Fundamental difficulty in the use of second-harmonic generation as a strictly surface probe

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We prove that an important component of forbidden bulk second-harmonic generation in homogeneous media is inseparable from the surface contribution in all practical experimental situations. Experimental evidence is presented. Consequences are discussed.

In a centrosymmetric material, second-harmonic generation (SHG) due to electric dipoles is forbidden, and the second-harmonic polarization sources have magnetic dipole and electric quadrupole symmetry.[1] Near a surface, however, inversion symmetry is broken and electric dipole sources are allowed. In addition, large gradients exist in the normal component of the electric field. The source polarization due to both these effects can be described phenomenologically by a dipole sheet, the amplitude of which depends on the fundamental electric field at the surface through a surface susceptibility tensor.

In the use of second-harmonic generation as a probe of surface (or bulk) properties, it is obviously desirable to employ experimental geometries which allow—as far as is possible—for the unambiguous and separate determination of the elements of the surface susceptibility tensor and the material constants characterizing the bulk sources. Indeed, a number of clever experimental protocols have been suggested to do this.[2,3] But there is an important limitation to the extent to which this is possible in a homogeneous medium; a proof of that limitation is the subject of this note. Several years ago, Wang[4] observed a special case of our result when he considered the second-harmonic signal observed in reflection from a linearly polarized plane wave impinging from the vacuum on a flat surface. He showed that, in this very restrictive geometry, the signal depended on one of the bulk coefficients only through its dependence on a particular linear combination with one of the surface coefficients. And, since this linear combination is the same for all angles of incidence and linear polarization, no experiment in the class considered by Wang could separately determine those terms. This result has been noticed, in such special classes of experimental geometries, by other workers since.[3]

Here we prove theoretically and demonstrate experimentally that the result is considerably more general than has been previously appreciated. It holds for arbitrary polarization, and in fact for any number of beams of any shape propagating in any direction. Indeed, essentially nothing need be assumed about the form of the fundamental field. Further, the result holds for an arbitrarily shaped medium, and can be generalized to treat sum and difference frequency generation. It is thus a fundamental and important result in the theory of optical parametric processes.

To present and prove this result, we first consider second-harmonic generation from an isotropic medium, in a geometry where only one (planar) surface is important (see Fig. 1). In the bulk of the medium the polarization at 2ω is given by[1]

$$\mathbf{P}(\mathbf{r}) = \gamma\nabla[\mathbf{e}(\mathbf{r})\cdot\mathbf{e}(\mathbf{r})] + \beta\mathbf{e}(\mathbf{r})[\nabla\cdot\mathbf{e}(\mathbf{r})] + \delta'[\mathbf{e}(\mathbf{r})\cdot\nabla]\mathbf{e}(\mathbf{r}) \ , \tag{1}$$

where $\mathbf{e}(\mathbf{r})$ is the electric field at the fundamental frequency ω, and γ, β, and δ' are material constants. The δ introduced by Bloembergen is $\delta=\delta'+\beta+2\gamma$; it is convenient to consider γ, β, and δ' as the independent constants. The polarization of the dipole sheet at the surface is

$$\mathbf{P}(\mathbf{r}) = \delta(z-0^+)\mathbf{p}(x,y) \ , \tag{2}$$

where we have assumed vacuum for $z>0$, medium for $z<0$, and

$$\mathbf{p}(x,y) = \boldsymbol{\chi}^s{:}\mathbf{e}(x,y,z=0^-)\mathbf{e}(x,y,z=0^-) \ . \tag{3}$$

The assumption of isotropy in the medium requires $\chi^s_{xxz}=\chi^s_{xzx}=\chi^s_{yyz}=\chi^s_{yzy}\equiv\chi^s_{\parallel\parallel\perp}$, $\chi^s_{zxx}=\chi^s_{zyy}\equiv\chi^s_{\perp\parallel\parallel}$; all other elements of the surface susceptibility tensor $\boldsymbol{\chi}^s$ except $\chi^s_{zzz}\equiv\chi^s_{\perp\perp\perp}$ vanish. (The subscripts $\parallel$ and $\perp$ refer to components parallel and perpendicular to the surface, respectively.)

The particular surface and bulk terms that appear together are $\chi^s_{\perp\parallel\parallel}$ and γ; we prove below that these terms always appear in the linear combination $\chi^s_{\perp\parallel\parallel}+\epsilon^{-1}(2\omega)\gamma$, where $\epsilon(2\omega)$ is the (in general, complex) dielectric constant at the second-harmonic frequency. This result has some surprising consequences. For example, consider a transparent material where SHG can be observed in reflection or transmission. In the latter case the condition of phase matching can be much more closely approximat-

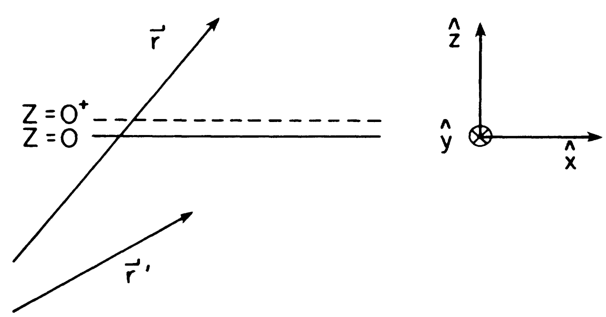

FIG. 1. A simple interface; the dipole sheet is placed at $z=0^+$ as indicated. The medium is in the region $z<0$.

ed than in the former. If fused silica is chosen as the material with a fundamental beam at 532 nm incident at 45°, the effective coherence length (the thickness of the bulk material that coherently contributes to the second-harmonic signal) is 3.0 μm in the forward direction and only 0.052 μm in the reverse.[5] Thus, one might naively expect of order $(3.0/0.052)^2=3300$ times more contribution form the γ term in the forward direction (SHG in transmission) than in the backward direction (SHG in reflection), with roughly comparable contributions from the surface terms. Yet this coherence-length factor is *always* canceled out (as can be shown by direct calculation) by geometric factors associated with the direction of the bulk source polarization, and in the end the signal is sensitive not to γ independently, but to $\chi^s_{\perp\parallel\parallel}+\epsilon^{-1}(2\omega)\gamma$.

Note that in an optics experiment $\nabla\cdot\mathbf{e}(\mathbf{r})=0$ in the bulk, and if s-polarized light is incident, there is no signal due to δ', $\chi^s_{\perp\perp\perp}$, or $\chi^s_{\parallel\parallel\perp}$, and only the $\chi^s_{\perp\parallel\parallel}+\epsilon^{-1}(2\omega)\gamma$ term remains. From this it follows that the *ratio* of the signal in a transmission experiment to that in a reflection experiment should only depend on Fresnel coefficients.

We have experimentally tested the validity of this assertion, on both Suprasil (fused silica), and BK-7 optical glass. Second-harmonic generation was performed, both in reflection and transmission, at a fundamental wavelength of 532 nm, with a 25-ps s-polarized Nd:YAG laser (where YAG is yttrium aluminum garnet) at 10 mJ/pulse and with a measured beam radius of 2.2 mm at the sample. In the case of the BK-7, a 6-mm-thick optical flat was used with fundamental beam incident at 45° to the normal [see Fig. 2(a)]. As BK-7 is opaque at 266 nm, only the first surface region contributes to the second harmonic detected in reflection, and only the second surface region to transmission. A detailed calculation,[5] using the

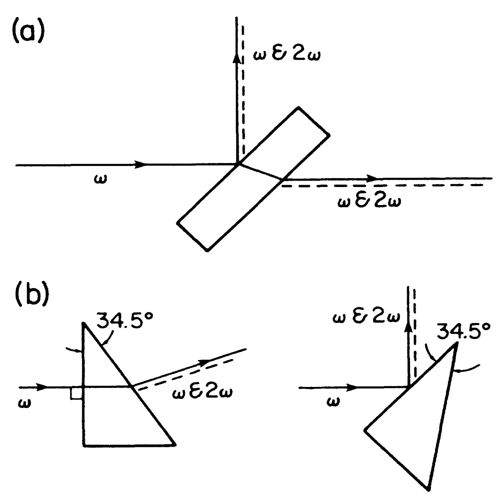

FIG. 2. (a) Experimental geometry employed with the BK-7 flat, which is opaque at 2ω. The solid line indicates the laser beam at ω. The dashed line, shown displaced for clarity, represents the generated second harmonic. (b) Experimental geometry employed with the Suprasil (fused silica) Littrow prism. In transmission the first surface is oriented at normal incidence to the beam, and so does not contribute to SHG. In reflection the first surface is rotated by 45°.

linear Fresnel factors associated with the vacuum-glass interface, predicts a value of 2.952 for the ratio of the second-harmonic intensity in the forward direction to that of the reverse. Note that we do not need to know the value of either $\chi^s_{\perp\parallel\parallel}$ or γ for this calculation. Experimentally we have measured this ratio to be 2.87 ± 0.15, in excellent agreement with this prediction.

In the case of fused silica, which is transparent at both 532 and 266 nm, a different geometry was employed to facilitate a clean separation of the two surface contributions (thus avoiding complications due to interference effects). The sample was a Littrow prism with a 34.5° apex angle. In transmission, the first face, set at normal incidence to the beam, did not contribute to SHG;[5] in reflection, the first face was rotated to 45°, with the second-surface contribution eliminated geometrically [see Fig. 2(b)]. For this experiment we calculated a ratio of forward to reverse second-harmonic intensities of 9.807, and measured 10.07 ±0.42; again excellent agreement. (The value differs from that of BK-7 largely due to the different forward geometry.)

Once the basic premise of this ratio depending only on the linear optical properties of the sample is accepted, it becomes possible to use the calculated ratio as an excellent and rigorous test of the experimental system, and to obtain a measure of systematic errors. This is a feature not normally available to the experimentalist.

We now turn to a proof of this result, dealing first with the simple geometry shown in Fig. 1. Denote by $\mathbf{G}(\mathbf{r};\mathbf{r}')$ the Green's function for a polarization source at $\mathbf{r}'$ and a detection point at $\mathbf{r}$. Then the second-harmonic field attributable to the γ term in Eq. (1) is

$$E_i(\mathbf{r})=\int_{-\infty}^{0^-}dz'\int\int_{-\infty}^{+\infty}dx'dy'G_{ij}(\mathbf{r};\mathbf{r}')\times\gamma\frac{\partial}{\partial r_j'}[\mathbf{e}(\mathbf{r}')\cdot\mathbf{e}(\mathbf{r}')]\ , \quad (4)$$

where subscripts denote Cartesian components, and are summed over if repeated. The Green's function $\mathbf{G}$ incorporates all the linear optical properties of the medium and vacuum at 2ω and the Maxwell saltus (boundary) conditions at the interface. In particular,

$$\frac{\partial G_{ij}(\mathbf{r};\mathbf{r}')}{\partial r_i}=0 \quad (5)$$

(any $\mathbf{r}'$ and $\mathbf{r}\neq\mathbf{r}'$) away from a source since the field generated by that source is divergenceless. The Green's function also satisfies a reciprocity condition,[6]

$$G_{ij}(\mathbf{r};\mathbf{r}')=G_{ji}(\mathbf{r}';\mathbf{r}) \quad (6)$$

(all $\mathbf{r},\mathbf{r}'$). That is, the ith component of the field at $\mathbf{r}$ due to the jth component of polarization at $\mathbf{r}'$ is the same as the jth component of the electric field that *would* be produced at $\mathbf{r}'$ if instead there *were* an ith component of polarization at $\mathbf{r}$.

Partially integrating Eq. (4), we find

$$E_i(\mathbf{r})=\gamma\int\int_{-\infty}^{+\infty}dx'dy'G_{iz}(\mathbf{r};x',y',z'=0^-)\times\mathbf{e}(x',y',z'=0^-)\cdot\mathbf{e}(x',y',z'=0^-) \quad (7)$$

plus a volume integral involving $\partial G_{ij}(\mathbf{r};\mathbf{r}')/\partial r'_j$. But that divergence vanishes using Eqs. (5) and (6), and so the contribution from the volume integral vanishes, leaving only Eq. (7)—regardless of the form of the function $\mathbf{e}(\mathbf{r})$. From this alone it is clear that the contribution to the second-harmonic signal from the γ term of Eq. (1) is behaving like some sort of surface term.

To see its nature in detail, we note that if there were a source at $\mathbf{r}(z>0)$, the z component of the electric field produced at $(x',y',z'=0^+)$, would be $\epsilon(2\omega)$ times that produced at $(x',y',z'=0^-)$, as follows from the Maxwell equations. Using this fact and the reciprocity condition (6), we can then write Eq. (7) as

$$E_i(\mathbf{r})=\gamma\epsilon^{-1}(2\omega)\int\int_{-\infty}^{+\infty}dx'dy'G_{iz}(\mathbf{r};x',y',z'=0^+)\mathbf{e}(x',y',z'=0^-)\cdot\mathbf{e}(x',y',z'=0^-)\ . \tag{8}$$

Now, using Eq. (2), we write down the second-harmonic signal from the surface source,

$$E_i(\mathbf{r})=\int\int_{-\infty}^{+\infty}dx'dy'G_{ij}(\mathbf{r};x',y',z'=0^+)p_j(x',y')\ , \tag{9}$$

and the similarity of the form of the bulk contribution (8) due to γ with that of the surface contribution (9) is apparent. In fact, writing out the form $\mathbf{p}(x',y')$ takes at the surface of an isotropic medium we find

$$\begin{aligned} p_z &= \chi^s_{\perp\perp\perp}e_ze_z+\chi^s_{\perp\parallel\parallel}(e_xe_x+e_ye_y)\\ &=\chi^s_{\perp\parallel\parallel}(\mathbf{e}\cdot\mathbf{e})+(\chi^s_{\perp\perp\perp}-\chi^s_{\perp\parallel\parallel})e_ze_z\ ,\\ p_x &= 2\chi^s_{\parallel\parallel\perp}e_xe_x\ ,\\ p_y &= 2\chi^s_{\parallel\parallel\perp}e_ye_z\ . \end{aligned} \tag{10}$$

where $\mathbf{e}$ of course refers to the fundamental field evaluated at $z=0^-$. Using Eq. (10) in Eq. (9) and comparing with Eq. (8), we see that γ appears only in the linear combination $\gamma\epsilon^{-1}(2\omega)+\chi^s_{\perp\parallel\parallel}\equiv\chi^{\text{eff}}_{\perp\parallel\parallel}$. From Eqs. (1), (9), and (10) we can then identify only four independent material parameters that can be measured in an optical $[\nabla\cdot\mathbf{e}(\mathbf{r})=0]$ experiment, namely, $\chi^{\text{eff}}_{\perp\parallel\parallel}$, $\chi^s_{\perp\perp\perp}-\chi^s_{\perp\parallel\parallel}$, $\chi^s_{\parallel\parallel\perp}$, and δ'. The parameter γ itself simply cannot be determined.

Although we have given the proof here only for a planar interface (Fig. 1), it is clear that it is easily generalized to any shape interface as long as a dipole sheet model can be used to phenomenologically describe the surface sources. For an interface of general shape, of course, the dipole sheet is considered "warped" to follow the shape of the interface. Further, it is clear that the proof can easily be generalized to sum and difference frequency generation: the Green's function $\mathbf{G}(\mathbf{r};\mathbf{r}')$ is then evaluated at the frequency generated, as is the ϵ that appears in going from Eq. (7) to Eq. (8). We emphasize we have assumed nothing about the form of $\mathbf{e}(\mathbf{r})$, the fundamental field. Thus, the proof holds for any number of beams in the medium, of any shape. Indeed, although in using a linear Green's function $\mathbf{G}(\mathbf{r};\mathbf{r}')$ we have implicitly assumed that the medium can be assumed to have linear optical properties at the frequency of the *generated* field, we have assumed nothing about the medium at the fundamental frequency. Even if $\mathbf{e}(\mathbf{r})$ satisfied a nonlinear wave equation in the medium, the proof would still hold. In the case of a medium-medium interface, as opposed to vacuum-medium, an analogous result would apply. Finally, we note that the proof can be generalized to anisotropic media where, in addition to the bulk and surface terms we have included, additional sources of lower symmetry are allowed. So in fact this result holds for all homogeneous media, including crystalline metals and semiconductors.

Because of the generality of our result, expectations that γ could be measured by using mixing experiments with noncolinear beams are seen to have been overly sanguine. Yet, our result does not imply that SHG cannot serve as a purely surface specific probe. For an isotropic system, a single-beam experiment (for which the δ' term gives no contribution) with an input polarization that is a combination of s and p polarization, and where only the s-polarized component of the generated field is measured, will be sensitive to only $\chi^s_{\parallel\parallel\perp}$. Unfortunately this combination of polarizations is not similarly surface specific for anisotropic systems such as crystalline silicon.[2] Therefore, since $\chi^s_{\perp\parallel\parallel}$ can never be measured directly and compared with theory, a direct consequence of our result is that the use of SHG as a probe of strictly surface phenomena is rendered more difficult. Indeed, it is interesting to note that if the surface were changed by material processing (changing χ^s) the ratio of forward to reverse SHG in the experiment described earlier (s-polarized fundamental) would not be affected. But if the processing affected the bulk material down to say a depth of order the coherence length for a reflection experiment, but rather less than that for a transmission experiment, that ratio *could* appreciably change [in going from Eq. (4) to Eq. (7) we assumed a uniform γ in the medium]. Whether this change would be more sensitive to bulk modification than would be changes in the linear optical properties is unclear; however if it were, then second-harmonic generation, which is usually promoted as a surface probe, would be insensitive to the surface and in fact probe the bulk.

Finally, we mention that since $\chi^s_{\perp\parallel\parallel}$ and γ describe different physical effects we would expect that, at least in principle, *some* experiment could measure them separately. And indeed this is true: if the detection point $\mathbf{r}$ were *inside* the medium, $\partial G_{ij}(\mathbf{r};\mathbf{r}')/\partial r'_j$ would contain a singular part at $\mathbf{r}'=\mathbf{r}$, giving a "local" contribution proportional to $\gamma\mathbf{e}(\mathbf{r})\cdot\mathbf{e}(\mathbf{r})$, in addition to the surface term. Measurement of the second-harmonic field at different points in the medium, then, could in principle lead to a determination of both $\chi^s_{\perp\parallel\parallel}$ and γ.

In summary, we have proved that for a wide class of experiments, γ *always* appears in the same linear combination with one component of $\boldsymbol{\chi}^s$, and hence the two terms cannot be measured separately. This key result, which had previously been derived by Wang[3] (see also Guyot-Sionnest, Chen, and Shen[3]) with a very restrictive set of assumptions, in fact holds for an arbitrary number of beams in an arbitrarily shaped medium, and is easily generalized to sum and difference frequency generation. The result restricts to some extent the use of second-harmonic generation as a probe of purely surface phenomena. Further, it leads to somewhat surprising and testable consequences. We have performed experiments to verify the validity of these assertions and obtain agreement to within the experimental uncertainty of 5%.

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[5]The detailed formalism employed in making such calculations is presented in V. Mizrahi and J. E. Sipe (unpublished).

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