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Ambiguities in surface nonlinear spectroscopy calculations

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ABSTRACT

Recent molecular simulations of liquid interfaces yield surface sum-frequency vibrational spectra that can be highly sensitive to the seemingly-arbitrary choice of molecular center in the calculation method. We show that the ambiguity arises because widely-used approaches, focusing exclusively on electric-dipole contributions from the surface, neglect coordinate-dependent quadrupole-order contributions of comparable magnitude from the bulk. The correct calculation includes both surface and bulk responses. With a judicious choice of molecular center, however, it may be possible to minimize the bulk contribution, allowing the surface-only calculation to produce a reasonably accurate spectrum. We use water as an example to elucidate the problem.

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1. Introduction

1.1. Background

Sum-frequency generation (SFG), including its special case of second-harmonic generation (SHG), has been established as a powerful technique for studying surfaces and interfaces [1] because of its ability to provide surface-specific electronic and vibrational spectra. The technique has already been widely used to probe systems with fundamental importance in physics, chemistry, biology, and geology. In some cases, however, interpretation of the spectra can be difficult. This is particularly true for surface vibrational spectra of liquids, such as water, where the diversity of molecular arrangements leads to a broad, but featured, spectrum. To understand such a spectrum and hence be able to deduce structural information about the surface or interface, we would need a theoretical calculation that can reproduce the experimental spectrum. Agreement between theory and experiment would lend weight to calculations which can then be further extended to predict new properties or phenomena about the surface. So far, molecular simulations have been the only theoretical technique used to calculate SF vibrational spectra of liquid interfaces, in particular the water interfaces because of their importance. However, their success in reproducing experimental spectra has been limited. Even in the case of the neat water/vapor interface, the calculated spectrum in the OH stretch range often does not fully agree with the experimental one, especially on the low-frequency side [2]

(however, more recent studies claim to have reconciled the low-frequency discrepancies [3,4]). Different groups have also reported somewhat different calculated spectra [2].

Recently, Noah-Vanhoucke et al. found that different seemingly-valid ways to perform the calculation could yield very different spectra [5]. Therefore it is appropriate to carefully reexamine the approach and assumptions used in the simulations. In this Letter, we show existing deficiencies in current computational approaches and suggest ways to minimize them. We shall focus on the neat water/vapor interface as a representative example, but our discussion is generally applicable to all interfaces.

Let us first briefly review the basic theory of reflected SFG from an interface (with more details presented in Section 2). Consider two input beams at frequencies ω_1 and ω_2 overlapping on the interface that generates a SF output at frequency $\omega_{\text{SF}} = \omega_1 + \omega_2$ in the reflected direction (Figure 1). The SF signal can be written as [1]:

$$S(\hat{e}_{\text{SF}}, \hat{e}_1, \hat{e}_2) \propto \left| \hat{e}_{\text{SF}} \cdot \vec{\chi}_{\text{S,eff}}^{(2)} : \hat{e}_1 \hat{e}_2 \right|^2, \quad \vec{\chi}_{\text{S,eff}}^{(2)} \equiv \vec{\chi}_{\text{S}}^{(2)} + \frac{\vec{\chi}_{\text{B}}^{(2)}}{-i|\Delta\vec{k}|}, \quad (1)$$

where $\vec{\chi}_{\text{S}}^{(2)}$ and $\vec{\chi}_{\text{B}}^{(2)}$ are defined as the second-order surface and bulk nonlinear susceptibilities, respectively, \hat{e}_i is the polarization unit vector of the i th field, $\Delta\vec{k} \equiv \vec{k}_{\text{SF}} - \vec{k}_1 - \vec{k}_2$ is the wave vector mismatch between input and output beams, and $\vec{\chi}_{\text{S,eff}}^{(2)}$ is the net “effective” surface susceptibility. The boundary between “surface” and “bulk” in this context is wherever the perturbing effects of the surface can no longer be felt (Figure 1), for example a few monolayers for neat water, or a screening length for ionic solutions. In centrosymmetric media, $\vec{\chi}_{\text{B}}^{(2)}$ vanishes under the electric-dipole approximation, and is therefore dominated by the electric-quadrupole

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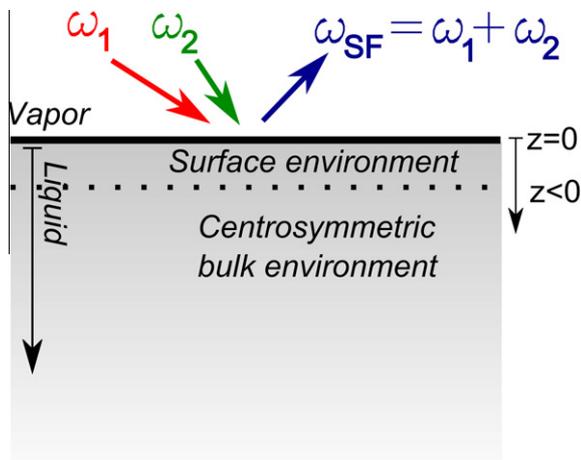


Figure 1. A schematic of the water/vapor interface probed by an SFG experiment. The water is depicted as infinitely deep, which corresponds to an experiment where light attenuation or spatial filtering suppresses the signal of the opposite (bottom) interface.

and magnetic-dipole response. On the other hand, $\vec{\chi}_S^{(2)}$ is dominated by the electric-dipole contribution because of the broken inversion symmetry at the interface. Its resonant spectrum, especially the vibrational one, can provide information about the interfacial structure as well as the orientation of the interfacial molecules. In some cases, the bulk term may be negligible compared with the surface term. In general, however, this is not necessarily true [1], and there is no simple theory that can be used to predict whether the bulk term can be neglected or not for a given interface. An order-of-magnitude estimate yields that the ratio of the bulk to the surface term is equal to the ratio of the geometric dimension of the induced electric-quadrupole on individual molecules to the average distance between molecules along the surface normal [6]. Thus, roughly speaking, if molecules are polar, electric-quadrupoles are well localized on the molecules and the surface layer thickness is large compared to a chromophore, the bulk term can be significantly smaller than the surface term. Experimentally, it is generally impossible to separate surface and bulk contributions [1,7–9]. We usually resort to the observed sensitivity of the spectrum to surface perturbations, for example by adsorbed molecules, to judge whether the surface term dominates or not.

More careful examination of the theory reveals that generally $\vec{\chi}_B^{(2)}/i|\Delta\vec{k}|$ consists of three separate terms: one comes from electric-quadrupole (and magnetic-dipole) contribution of interfacial molecules due to the strong field gradient at the interface between two media of different refractive indices [8]. It would vanish if the refractive indices were matched. Because this contribution is not relevant to the study here, we shall neglect it in our discussion. The other two come from bulk quadrupole contributions:

$$\frac{\vec{\chi}_B^{(2)}(\vec{k}_1, \vec{k}_2, \vec{k}_s)}{-i|\Delta\vec{k}|} = \vec{\chi}_{BS}^{(2)}(\vec{k}_1, \vec{k}_2, \vec{k}_s) + \frac{\vec{\chi}_{BB}^{(2)}}{-i|\Delta\vec{k}|}$$

$$\vec{\chi}_{BB}^{(2)} \equiv \vec{\chi}_B^{(2)}(\vec{k}_{10}, \vec{k}_{20}, \vec{k}_{s0})$$

$$\vec{\chi}_{BS}^{(2)}(\vec{k}_1, \vec{k}_2, \vec{k}_s) \equiv \left(\vec{\chi}_B^{(2)}(\vec{k}_1, \vec{k}_2, \vec{k}_s) - \vec{\chi}_{BB}^{(2)} \right) / -i|\Delta\vec{k}|$$

where $(\vec{k}_{10}, \vec{k}_{20}, \vec{k}_{s0})$ are nearby “reference” wavevectors that are perfectly phase-matched ($\Delta\vec{k}_0 = 0$), and therefore give a large SFG signal which can be unambiguously identified with the bulk. (Unless there is exactly one nearby phase-matched condition, there will be multiple choices for $(\vec{k}_{10}, \vec{k}_{20}, \vec{k}_{s0})$, and each will give a different $\vec{\chi}_{BB}^{(2)}$ and $\vec{\chi}_{BS}^{(2)}$. If there is no nearby phase-matched condition, the

above still works as a mathematical construction. See Ref. [7] for a similar but not identical construction.) The total effective susceptibility is then:

$$\vec{\chi}_{S,eff}^{(2)}(\vec{k}_1, \vec{k}_2, \vec{k}_s) = \vec{\chi}_S^{(2)} + \vec{\chi}_{BS}^{(2)}(\vec{k}_1, \vec{k}_2, \vec{k}_s) + \frac{\vec{\chi}_{BB}^{(2)}}{-i|\Delta\vec{k}|}$$

and it can be shown that $\vec{\chi}_S^{(2)}$ and $\vec{\chi}_{BS}^{(2)}$ are not separable in measurement, while $\vec{\chi}_{BB}^{(2)}$ can be measured by varying the k_i [7]. Actually, as we shall show below, $\vec{\chi}_S^{(2)}$ and $\vec{\chi}_{BS}^{(2)}$ are fundamentally inseparable because the division of electric dipole and electric quadrupole contributions from molecules is not unique, but depends on how the multipole expansion is defined [7]. In the remainder of the Letter, for simplicity and clarity, we shall use $\vec{\chi}_B^{(2)}$ in the analysis, but we note that the ambiguities under discussion are restricted more specifically to its $\vec{\chi}_{BS}^{(2)}$ component, while the $\vec{\chi}_{BB}^{(2)}$ component plays no role in the ambiguities.

1.2. Overview of molecular simulation ambiguities (fundamental cause)

Consider now the molecular simulation of SFG from surfaces. Conventional approaches were recently discovered to be ambiguous and ill-defined [5]. We will show that this problem arises from the neglect of electric-quadrupole and magnetic-dipole contributions, i.e., the calculations implicitly assume $\vec{\chi}_B^{(2)} = 0$ and $\vec{\chi}_{S,eff}^{(2)} = \vec{\chi}_S^{(2)}$. However, it is deeply problematic to ignore $\vec{\chi}_B^{(2)}$, not merely because it may lead to inaccuracies, but more fundamentally because it makes the whole calculation ill-defined. While $\vec{\chi}_{S,eff}^{(2)}$ of Eq. 1 is well-defined, $\vec{\chi}_S^{(2)}$ on its own and $\vec{\chi}_B^{(2)}$ on its own are not. Therefore, any attempt to calculate $\vec{\chi}_S^{(2)}$ by ignoring $\vec{\chi}_B^{(2)}$ will necessarily yield an incorrect and ambiguous result. The ambiguities in defining $\vec{\chi}_S^{(2)}$ and $\vec{\chi}_B^{(2)}$ are the main subject of this Letter, and in Section 2, we will explain and quantify their origins and their consequences.

These ambiguities stem from the usual ambiguity in multipole-expansion: the electromagnetic response of a system can be correctly described using different forms of multipole expansion [7,10–12]. The ambiguity in multipole expansions appears in many areas of physics—perhaps the most famous example is the fact that the dipole moment of a charged molecule is coordinate-system-dependent. Similarly, the electric-quadrupole moment of a polar molecule is also coordinate-system-dependent. In the case of SFG, different multipole expansions give different weights to the dipole response $\vec{\chi}_S^{(2)}$ versus the quadrupole response $\vec{\chi}_B^{(2)}$, but their combined response $\vec{\chi}_{S,eff}^{(2)}$ is constant, as we shall show later.

In Figure 2, we illustrate this classical ambiguity in multipole expansions with a simple example [7]: the same charge-distribution of a charge-neutral system (Figure 2a) can be described as having zero surface dipole and positive bulk quadrupole density (Figure 2b), or positive surface dipole and negative bulk quadrupole density (Figure 2c). These are two equally-valid descriptions of the same system [10–12].

1.3. Overview of molecular simulation ambiguities (specific cause)

As explained above, from a fundamental and general perspective, previous molecular-simulation calculations of SFG have been ambiguous because they calculated the ill-defined quantity $\vec{\chi}_S^{(2)}$, rather than the unambiguous quantity $\vec{\chi}_{S,eff}^{(2)}$. Different multipole expansion schemes (e.g., Figure 2) in simulation yield different values of $\vec{\chi}_S^{(2)}$. Such arbitrariness is often hidden deep within subtle details of the algorithms. We focus on the common case of molecular simulations in a slab geometry: here, the arbitrary part of the algorithm was recently discovered by Noah-Vanhoucke et al. [5].

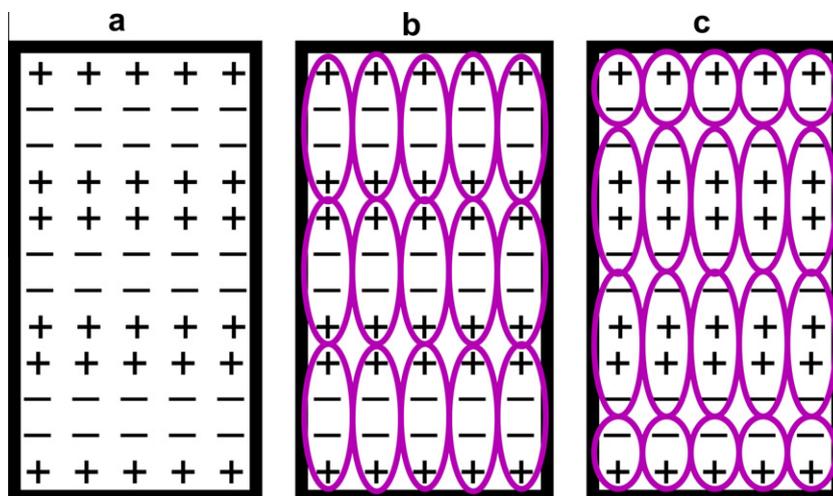


Figure 2. An example of the well-known ambiguity in multipole expansions: (a) a distribution of point charges in a box. (b) By grouping these charges as shown, the box appears to have zero surface dipole and positive bulk quadrupole. (c) By grouping these charges differently, the box now appears to have positive surface dipole and negative bulk quadrupole (after Ref. [7]).

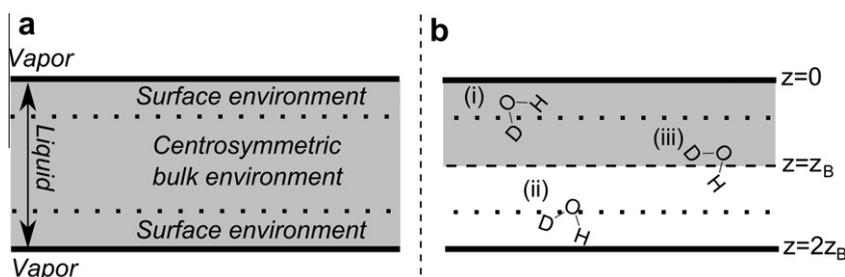


Figure 3. (a) A schematic of a simulated liquid slab, with vapor on both sides. (b) The SFG signal is typically calculated by neglecting molecules below the artificial boundary (long dashed line). Therefore the signal from molecule (i) would be included in the total, (ii) would not, and (iii) might or might not, depending on the molecular center used.

In the slab geometry, the real system is approximated by a thin slab with periodic boundary conditions (Figure 3a). In calculating many surface properties, such as surface tension, contributions from the two surfaces of the slab can be added and averaged, but this step is clearly not appropriate for SFG. The two surfaces, being opposite in orientation, will have their electric-dipole contributions cancelled by each other. Therefore, in molecular simulations of SFG, it is necessary to artificially break the symmetry of the slab. Typically, an artificial boundary surface is set up at the middle of the slab, and only electric-dipole responses of molecules between the top surface of the slab and the artificial boundary surface are assumed to contribute to SFG (Figure 3b). This way, it was thought, the SFG signal from just the top surface would be calculated. (The artificial boundary surface is not the only symmetry-breaking method, but it is the simplest, and other methods [13–15] are only superficially different as discussed further below.)

Since molecules residing around the artificial boundary surface are randomly oriented in an isotropic bulk-like environment, the detailed implementation of the artificial separation might seem unimportant. Unfortunately, this expectation is not true, as was highlighted by Noah-Vanhoucke et al. [5]. The problem arises because of an ambiguity in assigning molecules that straddle the artificial boundary to one interface or the other. In the simplest scheme, the assignment is based on whether a predetermined point within the molecule is above or below the artificial boundary. In using a single point to represent the molecule's position, one thus establishes a “molecular center”. In the case of an HOD molecule, this point could be placed on the H, O, or D atom, or any other fixed site in the molecular frame (Figure 3b). Surpris-

ingly, this choice can have a significant effect on the calculation. (A superficially similar ambiguity arises in DC electrostatic potential calculations [16,17].)

To illustrate the importance of this issue, we use the neat water/vapor interface as an example. Figure 4 shows two spectra of $\text{Im}\chi_s^{(2)}$, calculated using two different choices of molecular center (these simulations are discussed in more detail below). Taking the O atom as center yields a qualitatively different result than taking instead the H as the center. It is not clear which one (if either) gives the “correct” $\text{Im}\chi_s^{(2)}$ spectrum, i.e. the one that should be compared with experiment. (The sharp peak at $\sim 3700\text{ cm}^{-1}$ is

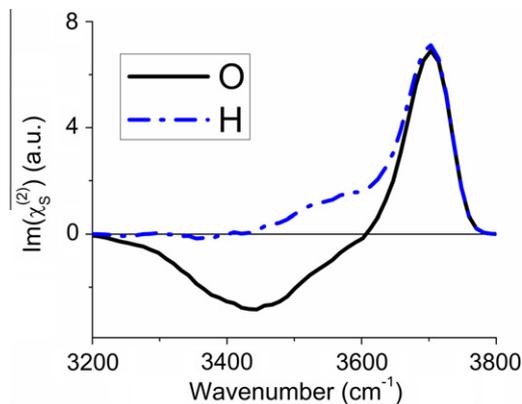


Figure 4. Slab-based MD-calculated SFG spectra, with oxygen (O) or hydrogen (H) as the molecular center. Light polarization is SSP.

the same in the two cases, because it is associated with a surface mode—dangling OH vibration—that does not exist near the artificial boundary surface [2].

Actually, the correct spectrum must come from calculation of $\vec{\chi}_{S,eff}^{(2)}$, which includes both $\vec{\chi}_S^{(2)}$ and $\vec{\chi}_B^{(2)}$. As we shall show in Section 2, both the $\vec{\chi}_S^{(2)}$ and $\vec{\chi}_B^{(2)}$ spectra depend on the choice of the molecular center, but that of $\vec{\chi}_{S,eff}^{(2)}$ does not. With current simulation approaches, it can be difficult to calculate $\vec{\chi}_B^{(2)}$. One therefore hopes that the $\vec{\chi}_B^{(2)}$ contribution can be negligible in comparison with $\vec{\chi}_S^{(2)}$. For this to be true, we must have a sufficiently large $\vec{\chi}_S^{(2)}$, such as in the cases of a surface layer of polar molecules with a significant net polar orientation, and quite importantly, a choice of molecular center that minimizes the absolute value of $\vec{\chi}_B^{(2)}$. For our example in Section 4, an SFG reflection measurement of the air/water interface, we shall suggest that the most appropriate molecular center is at the oxygen atom for SSP polarization (denoting S-, S-, and P-polarizations for the fields at ω_{SF} , visible ω_2 , and infrared ω_1 , respectively) and SPS polarization, but slightly displaced towards the hydrogen atom for PSS polarization.

The Letter is organized as follows: Section 2 describes the basics of sum-frequency generation. We first discuss SF response from individual molecules in terms of multipole expansion and show that the division into terms of electric-dipole, electric-quadrupole, and so on is not unique, but depends on the choice of molecular center. We then show the same ambiguity arises in describing nonlinear susceptibilities, $\vec{\chi}_S^{(2)}$ and $\vec{\chi}_B^{(2)}$, but that the effective surface susceptibility, $\vec{\chi}_{S,eff}^{(2)}$, which takes into account both surface and bulk contributions, is independent of the molecular center. Section 3 discusses how such ambiguities will lead to different SF vibrational spectra calculated by molecular simulation using different choices of molecular center. Section 4 presents molecular dynamics simulations of the air/water interface as an example, and shows how the effect of $\vec{\chi}_B^{(2)}$ can be minimized by a proper choice of molecular center.

2. Basics of sum-frequency generation

We describe in this section the basics of SF response of an interfacial system and show that $\vec{\chi}_{S,eff}^{(2)}$ of Eq. (1) does not depend on the choice of molecular center, but $\vec{\chi}_S^{(2)}$ and $\vec{\chi}_B^{(2)}$ do. We start from SF responses of individual molecules, and show that the sum of the electric-dipole and electric-quadrupole responses of an individual molecule is independent of the choice of molecular center, as any observable property should be.

2.1. SF response from individual molecules

The SF response of an individual molecule in the incoming fields $\vec{E}_1(\omega_1, \vec{k}_1)$ and $\vec{E}_2(\omega_2, \vec{k}_2)$ can be characterized by its effective electric dipole $\vec{p}_{eff}^{(2)}$, defined as the electric-dipole moment which, by itself, would give the same electromagnetic signal in the direction \vec{k}_{SF} as the combined effects of its true electric-dipole and higher-order moments together. The effective dipole is given in the form of a multipole expansion (i.e., power series in the wavevectors $\vec{k}_1, \vec{k}_2, \vec{k}_{SF}$) as [1]:

$$\begin{aligned} \vec{p}_{eff}^{(2)}(\omega_{SF}, \vec{k}_{SF}) &= \vec{p}^{(2)}(\omega_{SF}, \vec{k}_{SF}) - i\vec{k}_{SF} \cdot \vec{q}^{(2)}(\omega_{SF}, \vec{k}_{SF}) \\ &\quad - \frac{c}{\omega_{SF}} \vec{k}_{SF} \times \vec{\mu}^{(2)}(\omega_{SF}, \vec{k}_{SF}) + \dots \\ \vec{p}^{(2)} &= \vec{\alpha}^D : \vec{E}_1 \vec{E}_2 + \vec{\alpha}^{Q1,EQ} : (\nabla \vec{E}_1) \vec{E}_2 + \vec{\alpha}^{Q2,EQ} : \vec{E}_1 (\nabla \vec{E}_2) \\ &\quad + \vec{\alpha}^{Q1,MD} : \vec{B}_1 \vec{E}_2 + \vec{\alpha}^{Q2,MD} : \vec{E}_1 \vec{B}_2 \\ &= \vec{\alpha}^D : \vec{E}_1 \vec{E}_2 + i\vec{\alpha}^{Q1} : \vec{E}_1 \vec{E}_2 \vec{k}_1 + i\vec{\alpha}^{Q2} : \vec{E}_1 \vec{E}_2 \vec{k}_2 \\ \vec{q}^{(2)} &= \vec{\alpha}^{Qs,EQ} : \vec{E}_1 \vec{E}_2 \\ \vec{\mu}^{(2)} &= \vec{\alpha}^{Qs,MD} : \vec{E}_1 \vec{E}_2 \end{aligned} \quad (2)$$

where $\vec{p}^{(2)}$, $\vec{q}^{(2)}$, and $\vec{\mu}^{(2)}$ are the induced electric dipole, electric quadrupole, and magnetic dipole at the sum frequency, respectively; $\vec{\alpha}^D$, $\vec{\alpha}^{Q1,EQ}$, $\vec{\alpha}^{Q1,MD}$ are corresponding nonlinear electric-dipole, electric-quadrupole, and magnetic-dipole polarizabilities (see Figure 5); and $\vec{\alpha}^{Qi}$ is a linear combination of $\vec{\alpha}^{Qi,EQ}$ and $\vec{\alpha}^{Qi,MD}$ (see Appendix A for details). For simplicity, we shall henceforth use the term “quadrupole” to refer to both the electric-quadrupole and magnetic-dipole responses together, as described by the tensor $\vec{\alpha}^{Qi}$ which combines their effects.

Since $(a/\lambda) \ll 1$, where a is a molecular dimension and λ is a light wavelength, we are well justified in ignoring the higher-order multipoles beyond those shown in Eq. (2). More specifically, for a given molecule, each higher order in the multipole expansion is suppressed by an additional factor of order (a/λ) , as usual. On the other hand, when averaged over many molecules in a centrosymmetric bulk, the signal associated with odd-rank susceptibility tensors (like $\vec{\alpha}^D$) vanishes, while even-rank contributions (like $\vec{\alpha}^{Qi}$) do not. Since there are many more molecules in the bulk than the surface, the effect of even-rank tensors is boosted by a factor of order $(a/\lambda)^{-1}$ compared to odd-rank. From these two considerations, $\vec{\alpha}^D$ and $\vec{\alpha}^{Qi}$ together comprise the lowest-order term of an $(a/\lambda) \ll 1$ expansion, justifying the choice of terms shown in Eq. (2) [1].

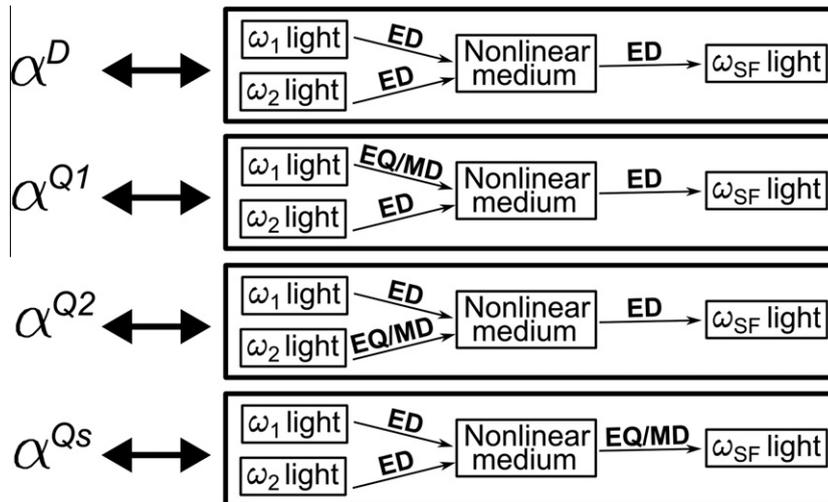


Figure 5. The four lowest-order contributions to SFG susceptibility in the multipole expansion. The light-matter interaction is specified by “ED” for “Electric Dipole”, or “EQ/MD” for “Electric Quadrupole or Magnetic Dipole”.

We can formally rewrite Eq. (2) in a way that distinguishes purely dipolar coupling between the molecule and input fields (yielding a response $\vec{p}_D^{(2)}$) from those involving a field gradient ($\vec{p}_Q^{(2)}$). We will soon see, however, that the division is not unique.

$$\begin{aligned}\vec{p}_{\text{eff}}^{(2)}(\omega_{\text{SF}}, \vec{k}_{\text{SF}}) &= \vec{p}_D^{(2)}(\omega_{\text{SF}}, \vec{k}_{\text{SF}}) + \vec{p}_Q^{(2)}(\omega_{\text{SF}}, \vec{k}_{\text{SF}}) \\ \vec{p}_D^{(2)} &= \vec{\alpha}^D : \vec{E}_1 \vec{E}_2 \\ \vec{p}_Q^{(2)} &= i[\vec{\alpha}^{Q1} : \vec{E}_1 \vec{E}_2 \vec{k}_1 + \vec{\alpha}^{Q2} : \vec{E}_1 \vec{E}_2 \vec{k}_2 - \vec{\alpha}^{Qs} : \vec{E}_1 \vec{E}_2 \vec{k}_{\text{SF}}]\end{aligned}\quad (3)$$

As a physical quantity, the magnitude of $\vec{p}_{\text{eff}}^{(2)}(\omega_{\text{SF}}, \vec{k}_{\text{SF}})$ should of course be independent of the origin for the multipole expansion of the molecular charge oscillations. However, those of $\vec{p}_D^{(2)}(\omega_{\text{SF}}, \vec{k}_{\text{SF}})$ and $\vec{p}_Q^{(2)}(\omega_{\text{SF}}, \vec{k}_{\text{SF}})$ may not be. For explicit discussion of the problem, we need to define a “molecular center” \vec{O} , which is taken as the origin for the multipole expansion above. (Usually, one would choose \vec{O} to be at a point on the molecule.) With \vec{O} chosen, we can write $\vec{p}_{\text{eff}}^{(2)}(\omega_{\text{SF}}, \vec{k}_{\text{SF}}) \equiv \vec{p}_{\text{eff}, \vec{O}}^{(2)}$, $\vec{p}_D^{(2)}(\omega_{\text{SF}}, \vec{k}_{\text{SF}}) \equiv \vec{p}_{D, \vec{O}}^{(2)}$ and $\vec{p}_Q^{(2)}(\omega_{\text{SF}}, \vec{k}_{\text{SF}}) \equiv \vec{p}_{Q, \vec{O}}^{(2)}$. Here, $\vec{p}_{\text{eff}, \vec{O}}^{(2)}$ is the effective dipole centered at \vec{O} , oscillating at the sum frequency, that is induced on the molecule by the fields $\vec{E}_1 \equiv \vec{E}_1^0 e^{i\vec{k}_1 \cdot \vec{O}}$ and $\vec{E}_2 \equiv \vec{E}_2^0 e^{i\vec{k}_2 \cdot \vec{O}}$ at \vec{O} , and \vec{E}_1^0, \vec{E}_2^0 are the amplitudes of the incoming waves. The SF radiation field at the detector is proportional to $\vec{\pi}_{\text{eff}, \vec{O}}^{(2)} \equiv \vec{p}_{\text{eff}, \vec{O}}^{(2)} e^{-i\vec{k}_{\text{SF}} \cdot \vec{O}}$; we therefore expect $\vec{\pi}_{\text{eff}, \vec{O}}^{(2)}$ to be independent of \vec{O} in both phase and magnitude.

To confirm that $\vec{\pi}_{\text{eff}, \vec{O}}^{(2)}$ is independent of \vec{O} , we rewrite Eq. (2) as

$$\vec{\pi}_{\text{eff}, \vec{O}}^{(2)} = [\vec{p}_{D, \vec{O}}^{(2)} + \vec{p}_{Q, \vec{O}}^{(2)}] e^{-i\vec{k}_{\text{SF}} \cdot \vec{O}} \quad (4)$$

with

$$\begin{aligned}\vec{p}_{D, \vec{O}}^{(2)} &= (\vec{\alpha}_O^D : \vec{E}_1^0 \vec{E}_2^0) e^{-i\Delta\vec{k} \cdot \vec{O}} e^{i\vec{k}_{\text{SF}} \cdot \vec{O}} \\ \vec{p}_{Q, \vec{O}}^{(2)} &= i(\vec{\alpha}_O^{Q1} : \vec{E}_1^0 \vec{E}_2^0 \vec{k}_1 + \vec{\alpha}_O^{Q2} : \vec{E}_1^0 \vec{E}_2^0 \vec{k}_2 - \vec{\alpha}_O^{Qs} : \vec{E}_1^0 \vec{E}_2^0 \vec{k}_{\text{SF}}) e^{-i\Delta\vec{k} \cdot \vec{O}} e^{i\vec{k}_{\text{SF}} \cdot \vec{O}}\end{aligned}\quad (5)$$

where $\Delta\vec{k} \equiv \vec{k}_{\text{SF}} - \vec{k}_1 - \vec{k}_2$. We can show that $\vec{\alpha}_O^D$ is independent of \vec{O} , but $\vec{\alpha}_O^{Qi}$ depends on \vec{O} : if \vec{O} and $\vec{O}' \equiv \vec{O} - \Delta\vec{O}$ are two molecular centers,

$$\vec{\alpha}_{\vec{O}'}^{Qi} = \vec{\alpha}_{\vec{O}}^{Qi} + \vec{\alpha}^D \Delta\vec{O}. \quad (6)$$

The explicit proof is given in Appendix A. The changes of $\vec{p}_D^{(2)}$ and $\vec{p}_Q^{(2)}$ due to the shift of \vec{O} to \vec{O}' are given by

$$\begin{aligned}\vec{p}_{D, \vec{O}'}^{(2)} e^{-i\vec{k}_{\text{SF}} \cdot \vec{O}'} - \vec{p}_{D, \vec{O}}^{(2)} e^{-i\vec{k}_{\text{SF}} \cdot \vec{O}} &= (\vec{\alpha}^D : \vec{E}_1^0 \vec{E}_2^0) (e^{-i\Delta\vec{k} \cdot \vec{O}'} - e^{-i\Delta\vec{k} \cdot \vec{O}}) \\ &= (\vec{\alpha}^D : \vec{E}_1^0 \vec{E}_2^0) [i\Delta\vec{k} \cdot \Delta\vec{O} + \dots] e^{-i\Delta\vec{k} \cdot \vec{O}} \\ \vec{p}_{Q, \vec{O}'}^{(2)} e^{-i\vec{k}_{\text{SF}} \cdot \vec{O}'} - \vec{p}_{Q, \vec{O}}^{(2)} e^{-i\vec{k}_{\text{SF}} \cdot \vec{O}} &= -i(\vec{\alpha}^D : \vec{E}_1^0 \vec{E}_2^0) (\Delta\vec{k} \cdot \Delta\vec{O}) e^{-i\Delta\vec{k} \cdot \vec{O}} + \dots\end{aligned}\quad (7)$$

We then see, in the limit of neglecting higher-order terms of $|\Delta\vec{k} \cdot (\vec{O} - \vec{O}')|$ (i.e., in the spirit of multipole expansion, neglecting responses of higher order than quadrupole), that the molecular-center dependences of $\vec{p}_D^{(2)}$ and $\vec{p}_Q^{(2)}$ cancel each other:

$$\vec{\pi}_{\text{eff}, \vec{O}}^{(2)} = [\vec{p}_{D, \vec{O}}^{(2)} + \vec{p}_{Q, \vec{O}}^{(2)}] e^{-i\vec{k}_{\text{SF}} \cdot \vec{O}} = [\vec{p}_{D, \vec{O}'}^{(2)} + \vec{p}_{Q, \vec{O}'}^{(2)}] e^{-i\vec{k}_{\text{SF}} \cdot \vec{O}'} = \vec{\pi}_{\text{eff}, \vec{O}'}^{(2)} \quad (8)$$

This confirms the earlier statement that $\vec{\pi}_{\text{eff}}^{(2)}$ does not depend on the choice of the molecular center \vec{O} of the coordinate system, but $\vec{p}_D^{(2)}$ and $\vec{p}_Q^{(2)}$ do. The latter often leads to ambiguity in distinguishing electric-dipole and quadrupole responses of a molecule.

2.2. Surface and bulk SF susceptibilities

The bulk SF susceptibility of a system is usually defined as

$$\vec{\chi}_B^{(2)}(\omega_{\text{SF}}, \vec{k}_{\text{SF}}) \equiv \frac{1}{V} \sum_j [\vec{p}_{\text{eff}, j}^{(2)} / \vec{E}_{1j} \vec{E}_{2j}], \quad (9)$$

where the sum is over individual molecules (j) in a mesoscopic bulk volume V with dimensions large compared to a molecule, and $\vec{E}_{1j} = \vec{E}_1^0 e^{i\vec{k}_1 \cdot \vec{O}_j}$, $\vec{E}_{2j} = \vec{E}_2^0 e^{i\vec{k}_2 \cdot \vec{O}_j}$. (The vector division in (9) is defined in the obvious way: for the (i, m, n) th Cartesian component of $\vec{\chi}_B^{(2)}$, use the i th component of $\vec{p}_{\text{eff}, j}^{(2)}$, m th of \vec{E}_{1j} , and n th of \vec{E}_{2j} .) For a medium with inversion symmetry, the electric-dipole part, $\vec{p}_D^{(2)}$, of $\vec{p}_{\text{eff}}^{(2)}$ vanishes in summation, but the quadrupole part, $\vec{p}_Q^{(2)}$, survives; as we showed in the preceding section, $\vec{p}_Q^{(2)}$ depends on the choice of molecular center. Hence, we expect that $\vec{\chi}_B^{(2)}$ must also depend on the choice of molecular center. From the expression for $\vec{p}_Q^{(2)}$ in Eq. (3), we obtain, for the choice of molecular center of the j th molecule at \vec{O}_j ,

$$\vec{\chi}_{B, \vec{O}}^{(2)} = \frac{1}{V} \sum_j i \left(\alpha_{j, \vec{O}_j}^{Q1} \cdot \vec{k}_1 + \alpha_{j, \vec{O}_j}^{Q2} \cdot \vec{k}_2 - \alpha_{j, \vec{O}_j}^{Qs} \cdot \vec{k}_{\text{SF}} \right). \quad (10)$$

If the molecular center is shifted from \vec{O}_j to $\vec{O}'_j = \vec{O}_j - \Delta\vec{O}$, then from Eq. (6) we have

$$\begin{aligned}\vec{\chi}_{B, \vec{O}'}^{(2)} - \vec{\chi}_{B, \vec{O}}^{(2)} &= \frac{-i}{V} \sum_j (\vec{\alpha}_j^D) (\Delta\vec{O}_j \cdot \Delta\vec{k}) \\ &\equiv -in \langle \vec{\alpha}^D \Delta\vec{O} \rangle \cdot \Delta\vec{k}\end{aligned}\quad (11)$$

where n denotes the density of molecules and angular brackets indicate an average over molecular orientations and arrangements in the bulk environment.

As mentioned above, $\vec{\chi}_B^{(2)}$ can be split into a $\vec{\chi}_{BB}^{(2)}$ term which can be measured by varying \vec{k}_i , and a $\vec{\chi}_{BS}^{(2)}$ term which cannot be measured separately from the surface [7]. The molecular-center dependence in Eq. (11) comes entirely from a change in $\vec{\chi}_{BS}^{(2)}$, not $\vec{\chi}_{BB}^{(2)}$. The components of $\vec{\chi}_{BS}^{(2)}$, such as $(\vec{\alpha}_{xyxy}^{Q2} - \vec{\alpha}_{xyxy}^{Qs})$ [7], are independent of molecular center by Eq. (6). This is consistent with our assertion that $\vec{\chi}_{BS}^{(2)}$ and $\vec{\chi}_S^{(2)}$ are fundamentally inseparable, while $\vec{\chi}_{BB}^{(2)}$ is separate.

It was already known in the early development of second-harmonic generation and SFG for surface studies that the surface and bulk terms in $\vec{\chi}_{S, \text{eff}}^{(2)}$ of Eq. (1) are not separable, either in theory or in measurement [8,9]. On the other hand, as a measurable physical quantity, $\vec{\chi}_{S, \text{eff}}^{(2)}$ naturally is independent of the choice of molecular center. Thus if $\vec{\chi}_B^{(2)}$ depends on the choice of molecular center, so must $\vec{\chi}_S^{(2)}$, but the sum of $\vec{\chi}_S^{(2)}$ and $\vec{\chi}_B^{(2)}/(-i\Delta k)$ must not. The explicit proof is briefly outlined here, with more details given in Appendix C.

Similar to the bulk case, the surface SF susceptibility is generally defined as

$$\vec{\chi}_S^{(2)}(\omega_{\text{SF}}, \vec{k}_{\text{SF}}) \equiv \frac{1}{A} \sum_j [\vec{p}_{\text{eff}, t}^{(2)} / \vec{E}_{1t} \vec{E}_{2t}] \quad (12)$$

where the summation is on molecules in a surface layer over a surface area A . The surface layer is a thin region at the interface that is structurally different from the bulk. For second-order nonlinear optical response of an isotropic liquid like water, for example, the surface layer is the layer that has broken inversion symmetry. In practice, the surface layer is microscopically thin, so that the quadrupole part, $\vec{p}_Q^{(2)}$, of $\vec{p}_{\text{eff}}^{(2)}$ can be neglected in the summation restricted to the surface layer. We then find, for the molecular center of the j th molecule taken at \vec{O}_t ,

$$\vec{\chi}_{S, \vec{O}}^{(2)} = \frac{1}{A} \sum_j \vec{\alpha}_j^D \quad (13)$$

Here, with $\vec{\alpha}_{j, \vec{O}_t}^D$ being independent of \vec{O}_j , the dependence on the choice of molecular center comes through counting of the set of molecules included in the summation: in reality, we should write Eq. (13) as

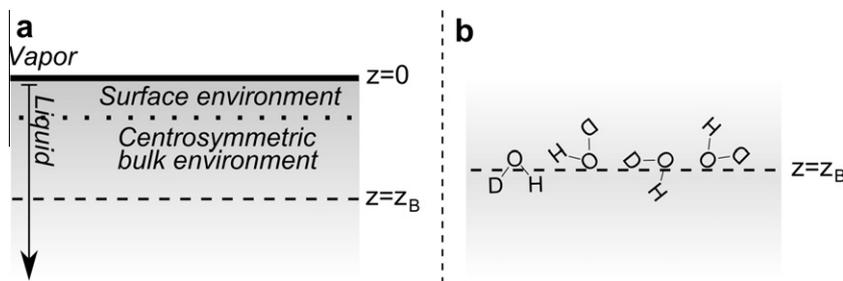


Figure 6. (a) An illustration for Eq. (14). The system is the same as the one described in Figure 1, with the plane $z = z_B$ indicated by a dashed line. The notional dividing plane $z = z_B$ could be placed at any arbitrary depth within the isotropic bulk environment. (b) A close-up view of the group of molecules with oxygen atoms immediately above the plane $z = z_B$. If oxygen is chosen as the molecular center, all of these molecules are included in Eq. (14); if hydrogen is chosen instead, only half are.

$$\vec{\chi}_{S,\vec{O}}^{(2)} = \frac{1}{A} \sum_{O_{jz} > z_B} \vec{\alpha}_j^D \quad (14)$$

(see Appendix B) Here, as sketched in Figure 6a, the interface is at $z = 0$, the semi-infinite bulk medium under discussion is at $z < 0$, and $z = z_B (< 0)$ is a plane sufficiently deep to be in the bulk environment, but separated from the interface only by a microscopically small distance. Changing the molecular center from \vec{O}_j to $\vec{O}'_j = \vec{O}_j - \Delta\vec{O}_j$, but keeping z_B unchanged for simplicity, will add some molecules near z_B to the sum in Eq. (A.10), and remove others. For illustration, we show in Figure 6b a system of HDO molecules, with the plane $z = z_B$ denoted by the dashed line. There are a number of randomly oriented HDO molecules with their oxygen (O) just above the plane (Figure 6b). If the molecular center of HDO is taken to be on O, these molecules will all be counted in the summation of Eq. (14). However, if the molecular center is taken to be on the hydrogen (H), then half of these molecules will no longer be counted in the sum, yielding a different value for $\vec{\chi}_S^{(2)}$. Since the effect of changing the molecular center on $\vec{\chi}_S^{(2)}$ is roughly from molecules within a layer of $|\Delta\vec{O}|$ thick, the change of $\vec{\chi}_S^{(2)}$ is expected to be of the order of $|\alpha^D \Delta\vec{O}|$. In Appendix C, we derive the net change of $\vec{\chi}_S^{(2)}$ due to the change from \vec{O}_j to \vec{O}'_j precisely as:

$$\vec{\chi}_{S,\vec{O}'}^{(2)} - \vec{\chi}_{S,\vec{O}}^{(2)} = -n \langle \alpha^D \Delta O_z \rangle \quad (15)$$

(consistent with Ref. [5]). Since $\langle \alpha^D \Delta O_z \rangle \neq 0$ in general, this explicitly shows that a different choice of \vec{O} will yield a different $\vec{\chi}_S^{(2)}$.

From Eqs. (11) and (15), we see readily

$$\vec{\chi}_{S,\vec{O}}^{(2)} + \frac{\vec{\chi}_{B,\vec{O}}^{(2)}}{-i|\Delta\vec{k}|} = \vec{\chi}_{S,\vec{O}'}^{(2)} + \frac{\vec{\chi}_{B,\vec{O}'}^{(2)}}{-i|\Delta\vec{k}|}. \quad (16)$$

As a result, $\vec{\chi}_{S,eff}^{(2)}$ is independent of the choice of molecular center \vec{O} .

3. Ambiguities in molecular-dynamics calculations

Discussion in the previous section provides the correct framework for calculation to compare with experiment of SFG, emphasizing the need to calculate $\vec{\chi}_{S,eff}^{(2)}$. Unfortunately, this is not the usual practice reported in the literature. Instead, it is simply assumed that $\vec{\chi}_{B,\vec{O}}^{(2)}$ would vanish and just $\vec{\chi}_S^{(2)}$ is calculated, ignoring the fact that $\vec{\chi}_S^{(2)}$ depends on the choice of molecular center. As noticed recently by Noah-Vanhoucke et al. [5], different choices of molecular center can yield significantly different SF surface spectra. We shall elucidate this by an example in a later section.

In practice, the ambiguity in $\vec{\chi}_S^{(2)}$ is typically resolved by arbitrarily choosing a molecular center to arrive at a definite answer. However, the arbitrary step (which may be subtle and uninten-

tional) depends on the simulation approach. Therefore we focus on molecular simulations using a slab model, as described in the Introduction. For surface SFG, these simulations often impose an artificial boundary surface at the middle of the slab to break the inherent inversion symmetry of the slab [5]. We can relate this procedure to Eq. (14) by assuming the artificial boundary surface is at $z = z_B$. The molecules with molecular centers above the artificial boundary surface are summed up, with the other molecules ignored. This procedure is consistent with Eq. (14), so it is a legitimate way to calculate $\vec{\chi}_S^{(2)}$. However, it also inherits the pathology that $\vec{\chi}_S^{(2)}$ is an ambiguous quantity whose value depends on the choice of molecular center. Consequently, as noted in Ref. [5], the SF spectrum calculated from $\vec{\chi}_S^{(2)}$ by molecular simulation depends on the choice of molecular center. Clearly, the correct SF spectrum must come from calculating $\vec{\chi}_{S,eff}^{(2)} \equiv \vec{\chi}_S^{(2)} + \vec{\chi}_B^{(2)} / (-i\Delta k)$, which is independent of the choice of molecular center.

The higher-order bulk nonlinear susceptibility, $\vec{\chi}_B^{(2)}$, given by Eq. (10) (with further details in Appendix A), is generally more difficult to calculate. Although detailed calculation procedures can be found in Refs. [18–21], the facts that $\vec{\chi}_B^{(2)}$ is an ambiguous quantity and that its value depends on the choice of molecular center have not been discussed in the literature. As shown in Appendix A, a proper quantum-mechanical calculation of $\vec{\chi}_{B,\vec{O}}^{(2)}$ should use the “relative” position operators $\vec{r}^{(O)} \equiv \vec{r} - \vec{O}$ in the expressions for the moment operators \vec{p} , \vec{q} , $\vec{\mu}$. Therefore, the result will in general depend on the choice of \vec{O} .

In a molecular-simulation calculation of SFG, one would ideally determine $\vec{\chi}_{S,eff}^{(2)}$ by calculating both $\vec{\chi}_S^{(2)}$ and $\vec{\chi}_B^{(2)}$ with a consistent choice of molecular center. The difficulty of computing $\vec{\chi}_B^{(2)}$, however, may render this approach impractical. A simpler approach is to choose a molecular center that will minimize $\vec{\chi}_B^{(2)}$, and therefore maximize $\vec{\chi}_S^{(2)}$, for the frequency-range and other parameters under investigation. Then, we may be able to argue that $|\vec{\chi}_{B,\vec{O}}^{(2)} / \Delta\vec{k}| \ll |\vec{\chi}_{S,\vec{O}}^{(2)}|$, and hence $\vec{\chi}_{S,eff}^{(2)} \approx \vec{\chi}_{S,\vec{O}}^{(2)}$, allowing us to obtain a fairly accurate SF surface spectrum from calculating only $\vec{\chi}_S^{(2)}$. This is likely the case for isotropic liquids composed of small molecules, or small functional groups on larger molecules. In the following section, we use water as an example to illustrate these points.

4. Water as an example

The air/neat-water interface has been studied extensively both in theory and in experiment. There are quite a few molecular simulations of the SF surface spectrum of the system reported in the literature, but to our knowledge, none of them includes $\vec{\chi}_B^{(2)}$ in the calculation. Here, we show that $\vec{\chi}_B^{(2)}$ is not negligible if the molecular center is not judiciously chosen. We begin by analyzing $\vec{\chi}_B^{(2)}$ more closely. The contribution of $\vec{\chi}_B^{(2)}$ to the experimental

signal can be calculated by appropriately combining its tensor elements, assuming an isotropic bulk. This contribution is proportional to [5]:

$$P_B^{(2)} \propto \frac{(\vec{k}_2 \cdot \hat{e}_1)\chi_{xyxy}^{Q2} - (\vec{k}_s \cdot \hat{e}_1)\chi_{xyxy}^{Qs}}{\Delta k} (\hat{e}_2 \cdot \hat{e}_s) + \frac{(\vec{k}_1 \cdot \hat{e}_2)\chi_{xyxy}^{Q1} - (\vec{k}_s \cdot \hat{e}_2)\chi_{xyxy}^{Qs}}{\Delta k} (\hat{e}_1 \cdot \hat{e}_s) + \frac{(\vec{k}_1 \cdot \hat{e}_s)\chi_{xyyx}^{Q1} + (\vec{k}_2 \cdot \hat{e}_s)\chi_{xyyx}^{Q2}}{\Delta k} (\hat{e}_1 \cdot \hat{e}_2), \quad (17)$$

where $\hat{e}_1, \hat{e}_2, \hat{e}_s$ are the polarizations of the three waves, and following Eq. (10), we define $\vec{\chi}^{Qi} = \frac{1}{V} \sum_t \vec{\alpha}_t^{Qi}$, a sum over a representative volume V in the bulk.

We now consider, for simplicity, an isotopically diluted HDO:-D₂O (in the infinite dilution limit) system and focus on SFG with one incoming wave ω_1 resonant with the OH stretch mode. In the OH stretch vibrational mode of HDO, the hydrogen atom oscillates along the OH bond, while the heavier oxygen atom is relatively stationary and the electronic wavefunction is not substantially perturbed. To the extent that one-dimensional hydrogen vibration dominates charge motion in this mode, we expect the corresponding transition quadrupole to be very small, $\vec{\alpha}_{\text{H}}^{Q1} \sim 0$, provided the molecular center is placed at the H atom's equilibrium position \vec{r}_{H} . On the other hand, the response of an HOD molecule at visible frequencies ω_2 and ω_s arises mainly from valence electron fluctuations, which are governed by wave functions centered nearly at the oxygen atom. Assuming these transitions do not have a strong *intrinsic* quadrupole character—for example, if the electron cloud shifts back and forth without much distortion in shape—we expect that $\vec{\alpha}_{\text{O}}^{Q2} \sim 0$ and $\vec{\alpha}_{\text{O}}^{Qs} \sim 0$, where \vec{r}_{O} is the oxygen atom position. If we now choose the molecular center at an arbitrary point \vec{O} , then we find from Eq. (6)

$$\begin{aligned} (\alpha_{\text{O}}^{Q1})_{jmn} &\approx \alpha_{jm}^D \cdot (\vec{r}_{\text{H}} - \vec{O})_n, \\ (\alpha_{\text{O}}^{Q2})_{jmn} &\approx \alpha_{jm}^D \cdot (\vec{r}_{\text{O}} - \vec{O})_n, \\ (\alpha_{\text{O}}^{Qs})_{jmn} &\approx \alpha_{jm}^D \cdot (\vec{r}_{\text{O}} - \vec{O})_n \end{aligned} \quad (18)$$

Substituting these idealized expressions for quadrupole susceptibilities into Eq. (17), assuming a typical experimental setup (45° angle of incidence, $\lambda_1 \approx 3 \mu\text{m}$, $\lambda_2 = 512 \text{ nm}$ [22]), we have

$$(\chi_{B,\vec{O}}^{(2)})_{\text{ssp}} \propto (\vec{k}_2 \cdot \hat{e}_1)\chi_{\vec{O},xyxy}^{Q2} - (\vec{k}_s \cdot \hat{e}_1)\chi_{\vec{O},xyxy}^{Qs} \propto |\vec{r}_{\text{O}} - \vec{O}|, \quad (19)$$

$$(\chi_{B,\vec{O}}^{(2)})_{\text{sps}} \propto (\vec{k}_1 \cdot \hat{e}_2)\chi_{xyxy}^{Q1} - (\vec{k}_s \cdot \hat{e}_2)\chi_{xyxy}^{Qs} \propto |(0.995\vec{r}_{\text{O}} + 0.005\vec{r}_{\text{H}}) - \vec{O}|, \quad (20)$$

$$(\chi_{B,\vec{O}}^{(2)})_{\text{pss}} \propto (\vec{k}_1 \cdot \hat{e}_s)\chi_{xyyx}^{Q1} + (\vec{k}_2 \cdot \hat{e}_s)\chi_{xyyx}^{Q2} \propto |(0.85\vec{r}_{\text{O}} + 0.15\vec{r}_{\text{H}}) - \vec{O}|, \quad (21)$$

where the abbreviations “ssp”, “sps”, “pss” each represent the polarizations for the SF, visible, and IR light, respectively. (For the various reflection-geometry experimental setups in the literature, the decimals in Eqs. (20) and (21) change only slightly.) The above equations suggest that $\vec{\chi}_B^{(2)}$ is nearly vanishing and $\vec{\chi}_{S,\text{eff}}^{(2)} \approx \vec{\chi}_S^{(2)}$ if the molecular center is chosen to be:

- At the O of HDO for SFG with ssp or sps polarizations,
- Near the O of HDO, but displaced 15% of the way towards H along the OH bond, for pss polarizations.

Thus, with the proper choice of molecular center, we may only need to find $\vec{\chi}_S^{(2)}$ to obtain an approximately correct OH stretch

spectrum for the air/HDO interface. This conclusion is supported by an MD calculation, as described below. We emphasize again, however, that this conclusion is contingent on the assumptions about HOD molecular transitions discussed above Eq. (18).

We have carried out MD simulations to calculate $\vec{\chi}_S^{(2)}$ for the air/HDO:D₂O interface with ssp polarization, using a slab model with different choices of molecular center. We closely followed the method of Ref. [5]. Specifically, we simulate an isotopically-diluted water system, comprising one HDO molecule together with 511 D₂O molecules. These SPC/E molecules were put in a $6 \times 6 \times 6 \text{ nm}^3$ box, with 4 nm of vacuum separating the 2 nm-thick slab from its periodic replicas. After Nosé-Hoover equilibration at 298 K, we integrated Newton's equations of motion for 100 ps with LAMMPS software [23]. The OH stretch frequencies were inferred from the local electric fields, which in turn were calculated in LAMMPS using slab-corrected Ewald summation [24]. The SFG signal of each bond was calculated from the full HOD hyperpolarizability tensor, using the vacuum values tabulated in Ref. [5]. $\text{Im}\vec{\chi}_S^{(2)}$ was calculated from the simulations, and $\text{Re}\vec{\chi}_S^{(2)}$ inferred from Kramers–Kronig relations to obtain $|\vec{\chi}_S^{(2)}|^2$. As discussed in Ref. [5], these simplified calculations neglect a host of effects including homogeneous broadening, motional narrowing, and intermolecular coupling. In addition to ssp polarization, an sps spectrum (not shown) was also calculated, but its correspondence with the experimental measurements [25] is too weak to draw useful conclusions on the merits of different molecular centers. This poor agreement may be due to an important motional effect [25] not included in our static simulations.

The center-of-mass plane of the slab was used as the “artificial boundary” at each time-step: molecules with their molecular centers above the plane were included in the top interface region, while molecules with molecular centers below the plane were ignored (but reused for a separate calculation for the bottom interface that was averaged into the final results).

Simulation results corresponding to different choices of molecular center are shown in Figure 7. The calculations performed with

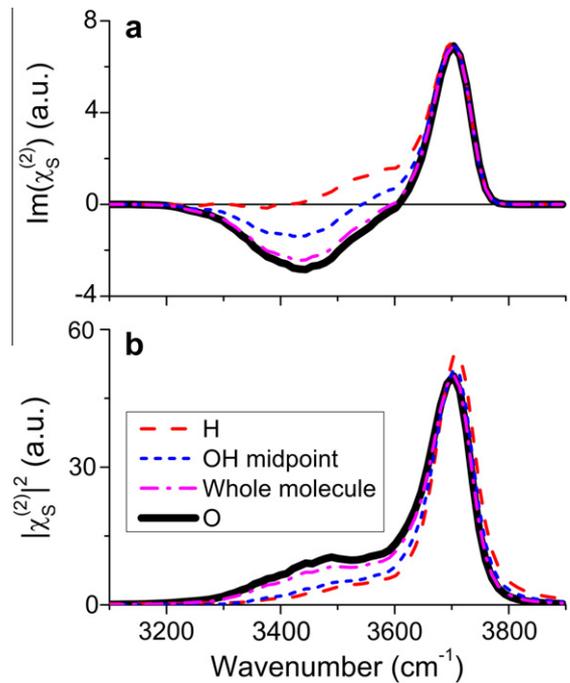


Figure 7. Calculated SFG spectra for HOD:D₂O with different molecular centers. Light polarization is SSP. See text for descriptions.

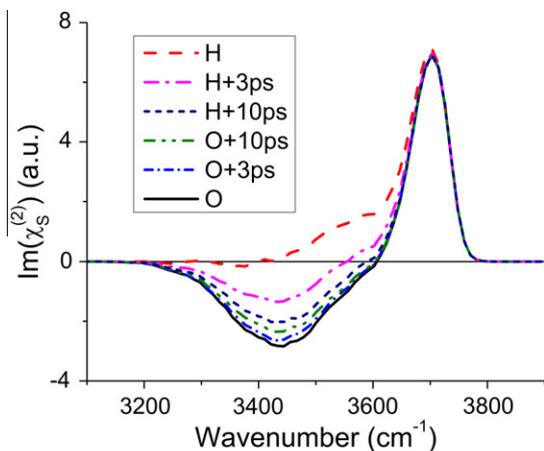


Figure 8. Effect of time-delayed molecular center. Each molecule is counted as above or below the slab center-of-mass using hydrogen or oxygen as the molecular center. Following equilibrium dynamics over 0, 3, or 10 ps, its contribution to the SFG signal is subsequently calculated. Polarization is SSP.

oxygen as molecular center are plotted with a thicker line in the graphs, highlighting the fact that this choice is suggested to be optimal for ssp polarization in the analysis above. Note that, as expected, the peak at 3700 cm^{-1} is independent of molecular center: it is due to dangling OH bonds at the surface, and therefore is insensitive to how molecules in the bulk environment near the artificial boundary surface are counted.

The plots in Figure 7 show the consequences of choosing O, H, or OH-midpoint as the molecular center. Also shown is the “whole molecule” result, where the contribution from HDO was included only if all three atoms of HDO were above the slab center-of-mass plane. We calculated as well the spectrum for which the center of mass of HDO served as the molecular center [26]; it is almost indistinguishable from the result for O as the molecular center.

Others have used a different approach: instead of choosing molecules nearest the interface in each configuration, the molecules are assigned to the top or bottom interface at the start of a short trajectory. The same molecules are counted as contributors throughout the time duration as they diffuse around [13–15]. In our formalism, we would say that the molecular center \vec{O} for a molecule is chosen based on where the molecule *was*, instead of where it *is*. We illustrate the effect of this method in Figure 8, where molecules are associated to an interface at one time-step, then allowed to freely evolve for a certain “delay”, before their signal is calculated.

It is clear from Figures 7 and 8 that the differences between $\text{Im}\overline{\chi}_s^{(2)}$ spectra calculated with different molecular centers can be comparable in magnitude to the spectra themselves. Therefore, we conclude that if the molecular center \vec{O} is not carefully chosen, then $|\overline{\chi}_{B,\vec{O}}^{(2)}/\Delta\vec{k}|$ can be as large as $|\overline{\chi}_{S,\vec{O}}^{(2)}|$. On the other hand, if \vec{O} is judiciously chosen, it is possible that $|\overline{\chi}_{B,\vec{O}}^{(2)}/\Delta\vec{k}| \ll |\overline{\chi}_{S,\vec{O}}^{(2)}|$.

Finally, we compare the calculated spectra with experimental measurements. For ssp, the $\text{Im}\overline{\chi}_{S,\text{eff}}^{(2)}$ spectrum for dilute HDO/D₂O isotopic mixtures has been measured directly [22], and shows a strong negative peak in the $3300\text{--}3600\text{ cm}^{-1}$ range. This feature is most consistent with our calculation that takes the oxygen molecular center. Therefore, our *a priori* reasoning about optimal choices for molecular centers appears well-founded. We note our calculation, similar to many others, is incapable of reproducing the experimentally observed positive band below 3300 cm^{-1} [2].

5. Conclusion

We have examined the formalism of SFVS in terms of multipole expansion, emphasizing that $\overline{\chi}_S^{(2)}$ and $\overline{\chi}_B^{(2)}$ are ambiguous, but their combination $\overline{\chi}_{S,\text{eff}}^{(2)}$ is unambiguous. Accordingly, a calculation of $\overline{\chi}_S^{(2)}$ alone to describe the SF response should yield ambiguous results, as is the case in practice. This analysis explains the recently-discovered troubling ambiguity in slab-based molecular simulations [5].

Ambiguity in separation of surface and bulk contributions in second-harmonic and SF reflection from a surface or interface is a famously problematic issue [1,7–9]. However, we show in this Letter that we can still discuss from a *physical* perspective how to optimally choose the molecular center to minimize $\overline{\chi}_B^{(2)}$ in favor of $\overline{\chi}_S^{(2)}$ in the division of $\overline{\chi}_{S,\text{eff}}^{(2)}$ into $\overline{\chi}_S^{(2)}$ and $\overline{\chi}_B^{(2)}$. In many cases, we can then argue from physical reasoning that $\overline{\chi}_{S,\text{eff}}^{(2)} \approx \overline{\chi}_S^{(2)}$, so that the spectrum calculated from $\overline{\chi}_S^{(2)}$ alone should compare well with experiment.

We have examined in particular the case of air/water interface, where choosing different molecular centers and calculating only $\overline{\chi}_S^{(2)}$ in SF response can result in very different SF vibrational spectra [5]. The problem was resolved, at least approximately, by consideration of the charge motion within the water molecule. Such considerations allow us to predict *a priori* which molecular center should be chosen to minimize the contribution of $\overline{\chi}_B^{(2)}$. We accordingly suggest that the O atom is an optimal molecular center for ssp and sps polarizations, while the point 0.15 \AA from O towards H is optimal for pss. Comparison between experimentally measured and computed spectra supports this expectation.

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Appendix A. Microscopic expressions for electric-dipole, electric-quadrupole, and magnetic-dipole polarizabilities and their relations to the choice of molecular center

We show here, from the microscopic expressions of the electric-dipole and the quadrupole SF polarizabilities of a molecule, $\overline{\alpha}^D$ and $\overline{\alpha}^{Qi}$, that $\overline{\alpha}^D$ does not depend on the choice of molecular center, but $\overline{\alpha}^{Qi}$ does. (The molecular-center dependence of $\overline{\chi}_S^{(2)}$ comes from the summation over $\overline{\alpha}^D$ in Eq. (14), not from the individual $\overline{\alpha}^D$ s themselves.) The derivation of $\overline{\alpha}^D$ and $\overline{\alpha}^{Qi}$ follows the usual perturbation-theory calculation with the light-molecule interaction Hamiltonian in the multipole expansion form [12]:

$$H = -p_j E_j - q_{j\ell} \partial_j E_\ell - \mu_j B_j + \dots \quad (\text{A.1})$$

with $p_j \equiv \sum_\beta e^{(\beta)} r_j^{(\beta)}$, $q_{j\ell} \equiv \frac{1}{2} \sum_\beta e^{(\beta)} r_j^{(\beta)} r_\ell^{(\beta)}$, $\mu_j \equiv \sum_\beta \frac{e^{(\beta)}}{2m^{(\beta)}} (\vec{r}^{(\beta)} \times \vec{\pi}^{(\beta)})_j$, with $e^{(\beta)}$, $r^{(\beta)}$, $\pi^{(\beta)}$, and $m^{(\beta)}$ denoting the charge, position, momentum, and mass of the electron or ion labeled β , and where j and ℓ are Cartesian indices. From second-order perturbation theory, induced moments $p_j^{(2)}(\omega_s)$, $q_{j\ell}^{(2)}(\omega_s)$, $\mu_j^{(2)}(\omega_s)$ at the sum frequency are given by

$$\begin{aligned}
p_j^{(2)}(\omega_s) &= \alpha_{j\ell n}^D E_{1\ell} E_{2n} + \alpha_{j\ell n}^{Q1,EQ} (\partial_t E_{1\ell}) E_{2n} + \alpha_{j\ell n}^{Q2,EQ} E_{1\ell} (\partial_t E_{2n}) \\
&\quad + \alpha_{j\ell n}^{Q1,MD} B_{1\ell} E_{2n} + \alpha_{j\ell n}^{Q2,MD} E_{1\ell} B_{2n} \\
q_{jt}^{(2)}(\omega_s) &= \alpha_{j\ell n}^{Qs,EQ} E_{1\ell} E_{2n} \\
\mu_j^{(2)}(\omega_s) &= \alpha_{j\ell n}^{Qs,MD} E_{1\ell} E_{2n}
\end{aligned} \tag{A.2}$$

with

$$\begin{aligned}
\alpha_{j\ell n}^D &= F(p_j, p_\ell, p_n) \\
\alpha_{j\ell n}^{Qs,EQ} &= F(q_{jt}, p_\ell, p_n) \\
\alpha_{j\ell n}^{Qs,MD} &= F(\mu_j, p_\ell, p_n) \\
\alpha_{j\ell n}^{Q1,EQ} &= F(p_j, q_{t\ell}, p_n) \\
\alpha_{j\ell n}^{Q1,MD} &= F(p_j, \mu_\ell, p_n) \\
\alpha_{j\ell n}^{Q2,EQ} &= F(p_j, p_\ell, q_{nt}) \\
\alpha_{j\ell n}^{Q2,MD} &= F(p_j, p_\ell, \mu_n)
\end{aligned} \tag{A.3}$$

$$\begin{aligned}
F(A, B, C) &= \frac{-1}{\hbar^2} \sum_{g,s,t} \left[\rho_{gg}^{(0)} \frac{(A)_{gs} (B)_{st} (C)_{tg}}{(\omega_2 - \omega_{tg} + i\Gamma_{tg})(\omega_s - \omega_{sg} + i\Gamma_{sg})} + \dots \right] \\
\end{aligned} \tag{A.4}$$

where “...” denotes five other similar terms, ω_{sg} and Γ_{sg} are the frequency and damping constant of the resonance between states s and g , and A, B , and C represent operators involved in the light-matter interaction (A.1) at frequencies ω_s, ω_1 , and ω_2 , respectively. (The conclusions would not be altered if the Γ 's were replaced with more sophisticated treatments of dephasing.) The effective induced electric-dipole moment at ω_s can be written as:

$$\begin{aligned}
p_{eff,j}^{(2)}(\omega_s = \omega_1 + \omega_2, \vec{k}_{SF}) &= p_j^{(2)} - (i\vec{k}_{SF} \cdot \vec{q}^{(2)})_j - \frac{C}{\omega_{SF}} (\vec{k}_{SF} \times \vec{\mu}^{(2)})_j \\
&= \left(\alpha_{j\ell n}^D + i \left(\alpha_{j\ell n}^{Q1} k_{1t} + \alpha_{j\ell n}^{Q2} k_{2t} - \alpha_{j\ell n}^{Qs} k_{SF,t} \right) \right) E_{1\ell} E_{2n}
\end{aligned} \tag{A.5}$$

in which $\vec{\alpha}^{Qi}$ includes both electric-quadrupole and magnetic-dipole parts:

$$\begin{aligned}
\alpha_{j\ell n}^{Qs} &= \alpha_{j\ell n}^{Qs,EQ} + \frac{i}{\omega_{SF}} \alpha_{j\ell n}^{Qs,MD} \epsilon_{btj} \\
\alpha_{j\ell n}^{Q1} &= \alpha_{j\ell n}^{Q1,EQ} - \frac{i}{\omega_1} \alpha_{j\ell n}^{Q1,MD} \epsilon_{bt\ell} \\
\alpha_{j\ell n}^{Q2} &= \alpha_{j\ell n}^{Q2,EQ} - \frac{i}{\omega_2} \alpha_{j\ell n}^{Q2,MD} \epsilon_{bt\ell}
\end{aligned} \tag{A.6}$$

where $\epsilon_{j\ell n}$ is the Levi-Civita tensor. We now show that $\vec{\alpha}^D$ does not depend on the choice of molecular center, while $\vec{\alpha}^{Qi}$ does. In calculating the matrix element $[f(\vec{r})]_{\alpha\beta}$ of an operator $f(\vec{r})$ representing a property of the molecule, we implicitly have \vec{r} referred to a molecular center. If the molecular center is at \vec{O} away from the origin of the coordinate system used in the calculation, then we must replace $f(\vec{r})$ by $f(\vec{r} - \vec{O})$. Thus, the operators $p_j \equiv \sum_\beta e^{(j\beta)} r_j^{(j\beta)}$, $q_{j\ell} \equiv \frac{1}{2} \sum_\beta e^{(j\beta)} r_j^{(j\beta)} r_\ell^{(j\beta)}$, and $\mu_j \equiv \sum_\beta \frac{e^{(j\beta)}}{2m^{(j\beta)}} (\vec{r}^{(j\beta)} \times \vec{\pi}^{(j\beta)})_j$ in the above equations should be replaced by $p_j^{(\vec{O})} \equiv \sum_\beta e^{(j\beta)} (r_j^{(j\beta)} - \vec{O})$, $q_{j\ell}^{(\vec{O})} \equiv \frac{1}{2} \sum_\beta e^{(j\beta)} (r_j^{(j\beta)} - \vec{O})(r_\ell^{(j\beta)} - \vec{O})$, and $\mu_j^{(\vec{O})} \equiv \sum_\beta \frac{e^{(j\beta)}}{2m^{(j\beta)}} ((\vec{r}^{(j\beta)} - \vec{O}) \times \vec{\pi}^{(j\beta)})_j$, respectively.

Since \vec{O} is a constant vector, we have $F(O_j, X, Y) = F(X, O_j, Y) = F(X, Y, O_j) = 0$ for any operators X, Y . It is then readily seen that $\vec{\alpha}^D$ is independent of \vec{O} , i.e., independent of the choice of molecular center.

However, $\vec{\alpha}^{Qi}$ does have molecular-center dependence. If we change the molecular center from \vec{O} to \vec{O}' , the electric quadrupole and magnetic dipole operators change from $q_{t\ell}^{(\vec{O})}$ and $\mu_j^{(\vec{O})}$ to

$$\begin{aligned}
q_{t\ell}^{(\vec{O}')} &= \frac{1}{2} \sum_\beta e^{(j\beta)} (r_\ell^{(j\beta)} - \vec{O}'_\ell)(r_t^{(j\beta)} - \vec{O}'_t) \\
&= q_{t\ell}^{(\vec{O})} + \frac{1}{2} (\vec{O} - \vec{O}')_{t\ell} p_\ell^{(\vec{O})} + \frac{1}{2} (\vec{O} - \vec{O}')_{\ell t} p_t^{(\vec{O})} \\
\mu_j^{(\vec{O}')} &= \sum_\beta \frac{e^{(j\beta)}}{2m^{(j\beta)}} (\vec{r}^{(j\beta)} - \vec{O}') \times \vec{\pi}^{(j\beta)} \\
&= \mu_j^{(\vec{O})} + (\vec{O} - \vec{O}') \times \sum_\beta \frac{e^{(j\beta)}}{2m^{(j\beta)}} \vec{\pi}^{(j\beta)}.
\end{aligned} \tag{A.7}$$

We apply these with the help of the identity $\sum_\beta \frac{e^{(j\beta)}}{m^{(j\beta)}} F(p_j, \pi_\ell^{(j\beta)}, p_n) = i\omega_1 F(p_j, p_\ell, p_n)$, which follows from $\vec{\pi}^{(j\beta)} = \frac{m_i}{\hbar} [H_0, \vec{r}^{(j\beta)}]$, where H_0 is the unperturbed Hamiltonian, $H_0 \equiv V(r^{(1)}, r^{(2)}, \dots) + \sum_\beta \frac{|\vec{\pi}^{(j\beta)}|^2}{2m^{(j\beta)}}$. The result is

$$\begin{aligned}
\alpha_{j\ell n}^{Q1,EQ,(\vec{O}')} &= \alpha_{j\ell n}^{Q1,EQ,(\vec{O})} + \frac{1}{2} \alpha_{j\ell n}^D (\vec{O} - \vec{O}')_t + \frac{1}{2} \alpha_{j\ell n}^D (\vec{O} - \vec{O}')_\ell \\
\alpha_{j\ell n}^{Q1,MD,(\vec{O}')} &= \alpha_{j\ell n}^{Q1,MD,(\vec{O})} + \frac{i\omega_1}{2} \epsilon_{t\ell b} \alpha_{j\ell n}^D (\vec{O} - \vec{O}')_t
\end{aligned}$$

and therefore

$$\begin{aligned}
\alpha_{j\ell n}^{Q1,(\vec{O}')} - \alpha_{j\ell n}^{Q1,(\vec{O})} &= \frac{1}{2} \alpha_{j\ell n}^D (\vec{O} - \vec{O}')_\ell + \frac{1}{2} \alpha_{j\ell n}^D (\vec{O} - \vec{O}')_t \\
&\quad + \frac{1}{2} \epsilon_{bt\ell} \epsilon_{bdf} \alpha_{j\ell n}^D (\vec{O} - \vec{O}')_t = \alpha_{j\ell n}^D (\vec{O} - \vec{O}')_t.
\end{aligned}$$

Likewise for all $\vec{\alpha}^{Qi}$,

$$\alpha_{j\ell n}^{Qi,(\vec{O}')} - \alpha_{j\ell n}^{Qi,(\vec{O})} = \alpha_{j\ell n}^D (\vec{O} - \vec{O}')_t. \tag{A.8}$$

Thus, $\vec{\alpha}^{Qi}$ depends on the choice of molecular center in a way that incorporates some part of the dipole susceptibility.

Appendix B. Effective surface susceptibility

The SF signals in transmission and reflection from a semi-infinite medium are proportional to $|\vec{\chi}_{S,eff}^{(2)}|^2$, where the effective surface nonlinear susceptibility $\vec{\chi}_{S,eff}^{(2)}$ is related to the surface and bulk nonlinear susceptibilities $\vec{\chi}_{S,0}^{(2)}$ and $\vec{\chi}_{B,0}^{(2)}$ by

$$\vec{\chi}_{S,eff}^{(2)} \equiv \vec{\chi}_{S,0}^{(2)} + \frac{\vec{\chi}_{B,0}^{(2)}}{-i\Delta k} \tag{B.1}$$

Macroscopically, this relation is usually derived from a three-layer model [27]. Here, we give a microscopic derivation valid for the simple case we have been considering, where the index of refraction is constant everywhere. The purpose of this is to show explicitly that (B.1) is consistent with Eqs. (10) and (14), the molecular expressions for $\vec{\chi}_{B,0}^{(2)}$ and $\vec{\chi}_{S,0}^{(2)}$, respectively.

The SF output field from the surface and the bulk of the medium can be considered as generated by an equivalent surface sheet of nonlinear polarization, $\vec{P}_{S,eff}^{(2)}$, which contains contributions from all molecules:

$$\begin{aligned}
\vec{P}_{eff}^{(2)} &= \frac{1}{A} \sum_t \vec{p}_{eff,j,\vec{O}_j}^{(2)} e^{-i\vec{k}_{SF} \cdot \vec{O}_j} \\
&= \frac{1}{A} \int_{z_B}^{0^+} \left(\sum_{(\vec{O}_j)_z=z} \vec{p}_{eff,j,\vec{O}_j}^{(2)} e^{-i\vec{k}_{SF} \cdot \vec{O}_j} \right) dz \\
&\quad + \frac{1}{A} \int_{-\infty}^{z_B} \left(\sum_{(\vec{O}_j)_z=z} \vec{p}_{eff,j,\vec{O}_j}^{(2)} e^{-i\vec{k}_{SF} \cdot \vec{O}_j} \right) dz
\end{aligned} \tag{B.2}$$

The second line of the above equation has the surface and bulk parts separately presented, each of which depends in general on how the molecular center \vec{O} is chosen within the molecule. Here, the coordinate system is defined so that the medium spans $z < 0$, and $|z_B|$ is the

thickness of the surface layer (Figure 6a), assumed to be much less than a wavelength. With the incoming fields given by $\vec{E}_1(\vec{r}) = \vec{E}_1^0 e^{i\vec{k}_1 \cdot \vec{r}}$ and $\vec{E}_2(\vec{r}) = \vec{E}_2^0 e^{i\vec{k}_2 \cdot \vec{r}}$, we can write, for the bulk part,

$$\begin{aligned} & \frac{1}{A} \int_{-\infty}^{z_B} \left(\sum_{(\vec{O}_j)_{z=z}} \vec{p}_{\text{eff},j,\vec{O}_j}^{(2)} e^{-i\vec{k}_{\text{SF}} \cdot \vec{O}_j} \right) dz \\ &= \left(\frac{1}{A} \int_{-\infty}^{z_B} \left(\sum_{(\vec{O}_j)_{z=z}'} e^{-i\Delta\vec{k} \cdot \vec{O}_j} i [\vec{\alpha}_{j,\vec{O}_j}^{Q1} \cdot \vec{k}_1 + \vec{\alpha}_{j,\vec{O}_j}^{Q2} \cdot \vec{k}_2 - \vec{\alpha}_{j,\vec{O}_j}^{Qs} \cdot \vec{k}_{\text{SF}}] \right) dz \right) : \vec{E}_1^0 \vec{E}_2^0 \\ &= (\vec{\chi}_{B,\vec{O}}^{(2)} : \vec{E}_1^0 \vec{E}_2^0) \int_{-\infty}^{z_B} e^{-i|\Delta k|z} dz \cong (\vec{\chi}_{B,\vec{O}}^{(2)} : \vec{E}_1^0 \vec{E}_2^0) \int_{-\infty}^0 e^{-i|\Delta k|z} dz \\ &= \left(\frac{\vec{\chi}_{B,\vec{O}}^{(2)}}{-i|\Delta k|} : \vec{E}_1^0 \vec{E}_2^0 \right) \end{aligned} \quad (\text{B.3})$$

(using Eq. (10)), and for the surface part,

$$\begin{aligned} & \frac{1}{A} \int_{z_B}^{0^+} \left(\sum_{(\vec{O}_j)_{z=z}} \vec{p}_{\text{eff},j,\vec{O}_j}^{(2)} e^{-i\vec{k}_{\text{SF}} \cdot \vec{O}_j} \right) dz \\ &= \frac{1}{A} \int_{z_B}^{0^+} \left(\sum_{(\vec{O}_j)_{z=z_B}} \vec{\alpha}_j^D e^{-i\Delta\vec{k} \cdot \vec{O}_j} \right) dz : \vec{E}_1^0 \vec{E}_2^0 \\ &\cong \frac{1}{A} \left(\sum_{(\vec{O}_j)_{z>z_B}} \vec{\alpha}_j^D \right) : \vec{E}_1^0 \vec{E}_2^0 \\ &= \vec{\chi}_{S,\vec{O}}^{(2)} : \vec{E}_1^0 \vec{E}_2^0 \end{aligned} \quad (\text{B.4})$$

(using Eq. (14)). With $\vec{P}_{S,\text{eff}}^{(2)} \equiv \vec{\chi}_{S,\text{eff}}^{(2)} : \vec{E}_1^0 \vec{E}_2^0$, we obtain Eq. (1).

Appendix C. Dependence of electric-dipole-order susceptibility on the choice of molecular center

To calculate the dependence of $\vec{\chi}_S^{(2)}$ on \vec{O} , we start with Eq. (14), $\vec{\chi}_{S,\vec{O}}^{(2)} = \frac{1}{A} \sum_{(\vec{O}_j)_{z>z_B}} \vec{\alpha}_j^D$. We assume that the molecular center \vec{O} for each molecule is fixed in molecular coordinates. Changing the molecular center from \vec{O} to $\vec{O}' = \vec{O} - \Delta\vec{O}$, but keeping z_B unchanged, will remove from the sum those molecules with $O_z > z_B$ but $O'_z < z_B$, i.e., molecules originally in the region $z_B < O_z < z_B + \Delta O_z$. Likewise, it will add to the sum molecules with $O_z < z_B$ but $O'_z > z_B$, i.e., molecules originally in the region $z_B > O_z > z_B + \Delta O_z$.

Consider an ensemble of molecules with a given orientation $\vec{\Omega}$. For this ensemble, ΔO_z has a constant value $\Delta O_z^{(\vec{\Omega})}$. If $\Delta O_z^{(\vec{\Omega})} > 0$, some molecules from this ensemble will be eliminated from the sum, namely those in the region $z_B < O_z < z_B + \Delta O_z^{(\vec{\Omega})}$. The volume of this region is $A \Delta O_z^{(\vec{\Omega})}$, so the change in $\vec{\chi}_S^{(2)}$ due to these eliminated molecules is $-n^{(\vec{\Omega})} \langle \vec{\alpha}^D \rangle_{\vec{\Omega}} \Delta O_z^{(\vec{\Omega})} d\vec{\Omega}$, where $n^{(\vec{\Omega})} d\vec{\Omega}$ is the differential number density of molecules with the given orientation $\vec{\Omega}$. Likewise, if $\Delta O_z^{(\vec{\Omega})} < 0$, some molecules from this ensemble will be added into the sum (14); namely those in the region $z_B > O_z > z_B + \Delta O_z^{(\vec{\Omega})}$. The volume of this region is $|A \Delta O_z^{(\vec{\Omega})}| = -A \Delta O_z^{(\vec{\Omega})}$, so the change in $\vec{\chi}_S^{(2)}$ due to these molecules is $-n^{(\vec{\Omega})} \langle \vec{\alpha}^D \rangle_{\vec{\Omega}} \Delta O_z^{(\vec{\Omega})} d\vec{\Omega}$, the same expression as before.

Altogether,

$$\vec{\chi}_{S,\vec{O}'}^{(2)} - \vec{\chi}_{S,\vec{O}}^{(2)} = \int d\vec{\Omega} \left(-n^{(\vec{\Omega})} \langle \vec{\alpha}^D \rangle_{\vec{\Omega}} \Delta O_z^{(\vec{\Omega})} \right) = -n \langle \vec{\alpha}^D \Delta O_z \rangle.$$

where the angle-brackets are a statistical average over molecules' orientations and local environments. This formula is consistent that derived in Noah-Vanhoucke et al. [5].

References

- [1] Y.R. Shen, Appl. Phys. B 68 (1999) 295.
- [2] C.S. Tian, Y.R. Shen, Chem. Phys. Lett. 470 (2009) 1.
- [3] T. Ishiyama, A. Morita, J. Chem. Phys. 131 (2009) 244714.
- [4] P.A. Pieniazek, C.J. Tainter, J.L. Skinner, J. Chem. Phys. 135 (2011) 044701.
- [5] J. Noah-Vanhoucke, J.D. Smith, P.L. Geissler, J. Phys. Chem. B 113 (2009) 4065.
- [6] Y.R. Shen, The Principles of Nonlinear Optics, John Wiley & Sons, Inc, Hoboken, 1984.
- [7] H. Held, A.I. Lvovsky, X. Wei, Y.R. Shen, Phys. Rev. B 66 (2002) 205110.
- [8] P. Guyot-Sionnest, Y.R. Shen, Phys. Rev. B 38 (1988) 7985.
- [9] J.E. Sipe, V. Mizrahi, G.I. Stegeman, Phys. Rev. B 35 (1987) 9091.
- [10] L.D. Landau, E.M. Lifshitz, Electrodynamics of Continuous Media, second edn., Butterworth-Heinemann, Oxford, 1960.
- [11] P.S. Pershan, Phys. Rev. 130 (1963) 919.
- [12] R.E. Raab, O.L. De Lange, Multipole Theory in Electromagnetism, Clarendon Press, Oxford, 2005.
- [13] B.M. Auer, J.L. Skinner, J. Chem. Phys. 129 (2008) 214705.
- [14] E.C. Brown, M. Mucha, P. Jungwirth, D.J. Tobias, J. Phys. Chem. B 109 (2005) 7934.
- [15] A. Perry, H. Ahlborn, B. Space, P.B. Moore, J. Chem. Phys. 118 (2003) 8411.
- [16] L.R. Pratt, J. Phys. Chem. 96 (1992) 25.
- [17] M.A. Kastenholz, P.H. Hünenberger, J. Chem. Phys. 124 (2006) 124106.
- [18] A. Morita, Chem. Phys. Lett. 398 (2004) 361.
- [19] C. Neipert, B. Space, A.B. Roney, J. Phys. Chem. C 111 (2007) 8749.
- [20] R.W. Munn, Mol. Phys. 89 (1996) 555.
- [21] X.D. Zhu, A. Wong, Phys. Rev. B 46 (1992) 2540.
- [22] C.S. Tian, Y.R. Shen, J. Am. Chem. Soc. 131 (2009) 2790.
- [23] S. Plimpton, J. Comput. Phys. 117 (1995) 1.
- [24] I.C. Yeh, M.L. Berkowitz, J. Chem. Phys. 111 (1999) 3155.
- [25] X. Wei, Y.R. Shen, Phys. Rev. Lett. 86 (2001) 4799.
- [26] A. Morita, J. Phys. Chem. B 110 (2006) 3158.
- [27] P. Guyot-Sionnest, W. Chen, Y.R. Shen, Phys. Rev. B 33 (1986) 8254.



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