Multipolar contributions to optical second-harmonic generation in isotropic fluids

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The general conclusions of the recent article by Andrews and Blake [Phys. Rev. A **38**, 3113 (1988)] on the forbidden nature of higher-order multipolar contributions to optical second-harmonic generation are misleading and not generally valid.

In a recent paper on second-harmonic generation (SHG) in isotropic fluids,[1] Andrews and Blake concluded that "(coherent) SHG is forbidden in isotropic fluids to all levels of multipolar approximation." They then asserted that "SHG in isotropic fluids is purely a surface phenomenon." These general conclusions are misleading as they contradict the fact that the bulk contribution to the so-called surface SHG in both transmission and reflection directions from an interface (even between two isotropic fluids) is often not negligible.[2-6] In view of the growing interest in applying SHG to studies of surfaces and interfaces, it is important and necessary to have the confusion clarified.

First, the conclusion of Andrews and Blake that SHG is strictly forbidden in an isotropic fluid actually resulted from their assumption of a single pump beam in the form of an infinite plane wave (specified by the wave vector $\mathbf{k}$), propagating in an infinite isotropic bulk medium. In practice, the pump beam is of finite size and the process is not strictly forbidden. It is known that a single pump beam with a single transverse mode or multimodes having the same polarization still yields some SHG in an isotropic medium,[7-9] but a single beam with multimodes having different polarizations or two noncollinear pump beams with different polarizations can produce significant SHG via electric quadrupole contribution.[9]

Next, we discuss the bulk contribution to the so-called surface SHG, for example, SHG in reflection direction from the surface of an isotropic fluid.[2-6] As shown in the classical paper by Bloembergen and Pershan,[10] the bulk nonlinear polarization $\mathbf{P}(2\omega)$ in a layer of the order of a coherent length next to the boundary surface should contribute to the surface SHG.[2-6] In this case, even if a single-mode pump beam in the form of infinite plane wave is used such that the induced $\mathbf{P}(2\omega)$ is parallel to the wave vector $2\mathbf{k}(\omega)$ and hence cannot yield coherent SHG in an infinite bulk, the same $\mathbf{P}(2\omega)$ can contribute to the surface SHG simply because $\mathbf{k}(2\omega)$ in the reflection direction is not parallel to $\mathbf{P}(2\omega)$.[10] An additional bulk contribution to the surface SHG output can result from a change in the density of the electric quadrupole moment across the interface separating two isotropic media.[11] It is solely determined by the bulk properties of the two media, and therefore can be regarded as a bulk contribution. This contribution can yield *s*-polarized as well as *p*-polarized SHG in the reflection direction. The second conclusion of Andrews and Blake is only true for incident and reflected beams along the surface normal.

In summary, we reassert here that higher-order multipole, especially electric-quadrupole contributions to SHG in an isotropic bulk medium are generally nonvanishing, and they are usually present in surface SHG from such a medium.

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