Polarization-based identification of bulk contributions in surface nonlinear optics

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We show that bulk and surface contributions in second-order surface nonlinear optics of isotropic materials can be identified unambiguously in a single measurement by their polarization signatures. The signatures follow from the isotropy of the material and are nearly independent of its linear optical properties. Interference between the contributions allows their relative magnitudes to be quantified. For second-harmonic generation from a glass surface, the surface (bulk) contribution dominates the reflected (transmitted) signal by a factor of ~160 (~40). The results also suggest that the inseparable, surfacelike bulk contribution can account for a significant fraction of the effective surface susceptibility of glass.

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Second-harmonic (SHG) and sum-frequency generation (SFG) are widely recognized tools to study surfaces and interfaces.[1–4] Their main features, surface specificity and sensitivity to surface conditions, arise from a powerful selection rule: as second-order nonlinear optical effects, SHG and SFG vanish in the bulk of materials with inversion symmetry but can occur at the surface, where the symmetry is broken.[1]

The selection rule, however, is only valid under the electric-dipole approximation. Once magnetic-dipole and electric-quadrupole interactions are taken into account, contributions to SHG or SFG can arise also from the bulk of centrosymmetric materials.[1,2,5–9] Although due to higher-order effects such bulk contributions can be comparable to (and sometimes dominant over) surface contributions, as the latter originate from a very thin surface layer.[2] Whenever SHG and SFG are used as surface probes, it is essential to verify that the measured signal does originate from the surface. Separation and quantification of bulk and surface contributions are therefore of utmost importance.

Unfortunately, some components of the bulk response of isotropic materials are indistinguishable from surface contributions in experiments where the surface cannot be modified.[2,7,8] However, it has been recognized that part of the bulk response can be identified experimentally.[2,9–12] Since all bulk contributions are expected to be of the same order of magnitude, the separable component allows assessing whether bulk contributions to the measured signals are significant.[10–13]

When present, the separable bulk component leads to radiation that builds up in the medium and therefore depends on the coherence length of the nonlinear process.[2] Such dependence can be used to separate the component from surface contributions, e.g., by performing measurements with different incident angles. The coherence length, however, usually does not vary strongly over the accessible angles.[2] The situation is somewhat simpler when both reflection and transmission measurements can be performed.[2,9] In the latter case, the phase-matching condition is better approximated than in the former, leading to an increased coherence length and, consequently, a larger bulk contribution.[2] Absolute comparison of reflected and transmitted signals relies, however, on accurate calibration of the experimental setup and requires detailed knowledge of the linear optical properties of the sample. For these reasons, the bulk and surface contributions have usually been separated by comparing reflected and transmitted spectra measured using visible-infrared SFG.[9–11,14,15] In addition to being limited to systems where the bulk and surface spectra are clearly different, the alignment of such experiments is quite involved.[10]

In this paper, we show that the separable bulk contribution and the effective surface contribution of isotropic materials can be identified in a direct and unambiguous way by detailed polarization measurements of the second-order response. Unlike methods relying on coherence length, we achieve separation from a single measurement, with no need to compare different signals. Moreover, no prior knowledge of the linear optical properties of the sample is required because the polarization signatures are essentially dictated by symmetry. We apply the technique to determine the relative magnitudes of the separable bulk contribution and the effective surface contribution to second-harmonic generation from a glass surface. This also allows the importance of the inseparable bulk contribution to the effective surface susceptibility to be estimated.

The theory of SHG at the interface between two isotropic and centrosymmetric dielectric media has been described earlier.[1,2,6–12,16,17] Usually, three regions are defined: the two bulk media and an interfacial layer (Fig. 1), which is assumed to have in-plane isotropy. A complete description assigns different linear optical properties to each region.[2] As we shall see, however, the linear properties have only a marginal effect on our results. To keep the mathematical expressions simple, we assume the refractive indices of all media to be unity and briefly discuss the effect of the linear properties separately.

At the interface, the inversion symmetry is broken and SHG is electric-dipole-allowed.[1] In addition, nonlocal (electric-quadrupole) contributions arise from the rapid variation of the electric field and of the material properties across the layer.[16,17] All these effects are described by an effective surface polarization[2,16]

$$\mathbf{P}^s(2\omega) = \boldsymbol{\chi}^s{:}\mathbf{E}(\omega,z=0)\mathbf{E}(\omega,z=0), \qquad (1)$$

where $\mathbf{E}(\omega,\mathbf{r})$ is the total fundamental incident field, x and y are the coordinates in the plane of the surface, and z is along

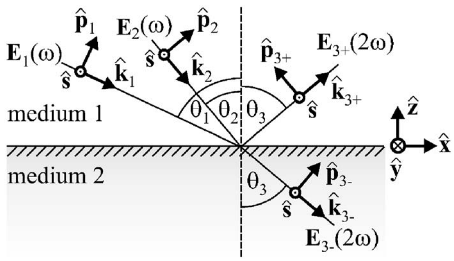

FIG. 1. Schematic representation of two-beam SHG at the interface between two isotropic media. Two input beams are incident on the interface from medium 1 at angles θ_1 and θ_2 (positive as drawn), and SHG light in transmission and reflection is emitted. The fields are divided into p and s components (parallel and normal to the plane of incidence, respectively). The coordinate system (x,y,z) associated with the sample is also shown.

the surface normal. For isotropic surfaces, the tensor $\boldsymbol{\chi}^s$ has only three independent components:[1,16] $\chi^s_{xxz}=\chi^s_{xzx}=\chi^s_{yyz}=\chi^s_{yzy}$, $\chi^s_{zxx}=\chi^s_{zyy}$, and χ^s_{zzz}.

We neglect the nonlinear response of bulk medium 1, as is commonly done when this medium is, e.g, air. The polarization at 2ω in the bulk of medium 2 is given by[1,2,6–8]

$$\mathbf{P}^b(2\omega,\mathbf{r}) = \beta\mathbf{E}(\omega,\mathbf{r})[\nabla\cdot\mathbf{E}(\omega,\mathbf{r})] + \gamma\nabla[\mathbf{E}(\omega,\mathbf{r})\cdot\mathbf{E}(\omega,\mathbf{r})] + \delta'[\mathbf{E}(\omega,\mathbf{r})\cdot\nabla]\mathbf{E}(\omega,\mathbf{r}), \quad (2)$$

where β, γ, and δ' are material parameters that depend on the electric-quadrupole and magnetic-dipole tensors of the medium.[2,6,12] Integrating Eq. (2) over the space occupied by medium 2 leads to a form that explicitly shows the dependence of the bulk contributions on coherence length.[2,9–11]

For homogeneous media, the first term in Eq. (2) can be neglected, since $\nabla\cdot\mathbf{E}=\varepsilon^{-1}\nabla\cdot\mathbf{D}$ vanishes. As realized by several authors,[2,7,8] it is impossible to separate the second term in Eq. (2) from the component P^s_z of the surface polarization in experiments that allow no modification of the surface. The γ contribution can therefore be included in the components χ^s_{zxx} and χ^s_{zzz} of the effective surface susceptibility.[2,7,8]

The third term in Eq. (2) vanishes when a single fundamental beam is present in the material but can be accessed using two input beams, as is typically the case for SFG.[2,8,18] Contrary to surfacelike contributions, it leads to radiation that builds up in the medium and therefore depends on the coherence length of the nonlinear process.[2,10,11] We will show below that this term also displays a polarization dependence which is completely different from that of surface contributions.

We consider a situation in which two noncollinear fundamental beams are incident on the surface and a joint (reflected or transmitted) SHG signal is detected (Fig. 1).[19,20] The total incident field is given by

$$\mathbf{E}(\omega,\mathbf{r}) = \mathbf{E}_1(\omega,\mathbf{r}) + \mathbf{E}_2(\omega,\mathbf{r}) = \mathbf{A}_1(\omega)e^{i(\omega/c)\hat{\mathbf{k}}_1\cdot\mathbf{r}} + \mathbf{A}_2(\omega)e^{i(\omega/c)\hat{\mathbf{k}}_2\cdot\mathbf{r}}. \quad (3)$$

The fundamental beams propagate in the x-z plane along $\hat{\mathbf{k}}_i=\sin\theta_i\hat{\mathbf{x}}-\cos\theta_i\hat{\mathbf{z}}$ $(i=1,2)$, with incident angles θ_1 and θ_2 (Fig. 1). Since the momentum parallel to the surface is conserved, the generated SHG field is

$$\mathbf{E}_{3\pm}(2\omega,\mathbf{r}) = \mathbf{A}_{3\pm}(2\omega)e^{i(2\omega/c)\hat{\mathbf{k}}_{3\pm}\cdot\mathbf{r}}, \quad (4)$$

with $\hat{\mathbf{k}}_{3\pm}=\sin\theta_3\hat{\mathbf{x}}\pm\cos\theta_3\hat{\mathbf{z}}$ (upper sign, transmission; lower sign, reflection) and $\sin\theta_3=(\sin\theta_1+\sin\theta_2)/2$. The field vectors are expressed in terms of p and s components (respectively, parallel and perpendicular to the plane of incidence) as $\mathbf{A}_i=A_{is}\hat{\mathbf{s}}+A_{ip}\hat{\mathbf{p}}_i$. While the s direction is the same for all beams $(\hat{\mathbf{s}}=-\hat{\mathbf{y}})$, the p_i directions depend on the propagation directions of the beams $(\hat{\mathbf{p}}_i=\hat{\mathbf{s}}\times\hat{\mathbf{k}}_i)$.

Let us first consider the SHG field arising from the effective surface polarization $\mathbf{P}^s$. For isotropic media, polarization effects due to linear light propagation can be neglected. The p component of the SHG field then arises from the components P^s_x and P^s_z, and therefore includes contributions from all three independent components of $\boldsymbol{\chi}^s$. The s component of the SHG field, on the other hand, is proportional to P^s_y and is therefore entirely determined by χ^s_{xxz}. A straightforward calculation shows that

$$P^s_y = -2\chi^s_{xxz}[\sin\theta_1 A_{1p}A_{2s} + \sin\theta_2 A_{1s}A_{2p}]. \quad (5)$$

Clearly, χ^s_{xxz} only appears as an overall scaling factor. The polarization dependence of the s-polarized SHG signals is therefore completely specified by the incident angles of the fundamental beams.

Inserting Eq. (3) into Eq. (2), we obtain the separable bulk polarization in medium 2:

$$\mathbf{P}^{\delta'}(2\omega,\mathbf{r}) = i\delta'\frac{\omega}{c}[(\mathbf{A}_2\cdot\hat{\mathbf{k}}_1)\mathbf{A}_1 + (\mathbf{A}_1\cdot\hat{\mathbf{k}}_2)\mathbf{A}_2]e^{i(\omega/c)(\hat{\mathbf{k}}_1+\hat{\mathbf{k}}_2)\cdot\mathbf{r}}, \quad (6)$$

whose y component is found to be

$$P^{\delta'}_y(2\omega,\mathbf{r}) = i\delta'\frac{\omega}{c}(\sin\theta_1\cos\theta_2 - \cos\theta_1\sin\theta_2)[A_{1p}A_{2s} - A_{1s}A_{2p}]e^{i(\omega/c)(\hat{\mathbf{k}}_1+\hat{\mathbf{k}}_2)\cdot\mathbf{r}}. \quad (7)$$

The reflected and transmitted s-polarized SHG fields are obtained by using Eq. (7) as a source in the wave equation and integrating over the portion of space occupied by medium 2.[2] This only affects the signal strength, not its polarization dependence, which is specified by the factor $[A_{1p}A_{2s}-A_{1s}A_{2p}]$ and does not, therefore, depend on experimental geometry.

To summarize, the polarization signatures of the surface and bulk contributions are

$$[A_{3s}]^{surface} \propto A_{1p}A_{2s} + \frac{\sin\theta_2}{\sin\theta_1}A_{1s}A_{2p} \quad (8)$$

and

$$[A_{3s}]^{bulk} \propto A_{1p}A_{2s} - A_{1s}A_{2p}. \quad (9)$$

Clearly, the differences between the signatures are accentuated when θ_1 and θ_2 have the same sign.

In the experiments, infrared radiation from a Q-switched Nd:YAG laser (1064 nm, ~20 mJ, 10 ns, 30 Hz) was used as a source for SHG. The s-polarized (transmitted or re-

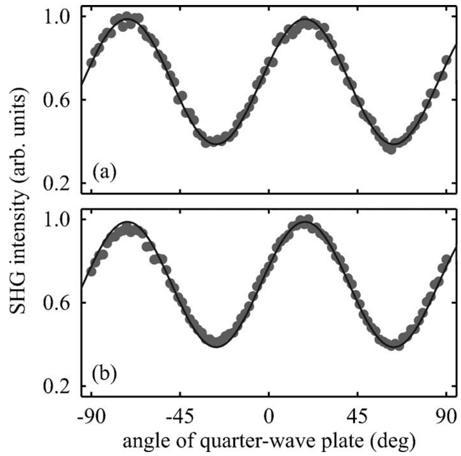

FIG. 2. Reflected (a) and transmitted (b) *s*-polarized SHG polarization patterns for a poled polymer film. The patterns are essentially identical and determined by the geometry of the experiment, indicating a response dominated by surface-type electric-dipole contributions. The solid lines are obtained by matching Eq. (8) to the signal level with no other fitting.

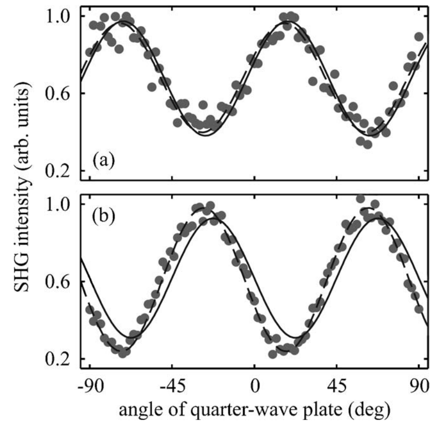

FIG. 3. Reflected (a) and transmitted (b) *s*-polarized SHG polarization patterns for a glass surface (BK7). The effective surface (separable bulk) contribution dominates the reflected (transmitted) signal by a factor of ~160 (~40). The solid lines in (a) and (b) are the predictions of, respectively, Eqs. (8) and (9), while the dashed lines are obtained by fitting Eq. (10) to the data.

flected) SHG signal at 532 nm was detected while the polarization of an initially *p*-polarized input $\mathbf{E}_2$ (probe) was varied by a continuously rotating zero-order quarter-wave plate and the polarization of input $\mathbf{E}_1$ (control) was held fixed at 45° from the plane of incidence. Calcite Glan polarizers (extinction ratio $\sim 4\times 10^{-6}$) were used to select the polarizations of the control and SHG beams and to clean the polarization of the probe beam before the quarter-wave plate. The incident angles of the control and probe beams were, respectively, 34.2° and 49.1°.

To verify our technique, we measured polarization patterns from a poled polymer film (octadecylamino cyanoazostilbene in PMMA, thickness ~1.4 μm) whose second-order response has electric-dipole origin with the uniaxial symmetry of an isotropic surface and should therefore follow Eq. (8). As expected, the reflected and transmitted polarization patterns are essentially identical (Fig. 2) and entirely determined by the experimental geometry. We emphasize that the solid lines in Fig. 2 do not involve any fitting except for an overall scaling factor used to match the measured signal level.

We then applied the technique to investigate the origin of the nonlinear response of a glass surface (BK7). In this case, the reflected pattern is again well described by the model of Eq. (8), with no apparent bulk contribution [Fig. 3(a)]. However, the transmitted pattern is completely different, indicating strong bulk contributions [Fig. 3(b)]. Although Eq. (9) [solid line in Fig. 3(b)] reproduces qualitatively the main features of the observed pattern, a better agreement is obtained by using a linear combination of surface [Eq. (8)] and bulk [Eq. (9)] contributions to account for their interference:

$$A_{3s} = [A_{3s}]^{surface} + S[A_{3s}]^{bulk}. \tag{10}$$

The parameter S is a measure of the relative importance of bulk and surface contributions in the experiment. By fitting Eq. (10) to the measured transmitted SHG pattern, a value of $S=6.54$ is obtained [dashed line in Fig. 3(b)]. In terms of intensities, this indicates that the signal arising from the bulk contribution in transmission is approximately 40 times larger than that from surface contributions.

The differences between transmitted and reflected SHG polarization patterns can be understood in terms of different coherence lengths. In our geometry, the coherence length in BK7 ($n=1.507$ and 1.519 at 1064 nm and 532 nm, respectively) is approximately 10 μm in transmission and 0.12 μm in reflection.[1] Therefore, the bulk contribution to the SHG field is expected to be approximately 85 times larger in transmission. This suggests that a weak bulk contribution should be observable in the reflected SHG pattern as well. When Eq. (10) is fitted to the pattern, we obtain a value of $S=-0.08$ [dashed line in Fig. 3(a)]. This result is in excellent agreement with the coherence length argument, despite the noise in the experimental data.

The parameter S is a measure of the integrated bulk contribution to the SHG field and can be estimated by integrating Eq. (7) over the coherence length l_c. This yields $S\approx 4l_c\delta'/\lambda$, where λ is the fundamental wavelength. Using the values for S and l_c in transmission or reflection and taking into account the geometrical factors appearing in Eqs. (5) and (7), we obtain the bulk parameter $\delta'\cong 0.76$ as referenced to the effective surface susceptibility. Since all bulk parameters are expected to be of the same order of magnitude,[10–13] this indicates that the inseparable γ contribution can account for a significant fraction of the effective surface susceptibility. This result complements previous work showing that nonlocal contributions arising from the structural and field discontinuities at the interface are important in the surface susceptibility of an air-glass interface.[2,7,17]

As stated above, the polarization signatures of bulk and surface contributions are almost independent of the linear optical properties of the media. This is verified by the excellent agreement between the experimentally determined polarization patters and the patterns simulated assuming unity refractive indices (Figs. 2 and 3). When one assigns different refractive indices to media 1 and 2, and assumes the index of the interface layer to be the same as that of medium 2, the second terms of Eqs. (8) and (9) must be multiplied by a factor

$$\kappa = \frac{t_1^s t_2^p}{t_1^p t_2^s}, \tag{11}$$

where, e.g., t_1^s is the Fresnel amplitude transmission coefficient for the s component of $\mathbf{E}_1$ and the field amplitudes $\mathbf{A}_i$ ($i=1,2$) are evaluated in medium 1. In our case, $\kappa=1.03$ and has practically no influence on the results. When the refractive index of the interface layer is different from that of the bulk, Eq. (11) needs to be modified. However, it can be shown that, even in this case, inclusion of the linear optical properties does not change significantly the polarization signatures provided that the two fundamental beams are applied at nearly the same angle of incidence.

In conclusion, we have shown that the separable bulk contribution and the effective surface contribution to the second-order nonlinear response of isotropic materials can be identified in a direct, unambiguous, and quantitative way in a single measurement by their polarization signatures. For second-harmonic generation from a glass surface, the surface (bulk) contribution was shown to dominate the reflected (transmitted) signal by a factor of ~160 (~40). This also suggests that the inseparable, surfacelike bulk contribution can account for a significant fraction of the effective surface susceptibility of glass. We expect our results to have two complementary applications in surface studies. First, the polarization signatures do not depend on the details of the surface, because they follow directly from the isotropy of the medium and are insensitive to its linear optical properties. Polarization measurements can therefore be exploited as a simple and unambiguous way to validate nonlinear surface and thin-film studies by verifying that there is no bulk interference in the measured signal. Second, combination of polarization measurements with theoretical models of the multipole tensors will allow fundamental properties of surface nonlinearities to be studied with unprecedented detail. Although the present results apply to SHG with two noncollinear input beams, extension to SFG, which is naturally performed in the same geometry, is straightforward.

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