

Bulk contribution in surface second-harmonic generation

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We study the bulk contribution to surface second-harmonic generation. It is shown that the formalism in the earlier literature neglected an important term in the bulk contribution which makes the separation of surface and bulk contributions impossible in experiments that allow no modification of the sample. Isotropic and cubic systems media are discussed in some detail for illustration. We also present a model for the bulk nonlinearity of molecular systems.

INTRODUCTION

Surface second-harmonic generation (SHG) is gaining popularity as a surface probe.¹ In applying the technique to real problems, the question one often encounters is how much the bulk contributes to the signal relative to the surface. For a medium with inversion symmetry, SHG is electric-dipole forbidden in the bulk, but the electric-quadrupole and magnetic-dipole contributions from the bulk could still be quite significant in comparison with the electric-dipole contribution from the surface. It is therefore important that we know how to assess the relative magnitudes of the two contributions. It would even be better if the two contributions can be separately determined.

In an important paper by Bloembergen *et al.*,² SHG in reflection from an isotropic medium was considered, and the bulk and surface contributions to SHG were explicitly derived. Subsequent publications, following their formalism, helped in improving the understanding of surface nonlinearities³⁻⁷ and extended the theory to crystalline media.⁸⁻¹¹ It was shown that with proper combinations of input and output polarizations, or from the output dependence on the angle of incidence, the surface contribution can be partly separated from the bulk contribution. In a recent publication,¹² however, we briefly mentioned that there is an omission in the expression of nonlinear polarization in Ref. 2, which to our knowledge, had been carried by all the subsequent publications on the subject. The corrected result suggests that SHG always has a mixed contribution from both the surface and the bulk. Thus, in actual experiments the surface information should be obtained by modifying the surface relative to the bulk and observing the SH signal change. If this is not possible, then one has to resort to theoretical models for assessing the relative contribution of surface versus bulk.

In this paper we show in detail the derivation of the correct expression for the second-order nonlinear polarization. We then discuss how it affects surface SHG from isotropic and cubic media. Finally, we consider two simple models that allow us to have an estimate of the bulk contribution.

Let us consider the nonlinear polarization at 2ω induced by the optical field $\mathbf{E}(\omega)$ in a medium. As is well

known, the effective nonlinear polarization $\mathbf{P}_{\text{eff}}^{(2)}(2\omega)$ generally should consist of a series of multipole terms,¹³

$$\mathbf{P}_{\text{eff}}^{(2)}(2\omega) = \mathbf{P}^{(2)}(2) - \nabla \cdot \vec{\mathbf{Q}}^{(2)}(2\omega) + \frac{c}{i2\omega} \nabla \times \mathbf{M}^{(2)}(2\omega) + \dots, \quad (1)$$

where \mathbf{P} , $\vec{\mathbf{Q}}$, and \mathbf{M} denote electric-dipole polarization, electric-quadrupole polarization, and magnetization, respectively. This expansion is valid when volume elements whose dimensions are small compared to the field variation length (in the bulk, it is the wavelength or the field-penetration depth) are used in averaging to obtain such macroscopic quantities. It may then be that, at the surface, terminating the expansion at a certain order is not justified. This will be discussed later and we will show that it is not a restriction in our case.

The terms in Eq. (1) are quadratic functions of the field and/or of their derivatives. Up to the first derivatives in $\mathbf{P}_{\text{eff}}^{(2)}$ we can write

$$\mathbf{P}^{(2)}(2\omega) = \vec{\chi}^D : \mathbf{E}(\omega)\mathbf{E}(\omega) + \vec{\chi}^P : \mathbf{E}(\omega)\nabla\mathbf{E}(\omega), \quad (2a)$$

$$\vec{\mathbf{Q}}^{(2)}(2\omega) = \vec{\chi}^Q : \mathbf{E}(\omega)\mathbf{E}(\omega), \quad (2b)$$

$$\mathbf{M}^{(2)}(2\omega) = \vec{\chi}^M : \mathbf{E}(\omega)\mathbf{E}(\omega). \quad (2c)$$

Such expressions can be related immediately to the microscopic expressions of the nonlinear susceptibility given, for example, by Adler.¹⁴ In a centrosymmetric medium, the first term in Eq. (2a), which is a pure electric-dipole term, vanishes identically in the bulk. Also, if there is inversion symmetry in both space and time, $\vec{\chi}^M$ is proportional to the unit antisymmetric tensor of the third rank,¹³ and as far as SHG is concerned, $\mathbf{M}(2\omega)$ vanishes. The bulk nonlinear polarization then takes the form

$$\mathbf{P}_{\text{eff}}^{(2)}(2\omega) = \vec{\chi}^P : \mathbf{E}(\omega)\nabla\mathbf{E}(\omega) - \nabla \cdot [\vec{\chi}^Q : \mathbf{E}(\omega)\mathbf{E}(\omega)]. \quad (3)$$

In previous works,¹⁻¹¹ the divergence in the second term of Eq. (3) was applied only to the field, thus omitting an effective surface contribution arising from an abrupt variation of $\vec{\chi}^Q$ at a surface or interface, and it is this omission that we will reinstate with detailed reasoning in this paper.

In a previous publication,⁷ we showed that we can

define an effective surface polarization for an interface when the interface layer thickness is much smaller than the wavelength:

$$\mathcal{P}_{si}^{(2)}(2\omega) = \int_I s_i(z, 2\omega) P_{\text{eff},i}^{(2)}(z, 2\omega) dz . \quad (4)$$

Here,

$$s_i(z, 2\omega) \equiv \begin{cases} 1 & \text{for } i=x, y , \\ D_z(z, 2\omega)/E_z(z, 2\omega) & \text{for } i=z , \end{cases}$$

D is the displacement current, and I is the interface layer over which the material constants can vary. Although this expression is phenomenological since the variation of $s(z, 2\omega)$ is certainly complicated near the surface, it has the merit of bringing out the importance of the linear dielectric effects at the interface. The field radiated by

the bulk region and the interface I is then conveniently written in terms of Green's functions as

$$\mathbf{E}(2\omega) = \vec{\mathbf{G}}_s \mathcal{P}_s^{(2)}(2\omega) + \int_B \vec{\mathbf{G}}_B \mathbf{P}_{\text{eff}}^{(2)}(2\omega) dz , \quad (5)$$

where both Green's functions $\vec{\mathbf{G}}_s$ and $\vec{\mathbf{G}}_B$ are uniquely determined by the bulk parameters and B denotes the bulk.⁷ The second term of Eq. (5) has already been treated in previous works.^{2,6,7,9,11} We will consider here only the first term of Eq. (5). From Eqs. (3) and (4), we have

$$\mathcal{P}_{si}^{(2)}(2\omega) = \int_I s_i(z, 2\omega) [\mathbf{P}^{(2)}(z, 2\omega) - \nabla \cdot \vec{\mathbf{Q}}^{(2)}(z, 2\omega)]_i dz . \quad (6)$$

Partial integration gives

$$\mathcal{P}_{si}^{(2)}(2\omega) = \int_I \left[s_i(z, 2\omega) P_i^{(2)}(z, 2\omega) + Q_{zi}^{(2)}(z, 2\omega) \frac{\partial}{\partial z} s_i(z, 2\omega) \right] dz - [s_i(z, 2\omega) Q_{zi}^{(2)}(z, 2\omega)]_{0^-}^{0^+} , \quad (7)$$

where 0^+ and 0^- define the boundaries of the interface layer I . In this expression the terms under the integral are clearly surface dependent. In general, $P_i^{(2)}$ consists of two contributions, one from a surface dipole layer⁶ and the other from an electromagnetic field gradient through χ^P .² The $Q_{zi}^{(2)}$ term also contributes only if there is a field gradient at the surface. On the other hand, the term in large parentheses is surface independent since we have

$$\begin{aligned} -[s_i(z, 2\omega) Q_{zi}^{(2)}(z, 2\omega)]_{0^-}^{0^+} &= \frac{Q_{zi}^{(2)}(0^-, 2\omega)}{[\epsilon(0^-, 2\omega)]^{\delta_{zi}}} - \frac{Q_{zi}^{(2)}(0^+, 2\omega)}{[\epsilon(0^+, 2\omega)]^{\delta_{zi}}} \\ &= \frac{\chi_{zilk}^Q E_l(0^-, 2\omega) E_k(0^-, 2\omega)}{[\epsilon(0^-, 2\omega)]^{\delta_{zi}}} - \frac{\chi_{zilk}^Q(0^+) E_l(0^+, 2\omega) E_k(0^+, 2\omega)}{[\epsilon(0^+, 2\omega)]^{\delta_{zi}}} , \end{aligned} \quad (8)$$

which is uniquely determined by the bulk material parameters. As a consequence, although this term appears in the calculation of the effective surface susceptibility, it is actually insensitive to any surface treatment and should therefore be called a bulk contribution.

We stated earlier that terminating the expansion of P_{eff} at the first derivatives would not affect our findings. This is true for the following reason: any higher-order derivative term in the expansion would have the form

$$P_{\text{eff},i}^{(2)} \simeq \partial^k a \partial^l b \quad \text{with } k+l \geq 2 \text{ and } k \geq 0, l \geq 0 , \quad (9)$$

where a and b are functions of the field and of some material constants. Again, for $P_{\text{eff},i}^{(2)}$ to give a significant contribution in the integral over I , one of the derivatives must be along z so that we can write

$$P_{\text{eff},i}^{(2)} = \partial^k a \partial_z^l b .$$

Equation (4) can then be integrated by parts to give

$$\begin{aligned} \mathcal{P}_{si}^{(2)}(2\omega) &= \int_I \frac{\partial}{\partial z} s_i(z, 2\omega) \partial^l a \partial^{k-1} b dz \\ &\quad - [s_i(z, 2\omega) \partial^l a \partial^{k-1} b]_{0^-}^{0^+} , \end{aligned} \quad (10)$$

and since $l+k > 2$ the term in square brackets is smaller

than the lowest-order contribution by a factor $(d/\lambda)^{l+k-1}$ if not identically zero, where d is the interface thickness and λ is the wavelength (or the field-penetration depth).

ISOTROPIC AND CUBIC SYSTEMS

In the following we will examine the particular cases of the isotropic and cubic centrosymmetric systems.

For an isotropic system the tensor elements of Eq. (2a) have some symmetry relations, such that with

$$P_i^{(2)}(2\omega) = \chi_{ijkl}^P E_j(\omega) \frac{\partial}{\partial l} E_k(\omega) , \quad (11a)$$

we have

$$\chi_{iiii}^P = \chi_1^P, \quad \chi_{ijjj}^P = \chi_2^P, \quad \chi_{ijij}^P = \chi_3^P, \quad \chi_{ijji}^P = \chi_4^P , \quad (11b)$$

$$\chi_1^P = \chi_2^P + \chi_3^P + \chi_4^P . \quad (11c)$$

In this expression the magnetic-dipole contribution would appear only in χ_3^P and χ_4^P with equal magnitude and opposite signs. For χ^Q in Eq. (2b) we similarly define

$$Q_{ij}^{(2)}(2\omega) = \chi_{ijkl}^Q E_l(\omega) E_k(\omega) , \quad (12a)$$

with the following symmetry relations:

$$\chi_{iii}^Q = \chi_1^Q, \quad \chi_{ijj}^Q = \chi_2^Q, \quad \chi_{ijij}^Q = \chi_3^Q, \quad \chi_{ijji}^Q = \chi_4^Q, \quad (12b)$$

$$\chi_1^Q = \chi_2^Q + \chi_3^Q + \chi_4^Q. \quad (12c)$$

The effective polarization is

$$P_{\text{eff},i}^{(2)}(2\omega) = P_i^{(2)}(2\omega) - \frac{\partial}{\partial j} Q_{ji}^{(2)}(2\omega). \quad (13)$$

With the substitutions

$$\delta = 2\chi_1^P - 2\chi_1^Q, \quad (14a)$$

$$\beta = 2\chi_2^P - (\chi_3^Q + \chi_4^Q), \quad (14b)$$

$$2\gamma = 2\chi_3^P - 2\chi_2^Q, \quad (14c)$$

$$\delta - \beta - 2\gamma = 2\chi_4^P - (\chi_3^Q + \chi_4^Q), \quad (14d)$$

we obtain

$$\begin{aligned} P_{\text{eff},i}^{(2)}(2\omega) = & (\delta - \beta - 2\gamma) E_i(\omega) \frac{\partial}{\partial i} E_j(\omega) \\ & + \beta E_i(\omega) \frac{\partial}{\partial j} E_j(\omega) + \gamma \frac{\partial}{\partial i} [E_j(\omega) E_j(\omega)] \\ & - \left[\frac{\partial}{\partial j} \chi_{jilk}^Q \right] E_l(\omega) E_k(\omega). \end{aligned} \quad (15)$$

In the homogeneous bulk where the derivatives of the material parameter χ^Q vanish, Eq. (15) is identical to the expression usually given for the bulk nonlinearity of an isotropic system.² However, as discussed earlier, in the presence of a surface the last term in Eq. (15) should also contribute.

As shown in previous works,^{6,7,9,11} the total SHG at a vacuum-substrate interface can be characterized by an effective surface susceptibility containing both bulk and “surface” terms. Defining⁷ $\mathcal{P}_{si}^{(2)}(2\omega) = \chi_{sijk} F_j(\omega) F_k(\omega)$ with

$$F_z(\omega) = \mathcal{D}_z(0, \omega),$$

$$F_x = E_x(0, \omega),$$

$$F_y = E_y(0, \omega)$$

(here the F fields are continuous across the interface and thus uniquely defined from the bulk parameters, leading to an unambiguous definition for χ_s),⁷ we find the nonvanishing effective surface susceptibility elements as

$$\chi_{zzz} = \chi_{zzzz} - \frac{\gamma}{\epsilon(2\omega)\epsilon(\omega)^2}, \quad (16a)$$

$$\chi_{zyy} = \chi_{zxx} = \chi_{szxx} - \frac{\gamma}{\epsilon(2\omega)}, \quad (16b)$$

$$\chi_{yzy} = \chi_{zxx} = \chi_{szxx}, \quad (16c)$$

where the γ terms comes from the bulk contribution. From Eq. (8) we know that the “surface” terms χ_s contain in effect also a bulk contribution. We can separate bulk and surface contributions by using Eqs. (4), (8), and (15), and we obtain

$$\chi_{zzz} = \chi_{s'zzz} - (\gamma + \chi_1^Q)/\epsilon(2\omega)\epsilon(\omega)^2, \quad (17a)$$

$$\chi_{zyy} = \chi_{zxx} = \chi_{s'zxx} - (\gamma + \chi_2^Q)/\epsilon(2\omega), \quad (17b)$$

$$\chi_{yzy} = \chi_{zxx} = \chi_{s'zxx} - \chi_4^Q/\epsilon(\omega), \quad (17c)$$

where $\chi_{s'}$ is the true surface susceptibility independent of the bulk nonlinearity. It is seen from the above expressions that all the effective surface susceptibility tensor components now contain some bulk contribution. This fact was not realized in the earlier publications that had held Eq. (16) as true. In particular, it was believed from Eq. (16c) that measuring the s -polarized output in a mixed-polarization input geometry would give a pure surface contribution. Equation (17c) now clearly indicates that such a geometry would still contain some electric-quadrupole contribution from the bulk.

A similar analysis also applies to a cubic medium with an inversion symmetry (e.g., Si, Ge, Cu, . . .). For a cubic system, we have the same tensor elements as in the isotropic case. Only Eqs. (11c) and (12c) are no longer true. Defining two additional parameters ζ^P and ζ^Q to account for the anisotropy, we now have

$$\chi_1^{P'} = \chi_2^P + \chi_3^P + \chi_4^P, \quad \chi_1^{Q'} = \chi_2^Q + \chi_3^Q + \chi_4^Q, \quad (18a)$$

$$\zeta^P = \chi_1^P - \chi_1^{P'}, \quad \zeta^Q = \chi_1^Q - \chi_1^{Q'}, \quad (18b)$$

$$\zeta = 2\zeta^P - 2\zeta^Q, \quad (18c)$$

where the axes are now fixed along the crystal axes. The effective nonlinear polarization is then the sum of the isotropic part (15) and the anisotropic part,

$$P_{\text{eff},i}^{\text{anis}} = \zeta E_i(\omega) \frac{\partial}{\partial i} E_i(\omega) - \left[\frac{\partial \zeta^Q}{\partial i} \right] E_i(\omega) E_i(\omega). \quad (19)$$

As in the isotropic case, away from the surface the second term of Eq. (19) vanishes and one is left with the usual expression for the bulk nonlinearity in a cubic medium.^{8,9,11} However, in the presence of a surface, its contribution may become nonvanishing. For a (100) face, this term does not contribute, but for a (111) face we find that ζ^Q gives an additional contribution to the anisotropic and isotropic components of the effective surface susceptibility. More explicitly, taking $\hat{\xi} \parallel [2\bar{1}\bar{1}]$ and $\hat{\eta} \parallel [01\bar{1}]$ as the axes in the plane of the surface, the anisotropic components of the surface susceptibility are^{8,9,15}

$$\chi_{s\xi\xi\xi} = -\chi_{s\eta\xi\eta} = -\chi_{s\eta\eta\xi}, \quad (20)$$

which contains an additional term $(1/3\sqrt{2})\zeta^Q$ arising from the $\partial\zeta^Q/\partial i$ term in Eq. (19). Similarly, for the isotropic components in Eq. (17) there is also an additional term, $\frac{1}{3}\zeta^Q$, coming from the $\partial\zeta^Q/\partial i$ term in Eq. (19).

In previous works,^{8,15} when SHG from a (111) face of a cubic medium was considered, the anisotropy was given as a combination of a surface term and a bulk anisotropy term as

$$\chi_{s\xi\xi\xi} + a\zeta, \quad (21)$$

where a is a function of the incidence angle, wavelength, and linear dielectric constants. Instead, we now have the expression

$$\chi_{s,\xi\xi\xi} + \frac{1}{3\sqrt{2}}\xi^Q + a\xi; \quad (22)$$

here only the first term is surface specific.

In the above two examples, isotropic and cubic, we have shown that for SHG with any polarization combinations it is not possible to separate the bulk and surface contributions if the surface has the same symmetry as the bulk. This modifies the views previously held that SHG from isotropic systems with the output *s* polarized results from a pure surface contribution. Similarly, for a cubic crystal, it was believed that probing different crystal faces would allow us to separate the surface and bulk contributions⁸ of the anisotropic term in the nonlinearity. It was also thought that the dependence of the coefficient *a* in Eq. (21) with the angle of incidence could be utilized for the separation.⁸ None of these methods would actually serve their purpose, as seen from Eq. (22).

These findings have different significance depending on the system studied. For clean surfaces of metals or semiconductors, it has been repeatedly shown that oxidation or disordering of the surface could easily decrease the SHG signals by 1 order of magnitude.¹⁵⁻¹⁸ This indicates that the surface contribution is dominant, and that the additional bulk contribution that we introduce in this paper is of little importance. When insulator surfaces are considered, or when the surfaces of metals or semiconductors are oxidized, it is likely that the surface and bulk contributions may have comparable magnitudes. In those cases our result is important. It shows that SHG cannot straightforwardly separate surface and bulk contributions. Only a careful modification of the surface could perhaps allow us to do so. An improved knowledge of the bulk nonlinearity in a centrosymmetric system would be helpful. In the next section we present two models for the bulk contribution. The second one, which we call the molecular model, has been successfully applied to the study of the surface polar ordering of a liquid crystal.¹⁹

MODELS FOR THE BULK NONLINEARITY

It is possible to relate a few tensor elements of χ^Q and χ^P using simplified models. The first model we shall discuss is based on the low-frequency approximation.² This approximation has been proposed for isotropic nonmagnetic systems. The nonlinearity is assumed to come from bound electrons, with electric-dipole and electric-quadrupole transition moments only. In this approximation one has²

$$\delta=0, \quad \beta = -2\gamma = 3(4n_b e)^{-1}[\chi^{(1)}(\omega)]^2, \quad (23)$$

where n_b is the density of valence electrons and $\chi^{(1)}$ is the linear susceptibility. In addition to Eqs. (11), (12), and (14), we find also the following relations:

$$\chi_1^P = \chi_1^Q, \quad \chi_2^P = \chi_2^Q, \quad \chi_3^P = \chi_4^P = \chi_3^Q = \chi_4^Q. \quad (24)$$

Although all the parameters can be expected to vary as $|\chi^{(1)}(\omega)|^2/n_b$, we were not able to find an expression further reducing the number of independent parameters.

The other model is the molecular model, which is based on the following approximation. We consider a system composed of individual moleculelike units such that each unit has a relatively strong intrinsic second-order polarizability $\vec{\alpha}^{(2)}$. The electric-quadrupole or magnetic-dipole contribution to $\vec{\alpha}^{(2)}$ is assumed negligible. In a medium with a centrosymmetric distribution of such individual units, their orientational average will then give rise to an effective electric-quadrupole nonlinearity. The field detected at point *r* is the sum of the radiative contributions of the individual dipoles in a volume Ω , so that we can write

$$E_m(\mathbf{r}, 2\omega) = \sum_{\mathbf{r}_1 \in \Omega} G_{mi}(\mathbf{r}_1, \mathbf{r}) \alpha_{ijk}^{(2)}(\mathbf{r}_1) E_{1j}(\mathbf{r}_1, \omega) E_{2k}(\mathbf{r}_1, \omega). \quad (25)$$

Now the orientational average can be performed in a volume V_0 with dimensions much smaller than the wavelength. We have

$$E_m(\mathbf{r}, 2\omega) = \sum_{\mathbf{r}_0 \in \Omega} \frac{1}{V_0} \sum_{\mathbf{r}_1 \in V_0(\mathbf{r}_0)} G_{mi}(\mathbf{r}_1, \mathbf{r}) \alpha_{ijk}^{(2)}(\mathbf{r}_1) E_{1j}(\mathbf{r}_1, \omega) E_{2k}(\mathbf{r}_1, \omega). \quad (26)$$

We now assume that G_{mi} , E_{1j} , and E_{2k} are smooth functions of the positions \mathbf{r}_1 . (This is equivalent to neglecting the local-field effects; the latter could be incorporated into the values of $\alpha^{(2)}$.) With this approximation, we can expand the functions G_{mi} , E_{1j} , and E_{2k} around \mathbf{r}_0 and stop at the first derivatives. We obtain

$$\begin{aligned} E_m(\mathbf{r}, 2\omega) = \sum_{\mathbf{r}_0 \in \Omega} \frac{1}{V_0} \sum_{\mathbf{r}_1 \in V_0(\mathbf{r}_0)} & \left[G_{mi}(\mathbf{r}_0, \mathbf{r}) \alpha_{ijk}^{(2)}(\mathbf{r}_1) E_{1j}(\mathbf{r}_0, \omega) E_{2k}(\mathbf{r}_0, \omega) \right. \\ & + G_{mi}(\mathbf{r}_0, \mathbf{r}) \alpha_{ijk}^{(2)}(\mathbf{r}_1) (r_{1l} - r_{0l}) \left[E_{1j}(\mathbf{r}_0, \omega) \frac{\partial}{\partial l} E_{2k}(\mathbf{r}_0, \omega) + \frac{\partial E_{1j}}{\partial l}(\mathbf{r}_0, \omega) E_{2k}(\mathbf{r}_0, \omega) \right] \\ & \left. + \frac{\partial}{\partial \rho} G_{mi}(\mathbf{r}_0, \mathbf{r}) \alpha_{ijk}^{(2)}(\mathbf{r}_1) (r_{1l} - r_{0l}) E_{1j}(\mathbf{r}_0, \omega) E_{2k}(\mathbf{r}_0, \omega) \right]. \quad (27) \end{aligned}$$

The first term vanishes because of the inversion symmetry and the third term can be integrated by parts over the whole volume so that it becomes

$$\sum_{\mathbf{r}_0 \in \Omega} \sum_{\mathbf{r}_1 \in V_0(\mathbf{r}_0)} G_{mi}(\mathbf{r}_0, \mathbf{r}) \frac{\partial}{\partial l} [\alpha_{ijk}^{(2)}(\mathbf{r}_1) (r_{1l} - r_{0l}) E_{1j}(\mathbf{r}_0, \omega) E_{2k}(\mathbf{r}_0, \omega)]$$

on the assumption that $V_0^{1/3} \ll \lambda$. We can define χ^P and χ^Q ,

$$\chi_{ijkl}^P = \chi_{ijkl}^Q = \frac{1}{V_0} \sum_{\mathbf{r}_i \in V_0(\mathbf{r}_0)} [\mathbf{i} \cdot \vec{\alpha}^{(2)}(\mathbf{r}_i) \cdot \mathbf{j} \cdot \mathbf{k}] [(\mathbf{r}_1 - \mathbf{r}_0) \cdot \mathbf{l}], \quad (28)$$

where $\mathbf{i}, \mathbf{j}, \mathbf{k}, \mathbf{l}$, are unit vectors, and Eq. (27) becomes

$$\mathcal{E}(\mathbf{r}, 2\omega) = \int_{\Omega} \vec{G} : (\vec{\chi}^P : \mathbf{E} \mathbf{V} \mathbf{E} + \nabla \cdot \vec{\chi}^Q : \mathbf{E} \mathbf{E}). \quad (29)$$

For an isotropic system, this gives the relation

$$\chi_1^P - \chi_1^Q, \quad \chi_2^P = \chi_2^Q = \chi_4^Q, \quad \chi_3^P = \chi_4^P = \chi_2^Q, \quad (30)$$

and, consequently, the following identities,

$$\delta = \beta = \gamma = 0. \quad (31)$$

From Eq. (17), the effective surface susceptibility then takes the simple form

$$\chi_{zzz} = \chi_{s'zzz} - \chi_1^Q / \epsilon(2\omega) \epsilon(\omega)^2, \quad (32a)$$

$$\chi_{zxx} = \chi_{s'zxx} - \chi_2^Q / \epsilon(2\omega), \quad (32b)$$

$$\chi_{xzx} = \chi_{s'xzx} - \chi_4^Q / \epsilon(\omega). \quad (32c)$$

In many cases the surface nonlinearity is dominated by the electric-dipole response of the surface layer, while the bulk nonlinearity is dominated by the electric-quadrupole contribution. The dipole response can be expressed in terms of the one-body distribution function, $f_1(\mathbf{r}, \theta)$, and the quadrupole response in terms of the pair distribution function, $f_2(\mathbf{r}_1, \theta_1, \mathbf{r}_2, \theta_2)$. Here we use the usual notation in the physics of liquids, with \mathbf{r} describing the position of the unit and θ its orientation. Note that $f_1(\mathbf{r}, \theta)$ may

vary in moving from the bulk to the surface. χ_s^P and χ^Q can then be written as

$$\chi_{s'ijk} = \int_I f_1(\mathbf{r}, \theta) [\mathbf{i} \cdot \vec{\alpha}^{(2)}(\mathbf{r}, \theta) \cdot \mathbf{j} \cdot \mathbf{k}] d\mathbf{r} d\theta, \quad (33a)$$

$$\chi_{ijk}^Q(\mathbf{r}_1) = \int f_2(\mathbf{r}_1, \mathbf{r}_2, \theta_1, \theta_2) [\mathbf{i} \cdot \vec{\alpha}^{(2)}(\mathbf{r}_2, \theta_2) \cdot \mathbf{j} \cdot \mathbf{k}] \times \mathbf{l} \cdot (\mathbf{r}_2 - \mathbf{r}_1) d\theta_1 d\theta_2. \quad (33b)$$

CONCLUSIONS

In this paper we have considered the bulk contribution to surface SHG from centrosymmetric substrates. We have found the omission of a bulk term in the literature on the subject. The presence of this term makes the separation of bulk and surface contributions by measurements on one sample impossible, contrary to the view previously held. This is particularly important when the two contributions are comparable. In studying the origin of the bulk nonlinearity in a centrosymmetric system, we have proposed a new model which applies to molecular solids and fluids with strong molecular nonlinear polarizability. This model relates the bulk nonlinearity to the pair-correlation functions of the molecules. It should be useful in the applications of SHG to the study of interfaces with molecular liquid or solid systems.

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¹See, for example, Y. R. Shen, *Annu. Rev. Mater. Sci.* **16**, 69 (1986); K. Kemnitz, K. Bhattacharyya, J. M. Hicks, G. R. Pinto, K. B. Eisenthal, and T. F. Heinz, *Chem. Phys. Lett.* **131**, 285 (1986); D. Heskett, K. J. Song, A. Burns, E. W. Plummer, and H. L. Dai, *J. Chem. Phys.* **85**, 7490 (1986); T. L. Mazely, and W. M. Hetherington III, *ibid.* **86**, 3640 (1987).

²N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, *Phys. Rev.* **174**, 813 (1968).

³C. C. Wang and W. W. Duminski, *Phys. Rev. Lett.* **20**, 668 (1968).

⁴C. C. Wang, *Phys. Rev.* **178**, 1457 (1969).

⁵J. M. Chen, J. R. Bower, C. S. Wang, and C. H. Lee, *Opt. Commun.* **9**, 132 (1973).

⁶T. F. Heinz, Ph.D. thesis, University of California, Berkeley, 1982.

⁷P. Guyot-Sionnest, W. Chen, and Y. R. Shen, *Phys. Rev. B* **33**, 8254 (1986).

⁸H. W. K. Tom, T. F. Heinz, and Y. R. Shen, *Phys. Rev. Lett.* **51**, 1983 (1983).

⁹H. W. K. Tom, Ph.D. thesis, University of California, Berkeley, 1984.

¹⁰D. Guidotti, T. A. Driscoll, and H. J. Gerritsen, *Solid State Commun.* **46**, 337 (1983).

¹¹J. E. Sipe, D. J. Moss, and H. M. Van Driel, *Phys. Rev. B* **35**, 1129 (1983).

¹²P. Guyot-Sionnest and Y. R. Shen, *Phys. Rev. B* **35**, 4420 (1987).

¹³P. S. Pershan, *Phys. Rev.* **130**, 919 (1963).

¹⁴E. Adler, *Phys. Rev.* **134**, A728 (1964).

¹⁵H. W. K. Tom and G. D. Aumiller, *Phys. Rev. B* **33**, 8818 (1986).

¹⁶H. W. K. Tom, C. M. Mate, X. D. Zhu, J. E. Crowell, T. F. Heinz, G. A. Somorjai, and Y. R. Shen, *Phys. Rev. Lett.* **52**, 348 (1984).

¹⁷H. W. K. Tom, X. D. Zhu, Y. R. Shen, and G. A. Somorjai, *Surf. Sci.* **167**, 167 (1986).

¹⁸T. F. Heinz, M. M. T. Loy, and W. A. Thompson, *Phys. Rev. Lett.* **54**, 63 (1985).