PHYSICAL REVIEW A VOLUME 42, NUMBER 10 15 NOVEMBER 1990

Comments

Comments are short papers which comment on papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Forbidden nature of multipolar contributions to second-harmonic generation in isotropic fluids"

T. F. Heinz and D. P. DiVincenzo
IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 4 April 1989)

Andrews and Blake [Phys. Rev. A **38**, 3113 (1988)] have presented an analysis suggesting that no coherent optical second-harmonic radiation is produced to any order in a multipole expansion by a fluid of noninteracting, randomly oriented molecules under excitation by a plane-wave electric field. We demonstrate to all orders of nonlocality that the correct description of any isotropic centrosymmetric medium in the field of a plane wave includes a *longitudinal* (generalized) nonlinear source polarization, which was not treated by Andrews and Blake. This bulk polarization does not give rise to a second-harmonic wave with a growing intensity in the medium; however, as has been recognized in the literature, it *cannot* be neglected in measurements of second-harmonic generation from surfaces and interfaces, since a longitudinal polarization is capable of exciting transverse electromagnetic waves at a discontinuity.

The application of second-order nonlinear processes to investigate surfaces and interfaces has attracted considerable attention in the past few years.[1-3] For centrosymmetric media, the second-order nonlinear effects of second-harmonic generation (SHG) and sum-frequency generation are forbidden in the electric-dipole approximation. A dipole-allowed contribution to the nonlinear radiation may, however, still appear at surfaces or interfaces where the inversion symmetry is no longer present. In addition to this source of nonlinear polarization, weak contributions to the second-order response are expected in the bulk of centrosymmetric media from electric-quadrupole, magnetic-dipole, and other higher-order terms. Since the bulk nonlinear polarization can arise in a much larger volume than the surface (electric-dipole-allowed) polarization, these weaker terms may still lead to a measurable contribution to the nonlinear radiation. For this reason, it is crucial to understand fully the nature of the bulk nonlinear response. Indeed, the effect of a polarization in the bulk on SHG from centrosymmetric media was already analyzed in the early literature on surface SHG.[4] In more current treatments, this issue has been examined further for isotropic,[5,6] as well as crystalline media.[7]

From the point of view of the analysis of surface and interface properties, the bulk nonlinear optical response constitutes a potential complication. In fact, in the usual measurement of SHG in reflection from the surface of an isotropic centrosymmetric material, it has been established that a bulk nonlinear polarization is present that is indistinguishable in terms of angular and polarization dependences from a surface term.[5,6] This result has been further generalized for other excitation geometries by Sipe *et al.*[8] The influence of this bulk polarization may complicate the interpretation of SHG measurements in some cases, particularly if it is not possible to modify experimentally the surface or interface conditions. Thus considerable importance is attached to the recent claim by Andrews and Blake[9] that coherent SHG is forbidden to any multipole order from the bulk of a fluid of noninteracting, randomly oriented molecules excited by a single plane wave. In this Comment, we present a general framework for treating the influence of bulk terms of all multipole orders. We prove that the bulk nonlinear source polarization induced by a single plane wave traveling through an isotropic centrosymmetric medium must lie in the direction of propagation of the pump beam, just as is the case when only the lowest-order nonlocal responses (electric-quadrupole and magnetic-dipole terms) are considered. Our analysis, based on symmetry considerations, demonstrates that a longitudinal (generalized) nonlinear source polarization is expected in any isotropic centrosymmetric medium, including the special case of a fluid of noninteracting molecules considered by Andrews and Blake. Within an infinite homogeneous medium, a longitudinal polarization will not give rise to transverse electromagnetic waves. In the presence of the discontinuity associated with a surface or interface, however, a longitudinal polarization can couple to radiative fields. Consequently, the bulk polarization cannot be neglected in measurements of surface or interface SHG. This finding, applicable to all orders of a multipole expansion in the bulk, confirms the known results for the leading-order nonlocal response; it contradicts the conclusion of Andrews and Blake that no coherent bulk contribution to surface SHG can arise from a fluid of noninteracting molecules.

To justify the statements made above, let us consider the nature of the (generalized) nonlinear source polarization induced in an isotropic centrosymmetric medium by a plane-wave electromagnetic field. In any homogeneous medium, the second-order nonlinear optical response can be expressed in terms of a nonlocal nonlinear susceptibility tensor $\chi^{(2)}$ defined by

$$\mathbf{P}^{(2)}(\mathbf{r})=\int d\mathbf{r}'d\mathbf{r}''\chi^{(2)}(\mathbf{r}-\mathbf{r}',\mathbf{r}-\mathbf{r}''):\mathbf{E}(\mathbf{r}')\mathbf{E}(\mathbf{r}'') , \qquad (1)$$

where $\mathbf{P}^{(2)}(\mathbf{r})$ represents the (generalized) nonlinear source polarization at the SH frequency induced at spatial position $\mathbf{r}$ by the pump electric field $\mathbf{E}$ acting at all pairs of locations $\mathbf{r}'$ and $\mathbf{r}''$. If the electric field is a plane wave with wave vector $\mathbf{k}$, we obtain

$$\mathbf{P}^{(2)}(\mathbf{r})=\left[\int d\mathbf{r}'d\mathbf{r}''e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}'')}\times\chi^{(2)}(\mathbf{r}-\mathbf{r}',\mathbf{r}-\mathbf{r}'')\right]:\mathbf{E}\mathbf{E}e^{2i\mathbf{k}\cdot\mathbf{r}}$$
$$\equiv\chi^{(2)}(\mathbf{k},\mathbf{k}):\mathbf{E}\mathbf{E}e^{2i\mathbf{k}\cdot\mathbf{r}} . \qquad (2)$$

The usual expression for a plane wave propagating in a homogeneous isotropic medium has been introduced in the first relation; the second equality constitutes a definition of the (double) Fourier transform of the nonlocal nonlinear susceptibility tensor. It should be noted that we treat here only the *coherent* contribution to SH radiation. Incoherent terms arising from fluctuations of the nonlinear polarization in the medium can be distinguished experimentally by their spatial (and spectral) characteristics[10] and are not considered here.

Up to this point, we have only assumed that we are dealing with a homogeneous medium excited by a plane wave. Let us now examine the effect of requiring the medium to be centrosymmetric and isotropic. To make the symmetry arguments more transparent, we write Eq. (2) for $\mathbf{r}=0$ with argument $\mathbf{k}$ in $\chi^{(2)}$ appearing only once:

$$\mathbf{P}^{(2)}=\chi^{(2)}(\mathbf{k}):\mathbf{E}\mathbf{E} . \qquad (3)$$

For a centrosymmetric medium, we then see immediately that $\chi^{(2)}(\mathbf{k})=-\chi^{(2)}(-\mathbf{k})$. This symmetry relation is obtained by considering an inversion operation, which reverses the signs of the vectors $\mathbf{P}^{(2)}$, $\mathbf{E}$, and $\mathbf{k}$ appearing in Eq. (3) without changing the nonlinear susceptibility tensor $\chi^{(2)}$ describing the material. In terms of a multipole expansion, the fact that $\chi^{(2)}(\mathbf{k})$ is an odd function of $\mathbf{k}$ means that the electric-dipole contributions (independent of $\mathbf{k}$) are absent, as are alternate higher-order terms. For an isotropic centrosymmetric medium, arbitrary reflections and rotations are also symmetry operations. We can identify the independent, nonvanishing elements of $\chi^{(2)}(\mathbf{k})$ by examining reflections through planes containing $\mathbf{k}$ and rotations about an axis parallel to $\mathbf{k}$, symmetry operations leaving $\mathbf{k}$ unchanged. In order to enumerate the tensor elements, we introduce a Cartesian coordinate system with X and Y axes running perpendicular to $\mathbf{k}$ and a Z axis parallel to $\mathbf{k}$. The independent tensor elements in this notation are $\chi^{(2)}_{ZZZ}$, $\chi^{(2)}_{ZXX}=\chi^{(2)}_{ZYY}$, $\chi^{(2)}_{XZX}=\chi^{(2)}_{XXZ}=\chi^{(2)}_{YZY}=\chi^{(2)}_{YYZ}$. It may be noted that these elements correspond precisely to those of a nonlinear susceptibility for an isotropic surface lying in the X-Y plane:[1-3] for both the surface and higher-order bulk response, the inversion symmetry is broken along the Z axis.

In the bulk of an isotropic medium, the electric field of the plane-wave pump beam is transverse, or, in our notation, $\mathbf{E}\cdot\hat{\mathbf{Z}}=0$. Thus only $\chi^{(2)}_{ZXX}=\chi^{(2)}_{ZYY}$ contributes to the nonlinear polarization, and

$$\mathbf{P}^{(2)}=P^{(2)}_Z\hat{\mathbf{Z}}=\chi^{(2)}_{ZXX}(E_X^2+E_Y^2)\hat{\mathbf{Z}}=\chi^{(2)}_{ZXX}(\mathbf{E}\cdot\mathbf{E})\hat{\mathbf{Z}} . \qquad (4)$$

This represents a longitudinal polarization, i.e., a polarization directed along $\mathbf{k}\|\hat{\mathbf{Z}}$. To make contact with the usual treatment of the bulk nonlinearity, let us recall that $\chi^{(2)}(\mathbf{k})$ is an odd function of $\mathbf{k}$. We can write, therefore, $\chi^{(2)}_{ZXX}(\mathbf{k}=k\hat{\mathbf{Z}})=2ik\gamma(k)$, with the new parameter $\gamma(k)$ being an even function of k. The nonlinear polarization induced by a plane wave $\mathbf{E}(\mathbf{r})$ can be expressed as

$$\mathbf{P}^{(2)}(\mathbf{r})=\gamma(k)\nabla[\mathbf{E}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})] . \qquad (5)$$

The nonlinear polarization of Eq. (5) has precisely the same form as has been derived previously for the nonlinear response of a homogeneous isotropic medium with inversion symmetry considering just the leading-order nonlocal terms.[4-6] The complete analysis presented here merely modifies the numerical value of the material parameter γ. From the practical point of view, the correction is expected to be small, since the successive terms of the multipole expansion at optical wavelengths converge rapidly in a homogeneous medium. Considering only the leading-order terms, formulas for $\gamma=\gamma(0)$ have been derived under various approximations. For example, in a dielectric medium at frequencies well below any electronic transitions, Bloembergen *et al.*[4] have obtained a simple estimate of the electronic contribution: $\gamma\approx\frac{3}{8}(Ne)^{-1}(\chi^{(1)})^2$, where Ne is the electronic charge density and $\chi^{(1)}$ denotes the linear susceptibility of the medium. This relation could be applied to describe the low-frequency response of an isotropic fluid of randomly oriented molecules treated by Andrews and Blake. It should be noted that the case of a gas of free electrons will give rise to a second-order nonlinear response of the form of Eq. (5). To leading order in k, we have $\gamma=Ne^3/8m^2\omega^4$, with N representing the density of electrons, m the electronic mass, and ω the frequency of the fundamental field.[4]

We now turn to the question of how the longitudinal nonlinear source polarization manifests itself in measurements of surface SHG. As mentioned earlier, a longitudinal polarization in an infinite medium does not lead to radiative electromagnetic fields, but only to a longitudinally polarized electric field. The situation is, however, quite different when one considers a longitudinal polarization in a half space, as one must in order to model the process of surface SHG. In this case, it is intuitively clear that the bulk nonlinear polarization may contribute to a transverse SH wave in the reflected direction, since the bulk polarization will generally have a finite projection perpendicular to the direction of propagation of the reflected SH wave. These elementary considerations indicate that a longitudinal polarization in the bulk will produce a p-polarized component of the reflected SH radiation except when the bulk polarization is parallel to the wave vector of the reflection, i.e., for all geometries other than that of normal-incidence excitation.

To describe the influence of the longitudinal nonlinear source polarization more precisely, we can make use of the result that a longitudinal polarization in a half space gives rise to a radiation pattern equivalent to that of a sheet of polarization at the surface.[5,6,8] In terms of a contribution to the surface nonlinear susceptibility tensor $\chi_s^{(2)}$, we find that the bulk polarization under plane-wave excitation can be represented by

$$(\chi_{s,\mathrm{eff}}^{(2)})_{\perp\perp\perp}=(\chi_s^{(2)})_{\perp\perp\perp}+\gamma(k)\ , \tag{6a}$$

$$(\chi_{s,\mathrm{eff}}^{(2)})_{\perp\|\|}=(\chi_s^{(2)})_{\perp\|\|}+\gamma(k)\ . \tag{6b}$$

Here $\perp$ and $\|$ refer to the (outward) surface normal and to a coordinate in the plane of the surface, respectively; and the surface nonlinear susceptibility tensor $\boldsymbol{\chi}_s^{(2)}$ is assumed to be embedded in the bulk medium. Equation (6) is identical to that derived previously for the bulk response of an isotropic centrosymmetric medium considering only the leading-order nonlocal response,[5,6,8] but with the coefficient γ replaced by $\gamma(k)$ to account for the higher-order nonlocal response. From the form of Eq. (6), it is apparent that under excitation by a single plane wave the bulk response (treated to all orders of the multipole expansion) appears whenever p-polarized SH radiation is produced by the surface.[11] Moreover, just as for the leading-order nonlocal bulk response, the full bulk response remains indistinguishable from the appropriate surface response specified by Eq. (6). The relative importance of the surface and bulk contributions has been discussed for the leading-order nonlocal approximation of the bulk response by Guyot-Sionnest *et al.*[5] and others. A simple argument can be presented demonstrating that the bulk contribution may be of the same order of magnitude as the surface contribution and, hence, must be considered in any careful investigation of the nonlinear optical response of a surface or interface. The same conclusion applies when higher-order nonlocal term contributions to the bulk nonlinear response are included.

In summary, we have demonstrated that in an isotropic centrosymmetric medium a longitudinal nonlinear source polarization is induced by excitation from a plane wave, even when the second-order nonlinear optical response is treated to all orders of a multipole expansion. In the analysis of a fluid of noninteracting molecules given by Andrews and Blake,[9] this longitudinal polarization was not considered, leading to the incorrect conclusion that the bulk nonlinear response could not affect the results of a measurement of surface SHG.

[1]Y. R. Shen, Annu. Rev. Mater. Sci. **16**, 69 (1986); in *New Laser and Optical Investigation of Chemistry and Structure of Interfaces,* edited by R. B. Hall and A. B. Ellis (Verlag Chemie, Weinheim, 1986), p. 151.
[2]G. I. Richmond, J. M. Robinson, and V. L. Shannon, Prog. Surf. Sci. **28**, 1 (1988).
[3]T. F. Heinz and M. M. T. Loy, in *Advances in Laser Science III,* edited by A. C. Tam, J. L. Gole, and W. C. Stwalley (AIP, New York, 1988), p. 452.
[4]N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, Phys. Rev. **174**, 813 (1968), and references therein.
[5]P. Guyot-Sionnest, W. Chen, and Y. R. Shen, Phys. Rev. B **33**, 8254 (1986).
[6]V. Mizrahi and J. E. Sipe, J. Opt. Soc. Am. B **5**, 660 (1988).
[7]J. E. Sipe, D. J. Moss, and H. M. van Driel, Phys. Rev. B **35**, 1129 (1987), and references therein.
[8]J. E. Sipe, V. Mizrahi, and G. I. Stegeman, Phys. Rev. B **35**, 9091 (1987).
[9]D. L. Andrews and N. P. Blake, Phys. Rev. A **38**, 3113 (1988).
[10]P. D. Maker, Phys. Rev. A **1**, 923 (1970).
[11]The s-polarized SH radiation from the surface will not include any contribution from the longitudinal bulk polarization, as has been recognized in analyses of the leading-order nonlocal bulk response.