

## Forbidden nature of multipolar contributions to second-harmonic generation in isotropic fluids

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Using a molecular theory of harmonic generation developed within the framework of quantum electrodynamics, we prove that second-harmonic generation is forbidden in isotropic fluids to all levels of multipolar approximation.

The use of second-harmonic generation (SHG) in characterizing surfaces has enjoyed an upsurge in interest in the past five years.<sup>1-13</sup> The technique's surface sensitivity arises when the bulk of the medium is isotropic. Under these conditions, it is not possible to observe the second harmonic in its coherent, forwardly scattered form. Molecules close to the surface or at the surface, however, are not isotropically distributed and may give rise to an observed second harmonic, providing the species itself does not possess inversion symmetry.<sup>14</sup>

In several recent papers, notably Sipe *et al.*,<sup>15</sup> Heinz *et al.*,<sup>16,17</sup> and Marowsky *et al.*,<sup>5</sup> it has been stated that although SHG is forbidden in centrosymmetric materials in the electric dipole approximation, it can still occur when electric quadrupole and magnetic dipole interactions are significant. Whilst this statement is correct for harmonic scattering by individual molecules with inversion symmetry, or centrosymmetric crystals where the nuclei have a fixed orientation in space, it is not a rule

which can generally be applied at the macroscopic level to isotropic gaseous or otherwise structurally fluid media. In these situations the molecules may freely tumble in space and in effecting the necessary rotational average it is found that coherent scattering of even harmonics is forbidden to all orders of the multipolar interaction Hamiltonian.<sup>18</sup> Exceptions to this rule can only arise where there is an induced anisotropy,<sup>19</sup> as, for example, may be conferred on a fluid through its interaction with the intense electric field of laser light.<sup>20,21</sup>

Within the confines of molecular quantum electrodynamics the intensity of the second harmonic can be expressed in terms of a series of molecular response tensors  $\Lambda$ , the propagation vectors for the incident light and emitted harmonic,  $\mathbf{k}$  and  $\mathbf{k}'$ , respectively (where  $\hat{\mathbf{k}} = \hat{\mathbf{k}}'$ , for coherent forward scattering), and the unit vectors  $\mathbf{w}^{(i)}$  disposed perpendicular to  $\hat{\mathbf{k}}$ . By taking the usual multipolar expansion of the interaction Hamiltonian,<sup>22</sup> the intensity of the second harmonic is

$$I^{(\text{SHG})} = \frac{2^5 \pi \omega^4 g^{(2)} I_0^2}{c^5 \epsilon_0^3} \left| \sum_{\xi} \left\langle \sum_p \sum_q \frac{2^q \omega^{p+q}}{c^{p+q+r/2}} \Lambda_{i_1 \dots i_{p+q+3}}^{\xi} \mathbf{w}_{i_1}^{(1)} \dots \mathbf{w}_{i_3}^{(3)} \hat{\mathbf{k}}_{i_4} \dots \hat{\mathbf{k}}_{i_{p+q+3}} \right\rangle \right|^2,$$

where  $g^{(2)}$  is the degree of second-order coherence,  $\omega$  is the circular frequency of the incident laser light,  $q = s - 1$ , where  $s$  represents the order to which the multipolar expansion of  $k'$  is taken,  $p = t - 2$ , where  $t$  is the order to which the multipolar expansion of  $k$  is taken (e.g.,  $t = 4$  when the matrix element comprises E1M3, E2M2, or E3M1 interactions with the incident light), and  $r$  is the number of magnetic interactions. The angular brackets  $\langle \rangle$  indicate that both phase and rotational averaging are required for each molecule,  $\xi$ , within the sample.

Assuming that there is *no orientational correlation* between different molecules, the result of rotationally averaging each of the terms in the angular brackets is independent of the particular molecule on which the average is performed, and hence with  $N$  molecules in the interaction volume we have

$$\begin{aligned} I^{(\text{SHG})} &= \frac{2^5 \pi \omega^4 g^{(2)} I_0^2}{c^5 \epsilon_0^3} N \left\langle \sum_{p,q} \frac{2^q \omega^{p+q}}{c^{p+q+r/2}} \Lambda_{i_1 \dots i_{p+q+3}} \mathbf{w}_{i_1}^{(1)} \dots \mathbf{w}_{i_3}^{(3)} \hat{\mathbf{k}}_{i_4} \dots \hat{\mathbf{k}}_{i_{p+q+3}} \right. \\ &\quad \times \left. \sum_{f,g} \frac{2^g \omega^{f+g}}{c^{f+g+r'/2}} \bar{\Lambda}_{o_1 \dots o_{f+g+3}} \bar{\mathbf{w}}_{o_1}^{(1)} \dots \bar{\mathbf{w}}_{o_3}^{(3)} \bar{\hat{\mathbf{k}}}_{o_4} \dots \bar{\hat{\mathbf{k}}}_{o_{f+g+3}} \right\rangle \\ &\quad + N(N-1) \left\langle \sum_{p,q} \frac{2^q \omega^{p+q}}{c^{p+q+r/2}} \Lambda_{i_1 \dots i_{p+q+3}} \mathbf{w}_{i_1}^{(1)} \dots \mathbf{w}_{i_3}^{(3)} \hat{\mathbf{k}}_{i_4} \dots \hat{\mathbf{k}}_{i_{p+q+3}} \right\rangle \\ &\quad \times \left\langle \sum_{f,g} \frac{2^g \omega^{f+g}}{c^{f+g+r'/2}} \bar{\Lambda}_{o_1 \dots o_{f+g+3}} \bar{\mathbf{w}}_{o_1}^{(1)} \dots \bar{\mathbf{w}}_{o_3}^{(3)} \bar{\hat{\mathbf{k}}}_{o_4} \dots \bar{\hat{\mathbf{k}}}_{o_{f+g+3}} \right\rangle, \end{aligned} \tag{2}$$

where the overbars represent complex conjugates. The two terms in the angular brackets, respectively, denote incoherent and coherent contributions to the second-harmonic intensity. The incoherent term is relatively weak, (due to

its linear dependence on  $N$ ) and can normally be ignored. The second term, however, is much larger, due to its quadratic dependence on  $N$ , and represents the situation where the scattered light from the molecules within the interaction volume interferes constructively. This coherent term normally represents the primary contribution to a harmonic signal.

When the medium is a fluid the result expressed in Eq. (2) needs to be rotationally averaged, and this can be done by using the tensor averaging results given by Andrews and Thirunamachandran.<sup>23</sup> If we assume that the coherent contribution to the second-harmonic intensity dominates, we can write

$$\begin{aligned} & \left| \langle \Lambda_{i_1 \dots i_{p+q+3}} \mathbf{w}_{i_1}^{(1)} \dots \mathbf{w}_{i_3}^{(3)} \hat{\mathbf{k}}_{i_4} \dots \hat{\mathbf{k}}_{i_{p+q+3}} \rangle \right|^2 \\ &= \left| \sum_{t,u} m_{tu}^{(p+q+3)} \mathbf{w}_{i_1}^{(1)} \dots \mathbf{w}_{i_3}^{(3)} \hat{\mathbf{k}}_{i_4} \dots \hat{\mathbf{k}}_{i_{p+q+3}} f_{i_1 \dots i_{p+q+3}}^{(p+q+3;t)} \Lambda_{\lambda_1 \dots \lambda_{p+q+3}} g_{\lambda_1 \dots \lambda_{p+q+3}}^{(p+q+3;u)} \right|^2, \quad (3) \end{aligned}$$

where

$$\sum_{t,u} m_{tu}^{(p+q+3)} f_{i_1 \dots i_{p+q+3}}^{(p+q+3;t)} g_{\lambda_1 \dots \lambda_{p+q+3}}^{(p+q+3;u)}$$

represents the rank  $(p+q+3)$  rotational average of the product of direction cosines relating the laboratory-fixed and molecule-fixed frames. The  $f^{(p+q+3;t)}$  and  $g^{(p+q+3;u)}$  tensors are isotropic, being constructed from products of Kronecker  $\delta$  tensors, with one Levi-Civita tensor if the rank is odd.<sup>23</sup> The resultant contraction of these isotropic tensors with the molecular and polarization tensors represents the isotropic average for the system. When  $p+q$  is even, then  $p+q+3$  is odd and the isotropic tensors  $f_{i_1 \dots i_{p+q+3}}^{(p+q+3;t)}$  involve one Levi-Civita tensor and  $(p+q)/2$  Kronecker  $\delta$  tensors. The Levi-Civita tensor must contract with two noncollinear  $\mathbf{w}$  vectors and one  $\hat{\mathbf{k}}$  vector to give a nonvanishing result; hence there is only one  $\mathbf{w}$  vector and  $p+q-1$   $\hat{\mathbf{k}}$  vectors to contract with the Kronecker  $\delta$  tensor. Since  $p+q-1$  is odd, the result must involve one  $\mathbf{w} \cdot \hat{\mathbf{k}}$  term, which is clearly zero and hence the result vanishes.

If  $p+q$  is odd then  $p+q+3$  is even and  $f_{i_1 \dots i_{p+q+3}}^{(p+q+3;t)}$  is a product of  $(p+q+3)/2$  Kronecker  $\delta$  tensors; consequently there will be a  $\mathbf{w} \cdot \hat{\mathbf{k}}$  term in each isomer, again leading to a vanishing result. Thus the rotational average necessary when considering free molecules forbids the observation of a coherent second harmonic within the bulk of the medium. It is in this respect that SHG in crystals differs from SHG in *free* molecules. This point appears to have been overlooked in a number of communications,<sup>5,15-17</sup> where it is assumed that SHG will be allowed in centrosymmetric media when higher multipolar contributions are considered. However, it is clear that this is not the case when one is considering isotropic fluids where SHG is forbidden to all orders of multipolar approximation.

One direct consequence of this is that SHG in isotropic fluids can only be a surface phenomenon. Many authors attribute the surface activity of SHG to the destruction of *inversion symmetry* which occurs at the surface. On a molecular level the orientational distribution is no longer random and therefore the orientational averaging procedure outlined above is inappropriate. Dipolar fluids at

metal-liquid interfaces, for example, will experience a certain degree of molecular order which arises as a result of preferential alignment of polar molecules with the electric field perpendicular to the metal surface. In this case the distribution can be described by the well-known *Langevin* function. The subsequent perturbation of the orientational distribution allows the coherent second harmonic to be observed.<sup>24-29</sup>

As is evident from the above treatment of SHG, the polarization formalism adopted in a great many papers obscures what is happening at the molecular level. The necessary rotational average shows that whilst *coherent* scattering of the second harmonic is forbidden to all orders of multipolar approximation, *incoherent* scattering of the second harmonic is allowed. The distinction between coherent and incoherent contributions to the scattered intensity is again something not immediately evident within the polarization formalism. For example, in a classic paper by Bloembergen and Jha,<sup>30</sup> the derivation of the nonlinear polarization  $P^{(NL)}(2\omega)$  only includes the coherent contribution [i.e.,  $E(2\omega) \propto N$ ]. Whilst entirely correct in its application to SHG in crystals, its apparent generalization to all homogeneous media<sup>15</sup> makes the treatment incomplete. In a recent paper<sup>15</sup> it has been concluded that "an important component of forbidden bulk second-harmonic generation in homogeneous media is inseparable from the surface contribution in all practical situations." Whilst this statement will be true for solid interfaces, this will clearly not be the case when the medium in question is an isotropic liquid, for then the bulk term will vanish.

In summary, using quantum electrodynamics we have shown that SHG is forbidden in fluids to *all* orders of multipolar approximation, provided there is no orientational correlation. This reinforces the view that SHG in isotropic fluids is purely a surface phenomenon, and within this context *can* therefore be used as a surface probe.

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