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David L. Andrews ^a

^a School of Chemical Sciences , University of East Anglia , Norwich, NR4 7TJ, UK

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The role of longitudinal polarization in surface second harmonic generation

DAVID L. ANDREWS

School of Chemical Sciences, University of East Anglia,
Norwich NR4 7TJ, UK

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Abstract. Use of the classical polarization concept is deeply entrenched in standard nonlinear optics. Nonetheless it establishes a framework for the formulation of theory which is not directly amenable to the resolution of certain kinds of question. In particular, it can obscure the difference between coherent and incoherent optical response. This has been forcefully illustrated by recent controversy over the issue of second harmonic generation involving surfaces or interfaces of isotropic fluids. It is the purpose of this paper, by formulating a theory cast directly in terms of the observable, the harmonic intensity, to resolve the issue. Through a unified treatment of both coherent and incoherent contributions to the second harmonic, it is unequivocally demonstrated that any signal classically associated with longitudinal polarization is necessarily incoherent.

1. Introduction

In considering the weak harmonic processes that can occur in fluids, the isotropy of the medium is commonly taken into account by considering the consequences of the macroscopic symmetry for the bulk nonlinear susceptibility. Important as this is, such considerations do not adequately account for the effects of local fluid structure and molecular tumbling. Although models based on a charge continuum, as in the free electron gas, are appropriate for describing media with macroscopically delocalized electronic structure, they are entirely inappropriate for dealing with most physical fluids. The inapplicability of such models is compounded where molecular fluids are concerned. Not only does the application to fluids sacrifice proper modelling of the electronic integrity of their constituent molecules, but it also rules out any consideration of local symmetry constraints and molecular tumbling. In molecular fluids it is the individual molecular centres that are responsible for harmonic emission, and it is crucial to take account of the powerful symmetry constraints which are associated with random molecular orientation.

The heart of the issue concerns the theoretical formulation of optical nonlinearity in terms of classical polarization, a concept that is deeply entrenched in standard nonlinear optics. Nonetheless it establishes a framework that is not directly amenable to the resolution of certain kinds of question. In particular, it can obscure the difference between coherent and incoherent optical response, leading in some cases to entirely incorrect conclusions. This has been forcefully illustrated by recent controversy over the issue of second harmonic generation involving surfaces or interfaces of isotropic fluids. It is the purpose of this paper, by formulating a theory cast directly in terms of the observable, the harmonic intensity, to resolve the issue. Through a unified treatment of both coherent and incoherent contributions to the

second harmonic, it is unequivocally demonstrated that any signal emitted in a non-forward direction, and therefore classically associated with longitudinal polarization, is necessarily incoherent.

Before proceeding with the theory, it may be observed that the use in this connection of the term 'longitudinal' is itself potentially misleading and open to criticism, though it is adopted here in conformity to current usage. It should therefore be emphasized at the outset that in the Coulomb gauge employed here, all radiative fields are transverse, and this of course applies to both pump and harmonic photons. The descriptor 'longitudinal' can only be appropriated when the *harmonic* field is, perhaps somewhat perversely, referred to the direction of propagation of the *pump* beam. It is the essentially classical inference of a nonlinear polarization giving rise to the harmonic field which leads to the apparent misnomer.

2. Coherent and incoherent second harmonic generation

In second harmonic generation, two photons of laser light with frequency ω (wave-vector \mathbf{k} and polarization vector $\mathbf{e}^{(\lambda)}$) are converted into a single photon of frequency 2ω (wave-vector \mathbf{k}' and polarization vector $\mathbf{e}^{(\lambda')}$). From the Fermi Golden Rule, the rate of harmonic conversion may be written as follows:

$$\Gamma = (2\pi\rho_f/\hbar) \left| \sum_{\xi} \epsilon_0^{-3} \chi_{(\xi)} \odot^3 \sigma \exp(i\Delta\mathbf{k} \cdot \mathbf{R}_{\xi}) \right|^2, \quad (1)$$

where the sum is taken over all N molecules ξ in the interaction volume. Here $\Delta\mathbf{k} = 2\mathbf{k} - \mathbf{k}'$ is the wave-vector mismatch, \mathbf{R}_{ξ} is the position vector of molecule ξ and the nonlinear susceptibility tensor $\chi = \chi(-2\omega, \omega, \omega)$. The radiation tensor σ defined through

$$\begin{aligned} \sigma \exp(i\Delta\mathbf{k} \cdot \mathbf{R}_{\xi}) &= \langle (n'+1)(\mathbf{k}', \lambda') | d^{\perp} | n'(\mathbf{k}', \lambda') \rangle_{\xi} \\ &\times \langle (n-2)(\mathbf{k}, \lambda) | d^{\perp} | (n-1)(\mathbf{k}, \lambda) \rangle_{\xi} \langle (n-1)(\mathbf{k}, \lambda) | d^{\perp} | n(\mathbf{k}, \lambda) \rangle_{\xi} \end{aligned} \quad (2)$$

is evaluated from the expansion for the electric displacement operator d^{\perp} [1];

$$\sigma = \frac{1}{2} i (\hbar\omega\epsilon_0/V)^{3/2} [(n'+1)(n-1)n]^{1/2} \bar{\mathbf{e}}' \mathbf{e} \mathbf{e}. \quad (3)$$

To take account of the random orientations of molecules in a fluid, (1) is first rewritten as a sum of diagonal and off-diagonal terms:

$$\Gamma = (2\pi\rho_f/\hbar\epsilon_0^6) \left\{ \sum_{\xi} |\chi_{(\xi)} \odot^3 \sigma|^2 + \sum_{\xi} \sum_{\xi'}^{N-1} [\chi_{(\xi)} \odot^3 \sigma][\bar{\chi}_{(\xi')} \odot^3 \bar{\sigma}] \exp(i\Delta\mathbf{k} \cdot \mathbf{R}_{\xi\xi'}) \right\}, \quad (4)$$

with $\mathbf{R}_{\xi\xi'} = \mathbf{R}_{\xi} - \mathbf{R}_{\xi'}$.

The first term in equation (4) represents the incoherent contribution. Although at any time the response from each molecule depends on its orientation with respect to the incident light, the averaged response from all N molecules must be identical, and the incoherent signal may therefore be expressed as

$$\Gamma_{\text{inc}} = N(2\pi\rho_f/\hbar\epsilon_0^6) \langle |\chi \odot^3 \sigma|^2 \rangle. \quad (5)$$

The second term in (4) represents the coherent contribution. With no time-averaged orientational correlation between different molecules, independent rotational averaging can be performed for molecules ξ and ξ' , giving

$$\Gamma_{\text{coh}} = (2\pi\rho_f/\hbar\epsilon_0^6) \langle |\chi \odot^3 \sigma|^2 \rangle \sum_{\xi} \sum_{\xi' \neq \xi}^{N-1} \exp(i\Delta\mathbf{k} \cdot \mathbf{R}_{\xi\xi'}). \quad (6)$$

(The case of correlated molecules requires a different treatment which has been described in detail [2] by Kielich.) Equation (6) may be concisely expressed as

$$\Gamma_{\text{coh}} = (2\pi\rho_f/\hbar\varepsilon_0^2) |\langle \chi \odot^3 \sigma \rangle|^2 (\eta_N - N), \quad (7)$$

where the parameter η_N defined by

$$\eta_N = \left| \sum_{\xi}^N \exp(i\Delta\mathbf{k} \cdot \mathbf{R}_{\xi}) \right|^2, \quad (8)$$

embodies the dependence on wave-vector mismatch which characterizes the coherent signal and ultimately leads to the familiar sinc^2 factor [3].

The above results for the rates of coherent and incoherent second harmonic emission evoke the following expressions for the second harmonic intensity:

$$I_{\text{inc}} = D \langle |\chi(-2\omega, \omega, \omega) \odot^3 \bar{\mathbf{e}}' \cdot \mathbf{e} \mathbf{e}|^2 \rangle, \quad (9)$$

$$I_{\text{coh}} = D(\eta_N - N) / N \langle |\chi(-2\omega, \omega, \omega) \odot^3 \bar{\mathbf{e}}' \cdot \mathbf{e} \mathbf{e}|^2 \rangle, \quad (10)$$

where the pump beam parameter D is defined by

$$D = N(c''\mathbf{k}'^4/8\pi^2\varepsilon_0)(I_{\omega}/2c'\varepsilon_0)^2 g_{\omega}^{(2)}, \quad (11)$$

with I_{ω} the irradiance and $g_{\omega}^{(2)}$ the degree of second-order coherence of the pump. Quite apart from the obvious difference in their dependence on wave-vector matching, it is crucial to notice that in contrast to the incoherent signal (9), the rotational average associated with the coherent signal (10) is taken over the matrix element before it is squared.

3. Consideration of random molecular orientation

Calculation of the tensor orientational averages in (9) and (10) requires a more detailed analysis of the tensor inner product $\chi \odot^m \sigma$. It is generally convenient to refer the molecular tensor to a molecule-fixed frame, denoted below by indices λ_r , in terms of which its own components are rotation-invariant. With radiation tensor components referred to a laboratory-fixed frame denoted by indices i_r , we thus have

$$\chi \odot^3 \sigma = \chi_{\lambda_1 \lambda_2 \lambda_3} \sigma_{i_1 i_2 i_3} l_{i_1 \lambda_1} l_{i_2 \lambda_2} l_{i_3 \lambda_3}, \quad (12)$$

where only the direction cosines $l_{i_r \lambda_r}$ vary with molecular rotation. The orientational averages in (9) and (10) now follow by averaging over the direction cosine products:

$$\begin{aligned} \langle |\chi \odot^3 \sigma|^2 \rangle &= \chi_{\lambda_1 \lambda_2 \lambda_3} \bar{\chi}_{\lambda_4 \lambda_5 \lambda_6} \sigma_{i_1 i_2 i_3} \bar{\sigma}_{i_4 i_5 i_6} \\ &\quad \times \langle l_{i_1 \lambda_1} \dots l_{i_6 \lambda_6} \rangle, \end{aligned} \quad (13)$$

$$|\langle \chi \odot^3 \sigma \rangle|^2 = |\chi_{\lambda_1 \lambda_2 \lambda_3} \sigma_{i_1 i_2 i_3} \langle l_{i_1 \lambda_1} l_{i_2 \lambda_2} l_{i_3 \lambda_3} \rangle|^2. \quad (14)$$

The former, incoherent case thus involves a sixth-rank average, but third-rank for the latter, coherent case.

One of the most crucial features of harmonic generation is its sensitivity by symmetry criteria, both on the local molecular and also the macroscopic level. Parity prohibits the electric dipole generation of even harmonics in any centrosymmetric crystal, and the same principle can be applied to individual atoms or centrosymmetric molecules. However such processes remain unobservable even in gases and liquids composed of non-centrosymmetric molecules. By extension of the classical electrodynamic principles normally reserved for solids, it is commonly

concluded that the coherent generation of even harmonics is forbidden in fluids because these too possess macroscopic inversion symmetry. The argument nonetheless obscures the fact that the coherent process is in any case forbidden by the random rotational motions of the molecules.

Where local symmetry permits harmonic generation based exclusively on electric dipole coupling, the inclusion of higher-order multipolar contributions in the coupling produces additional terms which are normally negligible. However, if electric dipole harmonic generation is forbidden, as is the case for even harmonics in a centrosymmetric species, these higher-order terms can become significant and may be manifest in weak harmonic emission, though not in fluids for other reasons outlined below. In general, if the multipolar expansions of the interactions involving the harmonic and pump waves are taken to order s and t respectively, then with $p=t-n$ and $q=s-1$, we obtain the following generalization of equation (12); [4, 2, 5]

$$I_{\text{coh}} = D(\eta_N - N)/N \times \left| \left\langle \sum_p \sum_q \mathbf{k}^p \mathbf{k}'^q \Lambda^{p,q}(-2\omega, \omega, \omega) \odot^{p+q+3} \prod_i \mathbf{w}^{(i)} \sum_j^{p+q} \mathbf{k}^{(j)} \right\rangle \right|^2, \quad (15)$$

where $\mathbf{w}^{(i)}$ are unit vectors perpendicularly disposed to the propagation direction and $\Lambda(-2\omega, \omega, \omega)$ is a generalized form of response tensor which accommodates any combination of multipolar couplings. For example second harmonic generation with electric dipole ($E1$) or magnetic dipole ($M1$) coupling gives $s=1$ and $t=2$, so that $p=0$ and $q=0$; however if one electric quadrupole ($E2$) coupling is included in the interaction with the pump, we have $s=1$ and $t=3$, giving $p=1$ and $q=0$.

When fluids are considered, the rotational averaging imposes further constraints. Consider first the case of pure electric dipole coupling ($E1^3$). The result requires evaluation of the rotational average in equation (10), which, using a method described in detail elsewhere [6], yields the result

$$\langle \chi(-2\omega, \omega, \omega) \odot^3 \bar{\mathbf{e}}' \mathbf{e} \mathbf{e} \rangle = \chi_{\lambda(\mu\nu)}(-2\omega, \omega, \omega) \bar{e}_i e_j e_k \varepsilon_{ijk} \varepsilon_{\lambda\mu\nu}. \quad (16)$$

The index contraction between the fully index-antisymmetric Levi-Civita tensor ε_{ijk} and the j, k -symmetric product of polarization components $e_j e_k$ invokes the cross product of \mathbf{e} with itself and is clearly zero. Macroscopic isotropy thus precludes observation of a *coherent* second harmonic signal even in the forward direction. Exceptions to this rule can arise only where there is an induced anisotropy, as for example may be conferred on any polar fluid by application of a static electric field or through a quadratic interaction with the electric fields associated with intense pump laser radiation.

Similar conclusions have to be drawn when higher-order multipolar contributions such as the magnetic dipole and electric quadrupole coupling terms are considered. Consider for example the possibility of a contribution to coherent second harmonic generation associated with one electric quadrupolar interaction in the pump photon annihilation process ($E1^2 E2$). This requires evaluation of a fourth rank orientational average entailing products of Kronecker delta pairs [6] giving the result

$$\begin{aligned} \tilde{\chi}_{\lambda(\mu\nu)\sigma}(-2\omega, \omega, \omega) \bar{e}'_i e_j e_k k_l \langle l_{i\lambda} l_{j\mu} l_{k\nu} l_{l\sigma} \rangle &= (1/15) [(3\tilde{\chi}_{\lambda(\lambda\mu)\mu} - \tilde{\chi}_{\lambda(\mu\mu)\lambda})(\bar{\mathbf{e}}' \cdot \mathbf{e})(\mathbf{k} \cdot \mathbf{e}) \\ &+ (2\tilde{\chi}_{\lambda(\lambda\mu)\lambda} - \tilde{\chi}_{\lambda(\lambda\mu)\mu})(\mathbf{k} \cdot \bar{\mathbf{e}}')(\mathbf{e} \cdot \mathbf{e})], \quad (17) \end{aligned}$$

and the result is again transparently zero since for emission in the *forward* direction which is necessary for phase-matched coherent response, \mathbf{k} is orthogonal to both \mathbf{e} and \mathbf{e}' . Analogous remarks apply when the contribution involving electric quadrupole emission of the *harmonic* photon is considered.

Rigorous treatment of the problem in fact shows that to all orders of multipolar approximation, the coherent generation of all even harmonics is forbidden in fluids [4, 5]; the same conclusion can be drawn on the basis of angular momentum considerations. [7] The result vindicates the use of second harmonic generation as a surface-specific probe. The whole issue has become obscured by treatments which, by dealing with nonlinear polarization rather than the observable harmonic intensity, fail to differentiate coherent and incoherent response [8, 9]. Within the bulk of an isotropic medium, any component associated with what would classically be regarded as *longitudinal* polarization (i.e. one which lies along the propagation vector of the pump radiation) can produce only *incoherent* emission.

4. Coherent second harmonic generation at fluid surfaces

As seen above, the generation of even harmonics is forbidden in a bulk medium possessing isotropic or cubic symmetry. However at the boundary of any such medium, as for example at a fluid interface, local symmetry is lowered and the exclusion of even harmonics no longer applies. For this reason extensive use has been made of the surface-selectivity of second harmonic generation, and it has become an important tool for studying the chemistry and physics of interfaces [10], both with regard to surfaces and surface-adsorbed layers. Although the harmonic is often studied by reflection, a host of experimental geometries have been systematically discussed by Mizrahi and Sipe [11].

At any two-dimensional boundary, the general expression for the intensity of n -harmonic emission associated with the surface can be obtained from (10), in which the coherence factor $\eta_N - N$ defined by

$$\eta_N - N = \sum_{\xi}^N \sum_{\xi' \neq \xi}^{N-1} \exp(i\Delta\mathbf{k} \cdot \mathbf{R}_{\xi\xi'}), \tag{18}$$

should be interpreted as being summing over surface molecules. Consequently, each $\mathbf{R}_{\xi\xi'}$ vector lies in the (X, Y) plane, where Z specifies the surface normal and where X is defined through identifying (X, Z) with the $(\mathbf{k}, \mathbf{k}')$ scattering plane. For any harmonic emission for which $\Delta\mathbf{k}$ is disposed in the Z direction, the argument of the exponential in (18) becomes zero and the factor $\eta_N - N$ attains the value $N(N-1)$ associated with coherent emission. If dispersion is neglected, this amounts to the usual rule for reflection at an angle equal to the angle of incidence. In general, however, we obtain for second harmonic generation

$$\sin \theta_i / \sin \theta_r = n_{2\omega} / n_{\omega}, \tag{19}$$

which is a special case of the general relationship for frequency addition [12].

The phase-matching requirement which leads to the reflection law applies to layers of molecules down to within a depth of approximately k^{-1} below the surface [13]. At optical frequencies, any coherent signal from layers further beneath the surface would invariably be destroyed through interference. In this connection some, but not all, of the confusion which has arisen over the issue of surface harmonic emission can be traced to the different usage of the term 'bulk' by various authors. Principally the ambiguity arises where surface second harmonic generation

is used in the study of adsorbed molecules, and the term ‘bulk’ is used to differentiate the substrate. For such a purpose the term ‘substrate’ is much to be preferred, however, since it does not imply the major part of the support medium. Such a distinction is crucial where the substrate has a bulk constitution that is isotropic.

For a surface harmonic produced by reflection from the surface of an isotropic fluid, it once again transpires that the molecular rotational average annihilates the signal associated with $E1^3$ coupling (if the molecules at the surface are isotropically oriented). This is because equation (16), which entails the factor $(\mathbf{e} \times \mathbf{e})$, still applies. However when the possible involvement of electric quadrupole coupling ($E1^2E2$) is entertained, the second term of (17) associated with the polarization factor $(\mathbf{k} \cdot \bar{\mathbf{e}}')$ ($\mathbf{e} \cdot \mathbf{e}$) will generally not vanish since \mathbf{k} is not parallel to \mathbf{k}' . In fact for a plane polarized pump with $(\mathbf{e} \cdot \mathbf{e}) = 1$ and the harmonic resolved for the component $\mathbf{e}' \parallel \mathbf{k}$, we have

$$\langle \tilde{\chi}(-2\omega, \omega, \omega) \odot^4 \bar{\mathbf{e}}' \mathbf{e} \mathbf{e} \mathbf{k} \rangle = (1/15)(2\tilde{\chi}_{\lambda(\mu\mu)\lambda} - \tilde{\chi}_{\lambda(\lambda\mu)\mu}). \quad (20)$$

In view of the condition $\mathbf{e}' \parallel \mathbf{k}$, this signal is from a classical viewpoint inferred as resulting from a longitudinal nonlinear polarization; however, such signals arise only at or close to the surface. For similar reasons there is a non-vanishing term arising from electric quadrupole emission, associated in this case with a factor $(\mathbf{k}' \cdot \mathbf{e})(\bar{\mathbf{e}}' \cdot \mathbf{e})$.

5. Incoherent second harmonic generation

Second harmonic emission associated with incoherent response imposes no condition on the pump and harmonic wave-vectors and is generally known as elastic second harmonic light scattering (ESHLS) or hyper-Rayleigh scattering. The absence of any requirement for wave-vector matching leads to one of the key features of the incoherent process, which is harmonic emission over 4π steradians, though this is not with an isotropic intensity distribution. This feature contrasts markedly with the laser-like emission associated with coherent response.

The equation for the ($E1^3$) incoherent signal, equation (9), requires evaluation of the rotational average

$$\begin{aligned} & \langle \chi(-2\omega, \omega, \omega) \bar{\chi}(-2\omega, \omega, \omega) \odot^6 \bar{\mathbf{e}}' \mathbf{e} \mathbf{e} \mathbf{e}' \bar{\mathbf{e}} \bar{\mathbf{e}} \rangle \\ & = \chi_{\lambda(\mu\nu)}(-2\omega, \omega, \omega) \bar{e}_i \bar{e}_j \bar{e}_k \bar{\chi}_{\alpha(\pi\rho)}(-2\omega, \omega, \omega) \bar{e}'_l \bar{e}'_m \bar{e}'_n \langle l_{i\lambda} l_{j\mu} l_{k\nu} l_{l\alpha} l_{m\pi} l_{n\rho} \rangle. \end{aligned} \quad (21)$$

The sixth-rank rotational average in this equation comprises products of Kronecker delta triplets [14, 6], each of which is referred to either the laboratory or the molecular frame. The laboratory frame deltas in particular contract with the polarization vector components to give scalar products amongst \mathbf{e} , $\bar{\mathbf{e}}$, \mathbf{e}' and $\bar{\mathbf{e}}'$. The full result for the ESHLS intensity is as follows;

$$\begin{aligned} I_{\text{inc}} = & (D/105) \{ [30(\bar{\mathbf{e}}' \cdot \mathbf{e})(\mathbf{e} \cdot \mathbf{e}')(\bar{\mathbf{e}} \cdot \bar{\mathbf{e}}) - 12(\bar{\mathbf{e}}' \cdot \mathbf{e})(\mathbf{e}' \cdot \bar{\mathbf{e}}) \\ & - 12(\mathbf{e} \cdot \mathbf{e}')(\bar{\mathbf{e}}' \cdot \bar{\mathbf{e}}) - 10(\mathbf{e} \cdot \mathbf{e})(\bar{\mathbf{e}} \cdot \bar{\mathbf{e}}) + 8] \chi_{\lambda(\lambda\mu)} \chi_{\mu(\nu\nu)} \\ & + [-12(\bar{\mathbf{e}}' \cdot \mathbf{e})(\mathbf{e} \cdot \mathbf{e}')(\bar{\mathbf{e}} \cdot \bar{\mathbf{e}}) + 16(\bar{\mathbf{e}}' \cdot \mathbf{e})(\mathbf{e}' \cdot \bar{\mathbf{e}}) \\ & + 2(\mathbf{e} \cdot \mathbf{e}')(\bar{\mathbf{e}}' \cdot \bar{\mathbf{e}}) + 4(\mathbf{e} \cdot \mathbf{e})(\bar{\mathbf{e}} \cdot \bar{\mathbf{e}}) - 6] \chi_{\lambda(\lambda\mu)} \chi_{\nu(\mu\nu)} \\ & + [-10(\bar{\mathbf{e}}' \cdot \mathbf{e})(\mathbf{e} \cdot \mathbf{e}')(\bar{\mathbf{e}} \cdot \bar{\mathbf{e}}) + 4(\bar{\mathbf{e}}' \cdot \mathbf{e})(\mathbf{e}' \cdot \bar{\mathbf{e}}) \\ & + 4(\mathbf{e} \cdot \mathbf{e}')(\bar{\mathbf{e}}' \cdot \bar{\mathbf{e}}) + 8(\mathbf{e} \cdot \mathbf{e})(\bar{\mathbf{e}} \cdot \bar{\mathbf{e}}) - 5] \chi_{\lambda(\mu\mu)} \chi_{\lambda(\nu\nu)} \\ & + [8(\bar{\mathbf{e}}' \cdot \mathbf{e})(\mathbf{e} \cdot \mathbf{e}')(\bar{\mathbf{e}} \cdot \bar{\mathbf{e}}) - 6(\bar{\mathbf{e}}' \cdot \mathbf{e})(\mathbf{e}' \cdot \bar{\mathbf{e}}) \end{aligned}$$

$$\begin{aligned}
& -6(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) - 5(\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) + 11\chi_{\lambda(\mu\nu)}\chi_{\lambda(\mu\nu)} \\
& + [-12(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) + 2(\bar{\mathbf{e}}'\cdot\mathbf{e})(\mathbf{e}'\cdot\bar{\mathbf{e}}) \\
& + 16(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}}) + 4(\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) - 6\chi_{\lambda(\mu\nu)}\chi_{\mu(\lambda\nu)}], \tag{22}
\end{aligned}$$

where use has been made of the symmetry in the last two indices of the nonlinear susceptibility tensor, whose components are for simplicity assumed to be real. The five independent quadratic parameters of the form $\chi \dots \chi$ appearing in (22) arise through abolition of the Kleinman symmetry implicit in early treatments. They were first identified and discussed by Bersohn *et al.* [15], and have also recently been the subject of a detailed analysis by Kielich and Bancewicz [16].

The polarization vector scalar products in (22) are generally non-zero, except that $(\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}})$ is zero when the pump is circularly polarized, and the result faithfully represents the detailed polarization- and angle-dependence of incoherent second harmonic emission [17–19]. Emission can occur in any direction, forward or non-forward. The latter can again be identified with a longitudinal polarization of the medium at the harmonic frequency. Indeed the size of the associated harmonic intensity produced by a plane polarized pump immediately follows from (22) with $\mathbf{e}\parallel\mathbf{k}$ and $(\mathbf{e}\cdot\mathbf{e})=1$;

$$\begin{aligned}
I_{\text{inc}} = (D/105)[& -2\chi_{\lambda(\lambda\mu)}\chi_{\mu(\nu\nu)} - 2\chi_{\lambda(\lambda\mu)}\chi_{\nu(\mu\nu)} + 3\chi_{\lambda(\mu\mu)}\chi_{\lambda(\nu\nu)} \\
& + 6\chi_{\lambda(\mu\nu)}\chi_{\lambda(\mu\nu)} - 2\chi_{\lambda(\mu\nu)}\chi_{\mu(\lambda\nu)}]. \tag{23}
\end{aligned}$$

As noted earlier, arguments about the possible role of higher multipoles in harmonic emission from fluids have tended to obscure the fact that such longitudinal polarizations arise even in the electric dipole approximation, and are invariably associated with incoherent emission.

It should be noted that incoherent second harmonic emission can occur even in fluid media comprising centrosymmetric molecules, through the involvement of fourth-rank molecular response tensors. One mechanism is associated with the application of a static electric field and entails the electric field induced second harmonic generation tensor $\tilde{\chi} \equiv \chi(-2\omega, 0, \omega, \omega)$. Even in the absence of any such applied field, the involvement of electric quadrupolar interactions can itself produce a signal. The calculation in this case calls for the evaluation of an eighth-rank tensor average; details are given by Kielich *et al.* [20]. The generation of local anisotropy through molecular orientational correlation can also play a role [18, 21]. The effect can most readily be understood on the basis of interactions between neighbouring molecules effectively reducing their inversion symmetry, leading to finite values for their hyperpolarizabilities.

6. Discussion

In comparing the theory described above with its classical counterpart, one of the key issues is that the distinction between coherent and incoherent harmonic emission is lost when the process is treated only in terms of a nonlinear polarization. The latter is essentially a bulk concept which, for example, it is not always appropriate to employ in the representation of molecular systems. In the particular case of an isotropic fluid, the necessary rotational averages must be enforced on the result for the observable, the harmonic intensity. Only in this way do the concomitant symmetry constraints become evident: such an approach cannot be employed where results are cast in terms of a nonlinear polarization.

From the analysis presented here it is clear that when second harmonic generation is studied in a *transmission* mode there can be no coherent (phase-matched) signal from the bulk of any isotropic medium. There is of course an incoherent (non-directed) signal associated with pure electric dipole ($E1^3$) coupling. However, when second harmonic generation is studied by *reflection* from the surface of an isotropic medium, there is a coherent signal associated with an interaction involving one electric quadrupole ($E1^2E2$). Both the surface-specific coherent ($E1^2E2$) and the non-specific incoherent ($E1^3$) signals are classically interpreted as arising from an induced longitudinal polarization. There is no coherent signal from the bulk associated with longitudinal polarization.

If the bulk medium from whose surface the harmonic is studied is structurally isotropic throughout its bulk, the second harmonic generation signal has to originate from molecules within a depth of about k^{-1} of the surface. However the nature of many fluid surfaces is such that a degree of orientational order may be present both at and just below the surface. In such circumstances a mechanism similar to that associated with electric field induced second harmonic generation (EFISHG) may produce a signal from within the bulk. This may account for some experimental results which appear to show a harmonic signal associated with the bulk of an isotropic medium; nonetheless the crucial point is that the signal in such cases derives from a region which is not truly isotropic.

In conclusion, it should be re-emphasized that a molecule-based theoretical description resolves the recent controversy over the role of longitudinal polarization in connection with surface second harmonic generation. The unfounded conjectures which appeared in the literature [9] serve only to highlight the shortcomings of the traditional approach in application to molecular fluids, principally through neglect of the distinctively molecular mechanism for nonlinear optical interactions in fluids. Where the detailed nonlinear optical response of molecules is required, recourse to molecular quantum electrodynamics brings both rigour and conceptual facility, despite its relative unfamiliarity to many involved in the field of nonlinear optics.

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