega)=E_p^I(\omega)\frac{t_{p13}^{\omega}r_{p32}^{\omega}\exp(i2w_3^{\omega}D)}{1-r_{p31}^{\omega}r_{p32}^{\omega}\exp(i2w_3^{\omega}D)}\ , \tag{25b}$$

$$E_s^{3-}(\omega)=E_s^I(\omega)\frac{t_{s13}^{\omega}}{1-r_{s31}^{\omega}r_{s32}^{\omega}\exp(i2w_3^{\omega}D)}\ , \tag{25c}$$

$$E_p^{3-}(\omega)=E_p^I(\omega)\frac{t_{p13}^{\omega}}{1-r_{p31}^{\omega}r_{p32}^{\omega}\exp(i2w_3^{\omega}D)}\ , \tag{25d}$$

and where the wave vectors are

$$\mathbf{k}_{3+}^{\omega}=w_3^{\omega}\hat{\mathbf{z}}+\kappa\hat{\boldsymbol{\kappa}}\ , \tag{26a}$$

$$\mathbf{k}_{3-}^{\omega}=-w_3^{\omega}\hat{\mathbf{z}}+\kappa\hat{\boldsymbol{\kappa}}\ . \tag{26b}$$

The unit vector for the s-polarized components of the fundamental field is again given by $\hat{\mathbf{s}}\equiv\hat{\boldsymbol{\kappa}}\times\hat{\mathbf{z}}$ as for the second-harmonic field, but the unit vectors for the p-polarized components are different and are

$$\hat{\mathbf{p}}_{i+}^{\omega}=\frac{\kappa\hat{\mathbf{z}}-w_i^{\omega}\hat{\boldsymbol{\kappa}}}{\tilde{\omega}n_i^{\omega}}\ , \tag{27a}$$

$$\hat{\mathbf{p}}_{i-}^{\omega}=\frac{\kappa\hat{\mathbf{z}}+w_i^{\omega}\hat{\boldsymbol{\kappa}}}{\tilde{\omega}n_i^{\omega}}\ , \tag{27b}$$

where

$$w_i^{\omega}=\tilde{\omega}n_i^{\omega}\cos\theta_i^{\omega}\ , \tag{28}$$

$$\kappa=\tilde{\omega}n_i^{\omega}\sin\theta_i^{\omega}\ . \tag{29}$$

The subscript i equals 1, 2, or 3.

Written in terms of $\boldsymbol{\kappa}$, the fundamental field is

$$\mathbf{E}^F(\mathbf{r},\omega)=\mathbf{E}^F(z,\omega)\exp(i\boldsymbol{\kappa}\cdot\mathbf{R})\ , \tag{30a}$$

$$\mathbf{B}^F(\mathbf{r},\omega)=\mathbf{B}^F(z,\omega)\exp(i\boldsymbol{\kappa}\cdot\mathbf{R})\ , \tag{30b}$$

for which

$$\mathbf{E}^F(z,\omega)=[\hat{\mathbf{s}}E_s^{3+}(\omega)+\hat{\mathbf{p}}_{3+}^{\omega}E_p^{3+}(\omega)]\exp(iw_3^{\omega}z)+[\hat{\mathbf{s}}E_s^{3-}(\omega)+\hat{\mathbf{p}}_{3-}^{\omega}E_p^{3-}(\omega)]\exp(-iw_3^{\omega}z)\ , \tag{31a}$$

$$\mathbf{B}^F(z,\omega)=n_3^{\omega}\hat{\mathbf{k}}_{3+}^{\omega}\times[\hat{\mathbf{s}}E_s^{3+}(\omega)+\hat{\mathbf{p}}_{3+}^{\omega}E_p^{3+}(\omega)]\exp(iw_3^{\omega}z)+n_3^{\omega}\hat{\mathbf{k}}_{3-}^{\omega}\times[\hat{\mathbf{s}}E_s^{3-}(\omega)+\hat{\mathbf{p}}_{3-}^{\omega}E_p^{3-}(\omega)]\times\exp(-iw_3^{\omega}z), \tag{31b}$$

where the s- and p-component amplitudes continue to be given by Eqs. (25). From this form of the fundamental field, we see that a quadratic nonlinearity will have phase factors of the form $\exp(i2\boldsymbol{\kappa}\cdot\mathbf{R})$. It is now clear why the nonlinear polarization [Eq. (5)] and magnetization [Eq. (6)] are each assumed to have this phase factor.

We need only the form of the fundamental field at the location of the nonlinear layer. For the second-harmonic wave, the thickness D was assumed earlier to be small such that $2Dw_3^{2\omega} \ll 1$. We assume that a similar condition $2Dw_3^{\omega} \ll 1$ is also valid for the fundamental waves, which also implies that $z_0 w_3^{\omega} \ll 1$ without actually specifying the exact location of the nonlinear layer. Hence, the specific form of the Cartesian components of the electric and magnetic-induction field at the fundamental frequency ω that are to be used in Eqs. (1) and (2) is

$$E_x^F(\omega)=E_p^I(\omega)\frac{t_{p13}^{\omega}}{1-r_{p31}^{\omega}r_{p32}^{\omega}}[1-r_{p32}^{\omega}]\cos\theta_3^{\omega} , \qquad (32a)$$

$$E_y^F(\omega)=-E_s^I(\omega)\frac{t_{s13}^{\omega}}{1-r_{s31}^{\omega}r_{s32}^{\omega}}[1+r_{s32}^{\omega}] , \qquad (32b)$$

$$E_z^F(\omega)=E_p^I(\omega)\frac{t_{p13}^{\omega}}{1-r_{p31}^{\omega}r_{p32}^{\omega}}[1+r_{p32}^{\omega}]\sin\theta_3^{\omega} , \qquad (32c)$$

$$B_x^F(\omega)=-E_s^I(\omega)\frac{t_{s13}^{\omega}}{1-r_{s31}^{\omega}r_{s32}^{\omega}}[1-r_{s32}^{\omega}]n_3^{\omega}\cos\theta_3^{\omega} , \qquad (32d)$$

$$B_y^F(\omega)=-E_p^I(\omega)\frac{t_{p13}^{\omega}}{1-r_{p31}^{\omega}r_{p32}^{\omega}}[1+r_{p32}^{\omega}]n_3^{\omega} , \qquad (32e)$$

$$B_z^F(\omega)=-E_s^I(\omega)\frac{t_{s13}^{\omega}}{1-r_{s31}^{\omega}r_{s32}^{\omega}}[1+r_{s32}^{\omega}]n_3^{\omega}\sin\theta_3^{\omega} . \qquad (32f)$$

V. EXPRESSIONS FOR THE SECOND-HARMONIC WAVES

We now have all the information needed to write explicit formulas for the second-harmonic waves as functions of the tensor components of the nonlinear susceptibilties. The substitution into Eqs. (20) of the specific form of the nonlinear surface polarization [Eq. (1)] and magnetization [Eq. (2)] found using Eqs. (32) for the fundamental field gives

$$\mathbf{E}^R(2\omega)=[\hat{\mathbf{s}}E_s^R(2\omega)+\hat{\mathbf{p}}_{1+}^{2\omega}E_p^R(2\omega)]\exp(i\mathbf{k}_{1+}^{2\omega}\cdot\mathbf{r}) \qquad (33)$$

for the reflected second-harmonic wave, where

$$E_j^R(2\omega)=\frac{i4\pi\tilde{\omega}}{n_3^{2\omega}\cos\theta_3^{2\omega}}\frac{t_{j31}^{2\omega}}{1-r_{j31}^{2\omega}r_{j32}^{2\omega}}[f_j^R F+g_j^R G+h_j^R H] , \qquad (34)$$

and

$$\mathbf{E}^T(2\omega)=[\hat{\mathbf{s}}E_s^T(2\omega)+\hat{\mathbf{p}}_{2-}^{2\omega}E_p^T(2\omega)]\exp(i\mathbf{k}_{2-}^{2\omega}\cdot\mathbf{r}) \qquad (35)$$

for the transmitted second-harmonic wave, where

$$E_j^T(2\omega)=\frac{i4\pi\tilde{\omega}}{n_3^{2\omega}\cos\theta_3^{2\omega}}\frac{t_{j32}^{2\omega}}{1-r_{j31}^{2\omega}r_{j32}^{2\omega}}[f_j^T F+g_j^T G+h_j^T H] . \qquad (36)$$

The subscripts j in Eqs. (34) and (36) represent either s or p. The dependence of the generated second-harmonic waves upon the incident fundamental wave is given by the factors

$$F=E_p^I E_p^I , \quad G=E_s^I E_s^I , \quad H=E_s^I E_p^I . \qquad (37)$$

Note that these three bilinear combinations are the only possible ones for a transverse fundamental field, which in a completely general manner can always be expanded in terms of s- and p-polarized unit vectors. The coefficients appearing in Eqs. (34) and (36) are

$$f_s^{R/T}=\left[\frac{t_{p13}^{\omega}}{1-r_{p31}^{\omega}r_{p32}^{\omega}}\right]^2\{2\chi_{xyz}^{eee}[1+r_{s3i}^{2\omega}][1+r_{p32}^{\omega}][1-r_{p32}^{\omega}]\sin\theta_3^{\omega}\cos\theta_3^{\omega}$$
$$+\chi_{xzx}^{eem}[1+r_{s3i}^{2\omega}][1+r_{p32}^{\omega}]^2 n_3^{\omega}\sin\theta_3^{\omega}\pm 2\chi_{xxz}^{mee}[1-r_{s3i}^{2\omega}]n_3^{2\omega}\cos\theta_3^{2\omega}[1+r_{p32}^{\omega}][1-r_{p32}^{\omega}]\sin\theta_3^{\omega}\cos\theta_3^{\omega}$$
$$-\chi_{zxx}^{mee}[1+r_{s3i}^{2\omega}]n_3^{2\omega}\sin\theta_3^{2\omega}[1-r_{p32}^{\omega}]^2\cos^2\theta_3^{\omega}-\chi_{zzz}^{mee}[1+r_{s3i}^{2\omega}]n_3^{2\omega}\sin\theta_3^{2\omega}[1+r_{p32}^{\omega}]^2\sin^2\theta_3^{\omega}\} . \qquad (38a)$$

$$g_s^{R/T}=-\left[\frac{t_{s13}^{\omega}}{1-r_{s31}^{\omega}r_{s32}^{\omega}}\right]^2\{\chi_{xxz}^{eem}[1+r_{s3i}^{2\omega}][1+r_{s32}^{\omega}]^2 n_3^{\omega}\sin\theta_3^{\omega}+\chi_{zxx}^{mee}[1+r_{s3i}^{2\omega}]n_3^{2\omega}\sin\theta_3^{2\omega}[1+r_{s32}^{\omega}]^2\} , \qquad (38b)$$

$$h_s^{R/T}=\frac{t_{s13}^{\omega}}{1-r_{s31}^{\omega}r_{s32}^{\omega}}\frac{t_{p13}^{\omega}}{1-r_{p31}^{\omega}r_{p32}^{\omega}}\{2\chi_{xxz}^{eee}[1+r_{s3i}^{2\omega}][1+r_{s32}^{\omega}][1+r_{p32}^{\omega}]\sin\theta_3^{\omega}$$
$$-\chi_{xzy}^{eem}[1+r_{s3i}^{2\omega}][1-r_{s32}^{\omega}][1+r_{p32}^{\omega}]n_3^{\omega}\sin\theta_3^{\omega}\cos\theta_3^{\omega}$$
$$-\chi_{xyz}^{eem}[1+r_{s3i}^{2\omega}][1+r_{s32}^{\omega}][1-r_{p32}^{\omega}]n_3^{\omega}\sin\theta_3^{\omega}\cos\theta_3^{\omega}$$
$$\mp 2\chi_{xyz}^{mee}[1-r_{s3i}^{2\omega}]n_3^{2\omega}\cos\theta_3^{2\omega}[1+r_{s32}^{\omega}][1+r_{p32}^{\omega}]\sin\theta_3^{\omega}\} , \qquad (38c)$$

$$f_p^{R/T}=\left[\frac{t_{p13}^{\omega}}{1-r_{p31}^{\omega}r_{p32}^{\omega}}\right]^2\{\mp 2\chi_{xxz}^{eee}[1-r_{p3i}^{2\omega}]\cos\theta_3^{2\omega}[1+r_{p32}^{\omega}][1-r_{p32}^{\omega}]\sin\theta_3^{\omega}\cos\theta_3^{\omega}$$
$$+\chi_{zxx}^{eee}[1+r_{p3i}^{2\omega}]\sin\theta_3^{2\omega}[1-r_{p32}^{\omega}]^2\cos^2\theta_3^{\omega}+\chi_{zzz}^{eee}[1+r_{p3i}^{2\omega}]\sin\theta_3^{2\omega}[1+r_{p32}^{\omega}]^2\sin^2\theta_3^{\omega}$$
$$\pm\chi_{xzy}^{eem}[1-r_{p3i}^{2\omega}]\cos\theta_3^{2\omega}[1+r_{p32}^{\omega}]^2 n_3^{\omega}\sin\theta_3^{\omega}-\chi_{zxy}^{eem}[1+r_{p3i}^{2\omega}]\sin\theta_3^{2\omega}[1+r_{p32}^{\omega}][1-r_{p32}^{\omega}]n_3^{\omega}\cos\theta_3^{\omega}$$
$$+2\chi_{xyz}^{mee}[1+r_{p3i}^{2\omega}]n_3^{2\omega}[1+r_{p32}^{\omega}][1-r_{p32}^{\omega}]\sin\theta_3^{\omega}\cos\theta_3^{\omega}\} , \qquad (38d)$$

$$g_p^{R/T}=\left[\frac{t_{s13}^{\omega}}{1-r_{s31}^{\omega}r_{s32}^{\omega}}\right]^2\{\chi_{zxx}^{eee}[1+r_{p3i}^{2\omega}]\sin\theta_3^{2\omega}[1+r_{s32}^{\omega}]^2\mp\chi_{xyz}^{eem}[1-r_{p3i}^{2\omega}]\cos\theta_3^{2\omega}[1+r_{s32}^{\omega}]^2n_3^{\omega}\sin\theta_3^{\omega}$$
$$-\chi_{zxy}^{eem}[1+r_{p3i}^{2\omega}]\sin\theta_3^{2\omega}[1+r_{s32}^{\omega}][1-r_{s32}^{\omega}]n_3^{\omega}\cos\theta_3^{\omega}\}\ , \tag{38e}$$

and

$$h_p^{R/T}=\frac{t_{s13}^{\omega}}{1-r_{s31}^{\omega}r_{s32}^{\omega}}\frac{t_{p13}^{\omega}}{1-r_{p31}^{\omega}r_{p32}^{\omega}}\{\pm 2\chi_{xyz}^{eee}[1-r_{p3i}^{2\omega}]\cos\theta_3^{2\omega}[1+r_{s32}^{\omega}][1+r_{p32}^{\omega}]\sin\theta_3^{\omega}$$
$$\pm\chi_{xxz}^{eem}[1-r_{p3i}^{2\omega}]\cos\theta_3^{2\omega}[1+r_{s32}^{\omega}][1-r_{p32}^{\omega}]n_3^{\omega}\sin\theta_3^{\omega}\cos\theta_3^{\omega}$$
$$\pm\chi_{xzx}^{eem}[1-r_{p3i}^{2\omega}]\cos\theta_3^{2\omega}[1-r_{s32}^{\omega}][1+r_{p32}^{\omega}]n_3^{\omega}\sin\theta_3^{\omega}\cos\theta_3^{\omega}$$
$$+\chi_{zxx}^{eem}[1+r_{p3i}^{2\omega}]\sin\theta_3^{2\omega}([1+r_{s32}^{\omega}][1+r_{p32}^{\omega}]n_3^{\omega}-[1-r_{s32}^{\omega}][1-r_{p32}^{\omega}]n_3^{\omega}\cos^2\theta_3^{\omega})$$
$$-\chi_{zzz}^{eem}[1+r_{p3i}^{2\omega}]\sin\theta_3^{2\omega}[1+r_{s32}^{\omega}][1+r_{p32}^{\omega}]n_3^{\omega}\sin^2\theta_3^{\omega}$$
$$+2\chi_{xxz}^{mee}[1+r_{p3i}^{2\omega}]n_3^{2\omega}[1+r_{s32}^{\omega}][1+r_{p32}^{\omega}]\sin\theta_3^{\omega}\}\ , \tag{38f}$$

where in the coefficients for the reflected wave $i=2$ and the upper sign should be used, while in that for the transmitted wave $i=1$ and the lower sign should be used.

The intensity of the reflected second-harmonic wave as measured in medium 1 is $I^R(2\omega)=(cn_1^{2\omega}/2\pi)|\mathbf{E}^R(2\omega)|^2$ and the intensity of the transmitted second-harmonic wave as measured in medium 2 is $I^T(2\omega)=(cn_2^{2\omega}/2\pi)|\mathbf{E}^T(2\omega)|^2$. In an actual experiment, an analyzing polarizer may be placed before the detection system in order to measure only the s- or p-polarized components of the second-harmonic light. For later discussion, we need consider only that the measured components will be of the functional form

$$I(2\omega)\propto|fF+gG+hH|^2\ . \tag{39}$$

Without the use of an analyzing polarizer the measured intensity will be the sum of the intensities of the s- and p-polarized components.

This completes the main theoretical development of the paper. The expressions derived here are as valid for an isotropic, achiral material as for an isotropic, chiral material. The only difference between the two cases is that for the achiral material more components of the nonlinear susceptibility tensors vanish.

We note that the linear optical activity of a chiral material is not included in this formalism. The assumption that the nonlinear layer is very thin allowed us to ignore changes in the amplitude and phase of the optical field due to propagation through the nonlinear layer. Thus the nature of propagation depending upon the handedness of the light is ignored completely. Where handedness effects might enter is through the Fresnel reflectivity and transmission coefficients. In principle, the Fresnel coefficients would need to be generalized to treat the sensitivity to the handedness of the light.[31] The difference between the indices of refraction n_{RHC} for the right-hand and n_{LHC} for the left-hand circularly-polarized light is assumed to be very small and thus only an average value of the linear index of refraction for the nonlinear layer is used (i.e., n_3). Note that it is a formidable task to model accurately the average value of the linear index of the nonlinear layer as it is known to depend upon the materials surrounding the layer, such as in the case of a fused-silica substrate supporting a dye film in air.[32]

VI. DISCUSSION

In this section, we investigate the conditions under which second-harmonic generation from an isotropic surface will exhibit a different response depending upon whether the fundamental beam is right- or left-hand circularly polarized. Such a circular-difference effect is of particular interest, because it may serve as a means of detecting the presence of chirality in material systems. In the pioneering work of Petralli-Mallow *et al.*,[15] surface second-harmonic generation from a surface known to be chiral did give a signal whose strength depended sensitively upon whether the fundamental light is right- or left-hand circularly polarized. This example of nonlinear optical activity was called second-harmonic-generation circular dichroism (SHG-CD). The SHG-CD effect was later observed using other material systems.[16,17] The comprehensive theory developed here provides the first opportunity to explore in detail the possible mechanisms or conditions that lead to the SHG-CD effect. Our specific arguments for the existence of the SHG-CD effect are based on the general form of the intensity of the components of the second-harmonic field given by Eq. (39). Hence, no assumptions are necessary about the actual values of the individual components of the three susceptibility tensors.

We first show that no SHG-CD effect exists for an achiral material. Through the use of Table I, only the coefficients $f_s^{R/T}$, $g_s^{R/T}$, and $h_p^{R/T}$ are seen to be unique to the presence of chirality; these coefficients vanish for an achiral surface. Thus for an isotropic, achiral material the s-polarized signal is

$$I_s^{R/T}(2\omega)\propto|h_s^{R/T}H|^2\ , \tag{40}$$

and the p-polarized signal is

$$I_p^{R/T}(2\omega) \propto |f_p^{R/T} F + g_p^{R/T} G|^2 . \quad (41)$$

In order to investigate the possibility of the SHG-CD effect, we model the incident circularly polarized electromagnetic field in a completely general manner by taking $E_p^I / E_s^I = e^{i\delta}$. The incident light is said[33] to be right-hand circularly (RHC) polarized for $\delta = \pi/2$ and left-hand circularly (LHC) polarized for $\delta = -\pi/2$. For circularly polarized fundamental light,

$$F = (E_s^I)^2 e^{i2\delta} , \quad G = (E_s^I)^2 , \quad \text{and } H = (E_s^I)^2 e^{i\delta} . \quad (42)$$

The s-polarized signal [Eq. (40)] becomes $I_s^{R/T}(2\omega) \propto |h_s^{R/T}|^2 |E_s^I|^4$, which is independent of δ and hence does not exhibit the SHG-CD effect. The p-polarized signal [Eq. (41)] becomes $I_p^{R/T}(2\omega) \propto |f_p^{R/T} e^{i2\delta} + g_p^{R/T}|^2 |E_s^I|^4$, which also does not exhibit the SHG-CD effect owing to $e^{i2\delta} = -1$ for both RHC- and LHC-polarized light. Therefore, the SHG-CD effect cannot be observed using an isotropic, achiral material, which is as expected.

We next show that in order for the SHG-CD effect to exist, it is necessary that a phase difference exist between the coefficients f, g, and h. The case of no phase difference is addressed by considering the limit of real-valued coefficients. In this limit, the intensities of the second-harmonic fields will be of the functional form

$$I(2\omega) \propto f^2 |F|^2 + g^2 |G|^2 + h^2 |H|^2 + 2fg\,\mathrm{Re}(F^* G) + 2gh\,\mathrm{Re}(G^* H) + 2fh\,\mathrm{Re}(H^* F) . \quad (43)$$

For circularly-polarized light, the use of Eqs. (42) gives Eq. (43) as

$$I(2\omega) \propto \{ f^2 + g^2 + h^2 + 2[fg \cos 2\delta + h(f+g)\cos\delta] \} |E_s^I|^4 , \quad (44)$$

which is again independent of whether RHC- or LHC-polarized light is used as the incident fundamental wave owing to the fact that the cosine function is an even function in δ. Hence, the SHG-CD effect cannot be observed if the coefficients f, g, and h are purely real valued. In order to observe the SHG-CD effect, one or more of the coefficients will have to be complex valued and, furthermore, a phase difference between the coefficients must exist.

A quantitative measure of the SHG-CD intensity asymmetry is[15]

$$\Delta I^{\text{SHG-CD}} = \frac{I^{\text{LHC}} - I^{\text{RHC}}}{\frac{1}{2}[I^{\text{LHC}} + I^{\text{RHC}}]} , \quad (45)$$

where I^{RHC} and I^{LHC} are either the transmitted or reflected second-harmonic signals measured for the cases of RHC- and LHC-polarized fundamental light, respectively. For measurements of either the s- or p-polarized second-harmonic light, the use of Eqs. (39), (42), and (45) gives

$$\Delta I^{\text{SHG-CD}} = \frac{4\,\mathrm{Im}(g^* h) + 4\,\mathrm{Im}(h^* f)}{|f|^2 + |g|^2 + |h|^2 - 2\,\mathrm{Re}(f^* g)} \quad (46)$$

to be the predicted strength of the SHG-CD effect. A more complicated expression is required to model the SHG-CD effect in the total intensity.

Equation (46) shows that a phase difference must exist between h and either f or g in order for the SHG-CD effect to exist, where a 90° phase difference is optimum. Careful examination of the detailed expressions for the coefficients [see Eqs. (38)] leads to the conclusion that they may be complex valued if the Fresnel coefficients, angles θ_3^ω and $\theta_3^{2\omega}$, or some of the susceptibility-tensor components are complex valued. Recall that the susceptibility χ^{eee} is a purely real-valued quantity for the condition of being nonresonant in the fundamental and second-harmonic frequencies, while the susceptibilities χ^{eem} and χ^{mee} are purely imaginary-valued quantities.[22,26] We assume that the angle of incidence is chosen such that total internal reflection does not occur, which would lead to complex-valued angles θ_3^ω and/or $\theta_3^{2\omega}$. A consequence of being near to a resonance for the fundamental or second-harmonic frequencies is that absorption leads to a complex value of the index of refraction n_3, and hence complex values of the Fresnel coefficients that depend upon n_3 and a complex value of the angle θ_3. Thus, there are two interesting regimes under which to examine whether a phase difference between h and either f or g will exist, the cases of the fundamental or second-harmonic frequencies being nearly resonant or nonresonant.

The first regime we consider is that the fundamental or second-harmonic frequency is nearly resonant, leading to complex-valued linear-optical quantities and a complex-valued susceptibility χ^{eee}. We are also supposing that there are no contributions from magnetic-dipole transitions so that χ^{eem} and χ^{mee} are zero. In this special case, the nonvanishing tensor component χ_{xyz}^{eee} is the only one that is unique to the presence of chirality. The SHG-CD effect can thus occur, in principle, provided that a sufficient phase difference exists between the coefficients f, g, and h. This possibility makes nonlinear optical activity very different from linear optical activity, which relies on the presence of contributions from magnetic-dipole transitions.[21] In general, χ^{eem} and χ^{mee} may also be nonzero and would no longer be purely imaginary valued due to absorption from the near-resonance condition. The tendency of χ^{eem} and χ^{mee} to be $\sim 90°$ out of phase with respect to χ^{eee} would hence further increase the phase differences between the coefficients, leading to a larger SHG-CD effect.

The second regime of interest is that both the fundamental and second-harmonic frequencies are nonresonant. Thus, the linear-optical quantities and the susceptibility χ^{eee} are purely real valued, while the susceptibilities χ^{eem} and χ^{mee} are purely imaginary valued. Therefore, this 90° phase difference between some of the components of the susceptibility tensors causes a phase difference to exist between f, g, and h, and the SHG-CD effect should be measurable.

We believe that the phase difference between the coefficients should be larger due to magnetic-dipole contributions than due to the influence of the near-resonance absorption on the linear- and nonlinear-optical quantities.

In addition, magnetic-dipole transitions provide the only mechanism that can give rise to the SHG-CD effect under arbitrary conditions of being near or far from a resonance for the fundamental or second-harmonic frequencies, such that absorption does or does not play a role. Certainly, for a completely lossless material, only magnetic-dipole transitions could be responsible for the observation of the SHG-CD effect. Therefore, the fundamental sensitivity of second-harmonic generation from chiral surfaces to the handedness of the fundamental excitation is due to the presence of magnetic dipoles.

In further detail, $g_s^{R/T}$ has only susceptibility elements with contributions from magnetic dipoles, namely, χ_{xxz}^{eem} and χ_{zxx}^{mee}. An experiment that could prove $g_s^{R/T}$ is nonzero would confirm the presence of magnetic dipoles independent of the influence of absorption. The coefficient $g_s^{R/T}$ is also unique to the presence of chirality. Thus the measurement of a nonzero value of $g_s^{R/T}$ should confirm both the presence of magnetic dipoles as well as chirality.

VII. CONCLUSIONS

We have presented a theory of second-harmonic generation from an isotropic, chiral surface. The formalism allows one to easily include the specific nature of the electromagnetic interfaces through the use of Fresnel coefficients. The formalism is also valid for an isotropic, achiral surface.

The formalism verifies that the presence of chirality may be proven by the measurement of a circular-difference effect in the second-harmonic signal. Thus, this SHG-CD effect may be used as an effective method of metrology of chiral materials.

The role of magnetic dipoles in the process of SHG in chiral materials has been elucidated. Magnetic-dipole transitions are traced to be the fundamental reason for chiral materials to exhibit the SHG-CD effect. However, it was also shown that, in principle, the SHG-CD effect could be observed from a chiral material that has a second-harmonic response due only to electric dipoles (i.e., χ^{eee}), but only for near-resonant excitation such that optical quantities become complex valued due to absorption.

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