Reply to "Multipolar contributions to optical second-harmonic generation in isotropic fluids"

David L. Andrews and Nick P. Blake
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, United Kingdom
(Received 22 June 1989)

The preceding Comment [Phys. Rev. A **41**, 4549 (1990)] by Zhu and Shen is incorrect on a number of issues.

Our recent paper[1] was specifically concerned with a rebuttal of current conjecture[2–5] that multipolar effects can result in second-harmonic generation (SHG) in isotropic fluids, where pure electric dipole coupling results in coherent emission being forbidden. Our molecular theory based on quantum electrodynamics[6] (QED) is not at variance with experimental fact. It does, however, throw doubt on the validity of certain theoretical models referred to in the above Comment.[7]

In failing to accommodate the molecular mechanism for harmonic emission in fluids the adoption of a macroscopic polarization formalism can lead to confusion between *coherent* SHG and *incoherent* second-harmonic scattering; however, the difference is of central importance in discussing bulk contributions to surface harmonic emission. Zhu and Shen assert that such contributions to surface SHG are often non-negligible.[7] However, the assertion is only correct in relation to second-harmonic emission in directions noncollinear with the pump. Except at the surface, such emission cannot, however, be phase matched[8,9] and is necessarily *incoherent* in any isotropic fluid.[10–14] It is therefore insignificant compared to the coherent surface harmonic. The correct theoretical treatment of fluids demands a distributional average of the result for the *observable*,[10,15–17] which here is the harmonic signal rather than the polarization. In this framework both the disappearance of the coherent signal and the persistence of the incoherent signal in nonforward directions are immediately evident.

It is not the case that our theory depends on the assumption of an infinite plane-wave pump. While for the sake of simplicity only the case of a single-mode uniphase beam has been discussed in our work, precisely the same conclusions result for any finite width beam where the photons have parallel wave vectors. The extension of our quantum electrodynamical calculations to multimode light, such as the physically important case of mode-locked laser radiation, only requires the application of QED methods described in detail by one of us elsewhere.[18] The extension in no way affects the validity of our conclusions concerning SHG in fluids.

It is also incorrect to state that our theory was based on the assumption of an infinite bulk medium. If it had been, this controversy could hardly have arisen, since such a theory could have nothing to say about *surface* harmonic generation. Our assumptions concerning the nature of the bulk phase are simply that there is no orientational correlation between molecules irradiated by the pump beam, as befits a material described as *isotropic.* Part of the confusion appears to stem from a misapplication of the term *isotropic* to regions close to the surface of a fluid medium. Regions of orientational correlation or electrical anisotropy associated with the proximity of the fluid surface clearly can give rise to a *local* surface harmonic signal.

Neither the possibility of the pump containing a mixture of polarizations, nor consideration of a finite physical width for the pump beam make any difference to our conclusions on the forbidden nature of multipolar contributions in SHG. When transverse modes are present, as is the case when there is focusing or significant beam divergence, weak coherent harmonic emission can occur; however, under such conditions the *incoherent* harmonic scattering contribution exceeds the coherent signal by several orders of magnitude. Thus for all practical purposes coherent SHG may be regarded as forbidden.

In conclusion Zhu and Shen have offered no proof for their contention that higher-order multipole contributions to SHG in an isotropic fluid are generally nonvanishing. We therefore reassert that SHG can be utilized as a probe of the surfaces and interfaces of isotropic fluids.

[1] D. L. Andrews and N. P. Blake, Phys. Rev. A **38**, 3113 (1988).
[2] T. F. Heinz, C. K. Chen, D. Ricard, and Y. R. Shen, Phys. Rev. Lett. **46**, 1010 (1981).
[3] T. F. Heinz, H. W. K. Tom, and Y. R. Shen, Phys. Rev. A **28**, 1883 (1983).
[4] G. Morowsky, A. Giersulski, and B. Dick, Opt. Commun. **52**, 339 (1985).
[5] J. E. Sipe, V. Mizrahi, and G. I. Stegeman, Phys. Rev. B **35**, 9091 (1987).
[6] D. L. Andrews, J. Phys. B **13**, 4091 (1980).
[7] X. D. Zhu and Y. R. Shen, preceding Comment, Phys. Rev. A **41**, 4549 (1990).
[8] D. Marcuse, *Principles of Quantum Electronics* (Academic, New York, 1980). The arguments concerning Rayleigh scattering as given on pp. 361–363 equally apply to SHG.
[9] D. P. Craig and T. Thirunamachandran, *Molecular Quantum*

Electrodynamics (Academic, New York, 1984), p. 131.
[10]S. Kielich, Acta Phys. Pol. **23**, 141 (1968).
[11]S. Kielich, M. Kozierowski, Z. Ozgo, and R. Zawodny, Acta Phys. Pol. A **45**, 9 (1974).
[12]S. Kielich and M. Kozierowski, Acta Phys. Pol. A **45**, 231 (1974).
[13]S. Kielich, in *Progress in Optics,* edited by E. Wolf (North-Holland, New York, 1983), Vol. 20, p. 157.
[14]D. L. Andrews and N. P. Blake (unpublished).
[15]D. L. Andrews and T. Thirunamachandran, J. Chem. Phys. **67** 5026 (1977).
[16]D. L. Andrews and M. J. Harlow, Phys. Rev. A **29**, 2796 (1984).
[17]D. L. Andrews and N. P. Blake, J. Phys. A **22**, 49 (1989).
[18]D. L. Andrews, J. Phys. A **11**, 2655 (1978).