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Basic Theory of Surface Sum-Frequency Generation

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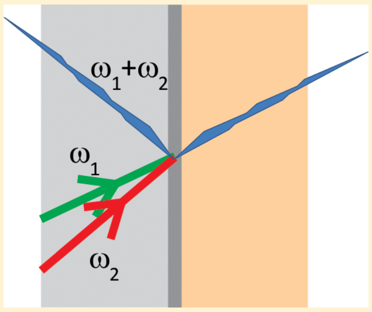
ABSTRACT: A detailed description on the basic theory of optical sum-frequency generation from an interfacial system is presented. Both the interface and the bulk generally contribute to the sum-frequency output. Two seemingly different approaches to specify bulk nonlinearity that includes electric-quadrupole and magnetic-dipole contributions are shown to yield the same sum-frequency output if surface nonlinearity is properly taken into account. The question of whether surface and bulk nonlinearities can be uniquely defined and separately measured is discussed. It is shown that the answer is affirmative. Truly bulk and truly surface nonlinear susceptibilities can be uniquely defined and separately deduced from measurements of transmitted and reflected sum-frequency generation.



Optical sum-frequency spectroscopy (SFS) has been developed into a powerful and versatile tool for surface and interface studies in past decades, as evidenced by the large number of review papers on the subject.[1−9] Second harmonic generation (SHG) is considered a special case of sum-frequency generation (SFG). It relies on the fact that the surface (interface) and bulk generally have different symmetries, such that, with the proper choice of input and output polarization combination, the electric-dipole-allowed bulk contribution to SFG can be suppressed and the corresponding surface contribution relatively enhanced. However, the electric-quadrupole and magnetic-dipole contributions of the bulk to SFG are always allowed and cannot generally be ignored, but this point has not been emphasized enough in the literature. In many reports, such a contribution to reflected SFG from a surface or interface is omitted or deemed negligible and ignored. This is perhaps because the basic theory of SFG from a surface in its more complex form has not attracted due attention of researchers. For future development and applications of SFS, this is certainly a situation that should be reversed.

The basic theory of surface SFG/SHG was developed in the early days of nonlinear optics.[10−12] It modeled an interfacial system as a three-layer system shown in Figure 1; the interfacial layer sandwiched between the two semi-infinite bulk media was much thinner than a wavelength. SF/SH radiation from the induced nonlinear polarizations in the interfacial system was obtained from solution of the wave equation with proper boundary conditions. It was believed that the nonlinearity of the interfacial layer was dominated by the electric-quadrupole contribution due to rapid variation of the fields across the interface, although the interfacial structure being noncentrosymmetric might also contribute.[11] The bulk nonlinearity was assumed to be electric-dipole-forbidden, so that electric-quadrupole and magnetic-dipole contributions to the nonlinearity become dominant and SFG/SHG from the interface and that from the bulk become comparable.

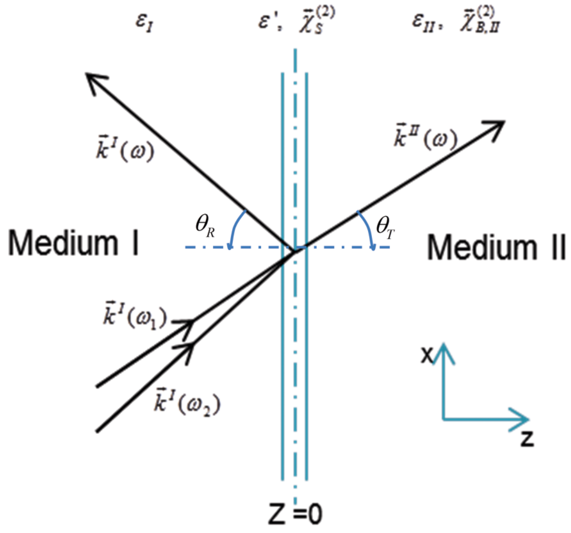


Figure 1. Schematics describing the beam geometry for sum-frequency generation from an interfacial system between media I and II.

In later years, after it was found that SFG/SHG could actually be used to probe surface adsorbates and interfacial structure,[13−16] the theory was expanded in great detail to describe how an interfacial system responds to incoming fields and contributes to SFG/SHG.[17−24] In particular, for development of SFG/SHG into a viable surface analytical tool, emphasis of the theory was on how to deduce surface nonlinearity from measurement and relate surface nonlinearity to interfacial structure. It was stressed that generally both bulk and interface nonlinearities would contribute to SFG/SHG, but this has not been taken very seriously by many researchers. Confusion stemming from the definition of bulk and surface nonlinearities has also arisen on a number of important aspects in the theory.[24,25] Presumably the reason is that not enough details of

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the formalism have been laid out in the publications and a few subtle problems in the formalism have not been ironed out. In this paper, we try to remedy the situation. We focus on the following basic issues: How do the transmitted SFG and reflected SFG from an interfacial system depend on induced nonlinear polarizations in the bulk and at the interface? How do we define the induced surface and bulk nonlinear polarizations and the corresponding nonlinear susceptibilities? Are the definitions unique, and is the surface nonlinear susceptibility clearly distinguishable from the bulk nonlinear susceptibility? If so, can the surface nonlinear susceptibility be separately deduced from measurement to provide information on the interfacial structure?

Different approaches have been used to find the output field of SFG/SHG from an interfacial system depicted in Figure 1.[11,17,18,20,22] It can be shown that both reflected and transmitted fields of SF at $\omega = \omega_1 + \omega_2$ can be expressed in the simple form[7,8]

$$\begin{aligned}
&\hat{e}\cdot\vec{E}^{\mathrm{M}}(\omega,\vec{r})\\
&\quad= \frac{\mathrm{i}2\pi\omega^2}{c^2k_z^{\mathrm{II}}}\left[\vec{e}^{\,*}(\omega)\cdot\left(\vec{P}_{\mathrm{S}}^{(2)} + \frac{\vec{P}_{\mathrm{B}}^{(2)}}{\mathrm{i}\Delta k_z^{\mathrm{II}}}\right):\vec{e}(\omega_1)\,\vec{e}(\omega_2)\right]\\
&\quad\times \mathrm{e}^{\mathrm{i}(\vec{k}^{\mathrm{M}}\cdot\vec{r}-\omega t)}\\
&\quad= \frac{\mathrm{i}2\pi\omega^2}{c^2k_z^{\mathrm{II}}}\left[\vec{e}^{\,*}(\omega)\cdot\left(\overleftrightarrow{\chi}_{\mathrm{S}}^{(2)} + \frac{\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}}{\mathrm{i}\Delta k_z^{\mathrm{II}}}\right):\vec{e}(\omega_1)\,\vec{e}(\omega_2)\right]\\
&\quad\times E^{\mathrm{I}}(\omega_1,0^-)\,E^{\mathrm{I}}(\omega_2,0^-)\,\mathrm{e}^{\mathrm{i}(\vec{k}^{\mathrm{M}}\cdot\vec{r}-\omega t)}\\
&\Delta k_z^{\mathrm{II}} = k_{1z}^{\mathrm{II}} + k_{2z}^{\mathrm{II}} - k_z^{\mathrm{II}}\\
&\vec{e}(\Omega) \equiv \overleftrightarrow{F}(\Omega)\cdot\hat{e}(\Omega)
\end{aligned}\tag{1}$$

Here, $\vec{P}_{\mathrm{S}}^{(2)}$ and $\vec{P}_{\mathrm{B}}^{(2)}$ denote the nonlinear polarizations at ω induced at the interface and in the bulk, respectively, $\overleftrightarrow{\chi}_{\mathrm{S}}^{(2)}$ and $\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}$ are the corresponding nonlinear susceptibilities, the superscript M = I or II describes in which medium a quantity is specified, the wave vectors are generally complex in the presence of absorption, $k_z^{\mathrm{II}} > 0$ and $k_z^{\mathrm{II}} < 0$ are for forward and backward SFG, respectively, and $\overleftrightarrow{F}(\Omega)$ corresponds to the transmission Fresnel coefficient from medium I to medium II for the case of reflected SFG, but equals 1 for transmitted SFG. If medium II has a finite length l, $\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}/\mathrm{i}\Delta k_z^{\mathrm{II}}$ in eq 1 for transmitted SFG should be replaced by $(\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}/\mathrm{i}\Delta k_z^{\mathrm{II}})(\mathrm{e}^{\mathrm{i}\Delta k_z^{\mathrm{II}}l} - 1)$.[26] However, for SF spectroscopy, either one or both inputs or the SF output is strongly absorbed in medium II, and if the absorption length is much shorter than the length of medium II, then eq 1 is still valid. For simplicity of presentation, we have assumed that medium I ($z < 0^-$) is linear and the dielectric constant of the interfacial layer ($0^- < z < 0^+$) is $\varepsilon' = \varepsilon_{\mathrm{II}}$. Among the various approaches to derive eq 1, the most physically transparent one is to calculate the output SF field as the sum of the radiation fields from a polarization sheet of $\vec{P}_{\mathrm{S}}^{(2)}$ at the interface and from a stack of polarization sheets of $\vec{P}_{\mathrm{B}}^{(2)}(z)\,\mathrm{d}z$ in the bulk.[20] There is, however, a rather subtle question of how $\vec{P}_{\mathrm{S}}^{(2)}$ and $\vec{P}_{\mathrm{B}}^{(2)}$, and hence $\overleftrightarrow{\chi}_{\mathrm{S}}^{(2)}$ and $\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}$, in eq 1 are defined. As we shall see later, the definitions may appear ambiguous or nonunique if we go beyond the electric-dipole approximation.

The bulk part of eq 1 is usually derived by assuming that the input fields $\vec{E}_1(\omega_1,\vec{k}_1)\exp[\mathrm{i}\vec{k}_1\cdot\vec{r} - \mathrm{i}\omega_1 t]$ and $\vec{E}_2(\omega_2,\vec{k}_2)\exp[\mathrm{i}\vec{k}_2\cdot\vec{r} - \mathrm{i}\omega_2 t]$ induce in the bulk a nonlinear polarization[11,17−20]

$$\begin{aligned}
&\vec{P}_{\mathrm{B}}^{(2)}(\vec{r},t)\\
&\quad= \overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}(\omega{=}\omega_1{+}\omega_2,\ \vec{k}{=}\vec{k}_1{+}\vec{k}_2):\vec{E}_1(\omega_1,\vec{k}_1)\,\vec{E}_2(\omega_2,\vec{k}_2)\\
&\quad\times \mathrm{e}^{\mathrm{i}(\vec{k}_1+\vec{k}_2)\cdot\vec{r}-\mathrm{i}(\omega_1+\omega_2)t}\\
&\quad= \vec{P}_{\mathrm{B}}^{(2)}(\omega{=}\omega_1{+}\omega_2,\ \vec{k}{=}\vec{k}_1{+}\vec{k}_2)\mathrm{e}^{\mathrm{i}(\vec{k}_1+\vec{k}_2)\cdot\vec{r}-\mathrm{i}(\omega_1+\omega_2)t}
\end{aligned}\tag{2}$$

and $\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}$ can be expressed in terms of the molecular nonlinear polarizability $\overleftrightarrow{\alpha}^{(2)}$ as

$$\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)} = N\left\langle \overleftrightarrow{\alpha}^{(2)}\right\rangle \tag{3}$$

where N is the molecular density and the angular brackets denote an orientation average. The wave vector dependence of $\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}$ comes in when it is necessary to go beyond the electric-dipole approximation in describing the medium response. Equation 3 however suggests that $\vec{P}_{\mathrm{B}}^{(2)}(\vec{r},t)$ may also be expressed as[24,25]

$$\begin{aligned}
&\vec{P}_{\mathrm{B}}^{(2)}(\vec{r},t)\\
&\quad= \vec{P}_{\mathrm{B}}^{(2)}(\omega{=}\omega_1{+}\omega_2,\ \vec{k}{\neq}\vec{k}_1{+}\vec{k}_2)\mathrm{e}^{\mathrm{i}(\vec{k}\cdot\vec{r}-\omega t)}\\
&\quad= \overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}(\omega{=}\omega_1{+}\omega_2,\ \vec{k}{\neq}\vec{k}_1{+}\vec{k}_2):\vec{E}_1(\omega_1,\vec{k}_1)\,\vec{E}_2(\omega_2,\vec{k}_2)\\
&\quad\times \mathrm{e}^{\mathrm{i}\Delta k_z z}\mathrm{e}^{\mathrm{i}(\vec{k}\cdot\vec{r}-\omega t)}
\end{aligned}\tag{4}$$

with $\vec{k}$ specified to be along the radiated SF direction, because in describing molecular SF or hyper Rayleigh scattering, $\overleftrightarrow{\alpha}^{(2)}$ should have the form $\overleftrightarrow{\alpha}^{(2)}(\omega{=}\omega_1{+}\omega_2,\vec{k}{\neq}\vec{k}_1{+}\vec{k}_2)$ with $\vec{k}$ along the radiated direction. The expression of $\vec{P}_{\mathrm{B}}^{(2)}(\vec{r},t)$ in eq 2 emphasizes the fact that $\vec{P}_{\mathrm{B}}^{(2)}$ is locally induced by $\vec{E}_1$ and $\vec{E}_2$, and that in eq 4 emphasizes the role $\vec{P}_{\mathrm{B}}^{(2)}$ plays as a source for SF radiation along $\vec{k}$. The two forms of $\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}(\omega,\vec{k})$, and hence the two forms of $\vec{P}_{\mathrm{B}}^{(2)}(\omega,\vec{k})$, are obviously different. For example, in the case of reflected SFG from an interfacial system, $\vec{k}$ is very different from $\vec{k}_1 + \vec{k}_2$. Following eq 1, they seemingly would result in very different SF outputs. This has led to the question or confusion of which form of $\vec{P}_{\mathrm{B}}^{(2)}$ is correct or whether both are.

The two different expressions of $\vec{P}_{\mathrm{B}}^{(2)}(\vec{r},t)$ in eqs 2 and 4 actually originate from different physical considerations. The problem arises because we are dealing with a semi-infinite bulk medium. We know that the Fourier transform of $\vec{P}_{\mathrm{B}}^{(2)}(\vec{r},t)$ to yield $\vec{P}_{\mathrm{B}}^{(2)}(\omega,\vec{k})$ must be carried out in an infinite space:

$$\vec{P}_{\mathrm{B}}^{(2)}(\omega,\vec{k}) = \left(\frac{1}{2\pi}\right)^4 \int_{-\infty}^{\infty} \vec{P}_{\mathrm{B}}^{(2)}(\vec{r},t)\mathrm{e}^{-\mathrm{i}(\vec{k}\cdot\vec{r}-\omega t)}\,\mathrm{d}\vec{r}\,\mathrm{d}t$$

In an infinite homogeneous medium, if $\vec{P}_{\mathrm{B}}^{(2)}(\vec{r},t)$ is induced by input fields $\vec{E}_1(\omega_1,\vec{k}_1)\exp[\mathrm{i}\vec{k}_1\cdot\vec{r} - \mathrm{i}\omega_1 t]$ and $\vec{E}_2(\omega_2,\vec{k}_2)\exp[\mathrm{i}\vec{k}_2\cdot\vec{r} - \mathrm{i}\omega_2 t]$, SFG can only appear in the phase-matched direction and $\vec{P}_{\mathrm{B}}^{(2)}(\omega,\vec{k}{\neq}\vec{k}_1{+}\vec{k}_2)$ vanishes. In a semi-infinite medium, however, the Fourier transform of $\vec{P}_{\mathrm{B}}^{(2)}(\vec{r},t)$ as a radiation source has Fourier components not with a single $\vec{k}$, but with a spread of $\vec{k}$. Only the one with $\vec{k}$ in the SF output direction contributes to the SFG and is retained (other Fourier components omitted) in eq 3. On the other hand, $\vec{P}_{\mathrm{B}}^{(2)}(\vec{r},t)$ of eq 2 describes the local nonlinear polarization, rather than a Fourier component of $\vec{P}_{\mathrm{B}}^{(2)}(\vec{r},t)$, induced in the medium and has its wave vector $\vec{k} = \vec{k}_1 + \vec{k}_2$ generally not in the SF output direction. From the physical point of view, we know that the end result on SFG should not depend on which expression of $\vec{P}_{\mathrm{B}}^{(2)}$ we use, as long as all induced nonlinear polarizations for SFG in the medium have been properly taken into account in the calculation. This then indicates that the difference between the two expressions of $\vec{P}_{\mathrm{B}}^{(2)}$

for the bulk must be compensated by the difference in specifying correspondingly the induced surface polarization at the surface or interface, as we shall see below.

To resolve the confusion, we need first to show explicit expressions of $\vec{P}_{\mathrm{B}}^{(2)}(\omega,\vec{k})$ and $\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}(\omega,\vec{k})$ The wave vector dependence of $\vec{P}_{\mathrm{B}}^{(2)}(\omega,\vec{k})$ that causes the confusion arises from the nonlocal response of the medium. To the first order, it comes from the electric-quadrupole and magnetic-dipole response in the multipole expansion, which has the expression[26−29]

$$\frac{\partial P_{\mathrm{B}}^{(2)}}{\partial t} = \frac{\partial P_{\mathrm{B,D}}^{(2)}}{\partial t} + c\nabla \times \vec{M}_{\mathrm{B}}^{(2)} - \frac{\partial \nabla \cdot \overleftrightarrow{Q}_{\mathrm{B}}^{(2)}}{\partial t} + \dots \tag{5}$$

where $\vec{P}_{\mathrm{B,D}}^{(2)}$, $\vec{M}_{\mathrm{B}}^{(2)}$, and $\overleftrightarrow{Q}_{\mathrm{B}}^{(2)}$ denote the induced electric-dipole polarization, magnetization, and electric-quadrupole polarization, respectively. Note that $\vec{P}_{\mathrm{B,D}}^{(2)}$also contains magnetic-dipole and electric-quadrupole terms that are induced by $\vec{E}_1(\nabla\vec{E}_2)$, $\vec{E}_2(\nabla\vec{E}_1)$, $\vec{E}_1(\nabla \times \vec{E}_2)$, and $\vec{E}_2(\nabla \times \vec{E}_1)$.[20] The corresponding equation for the Fourier components is

$$\begin{aligned}&\vec{P}_{\mathrm{B}}^{(2)}(\omega, \vec{k})\\ &\quad = \vec{P}_{\mathrm{B,D}}^{(2)}(\omega, \vec{k}) - \frac{c}{\omega}\vec{k} \times \vec{M}_{\mathrm{B}}^{(2)}(\omega, \vec{k}) - \mathrm{i}\vec{k}\cdot\overleftrightarrow{Q}_{\mathrm{B}}^{(2)}(\omega, \vec{k}) + \dots\end{aligned} \tag{6}$$

with

$$\begin{aligned}&\vec{P}_{\mathrm{BD}}^{(2)}(\omega, \vec{k})\\ &\quad = \overleftrightarrow{\chi}_{\mathrm{D}}^{(2)}(\omega{=}\omega_1{+}\omega_2){:}\vec{E}(\omega_1, \vec{k}_1)\, \vec{E}(\omega_2, \vec{k}_2)\\ &\quad + \overleftrightarrow{\chi}_{\mathrm{Q1}}^{(2)}(\omega{=}\omega_1{+}\omega_2;\vec{k}, \vec{k}_1, \vec{k}_2){:}\mathrm{i}\vec{k}_1\vec{E}(\omega_1, \vec{k}_1)\, \vec{E}(\omega_2, \vec{k}_2)\\ &\quad + \overleftrightarrow{\chi}_{\mathrm{Q2}}^{(2)}(\omega{=}\omega_1{+}\omega_2;\vec{k}, \vec{k}_1, \vec{k}_2){:}\mathrm{i}\vec{k}_2\vec{E}(\omega_1, \vec{k}_1)\vec{E}(\omega_2, \vec{k}_2)\\ &\quad + \overleftrightarrow{\chi}_{\mathrm{M1}}^{(2)}(\omega{=}\omega_1{+}\omega_2;\vec{k}, \vec{k}_1, \vec{k}_2){:}(\mathrm{i}\vec{k}_i \times \vec{E}(\omega_1, \vec{k}_1))\vec{E}(\omega_2, \vec{k}_2)\\ &\quad + \overleftrightarrow{\chi}_{\mathrm{M2}}^{(2)}(\omega{=}\omega_1{+}\omega_2;\vec{k}, \vec{k}_1, \vec{k}_2){:}\vec{E}(\omega_1, \vec{k}_1)(\mathrm{i}\vec{k}_2 \times \vec{E}(\omega_2, \vec{k}_2))]\\ &\vec{M}_{\mathrm{B}}^{(2)}(\omega, \vec{k}) = \overleftrightarrow{\chi}_{\mathrm{M}}^{(2)}(\omega{=}\omega_1{+}\omega_2;\, \vec{k}, \vec{k}_1, \vec{k}_2){:}\vec{E}(\omega_1, \vec{k}_1)\, \vec{E}(\omega_2, \vec{k}_2)\\ &\vec{Q}_{\mathrm{B}}^{(2)}(\omega, \vec{k}) = \overleftrightarrow{\chi}_{\mathrm{EQ}}^{(2)}(\omega{=}\omega_1{+}\omega_2;\, \vec{k}, \vec{k}_1, \vec{k}_2){:}\vec{E}(\omega_1, \vec{k}_1)\, \vec{E}(\omega_2, \vec{k}_2)\end{aligned} \tag{7}$$

Equation 6 can be recast into the form[20,22,24]

$$\begin{aligned}&\vec{P}_{\mathrm{B}}^{(2)}(\omega, \vec{k}) = \vec{P}_{\mathrm{B,d}}^{(2)}(\omega, \vec{k}) + \vec{P}_{\mathrm{B,q}}^{(2)}(\omega, \vec{k})\\ &\vec{P}_{\mathrm{B,d}}^{(2)}(\omega, \vec{k}) = \overleftrightarrow{\chi}_{\mathrm{B,D}}^{(2)}(\omega{=}\omega_1{+}\omega_2){:}\vec{E}_1(\omega_1, \vec{k}_1)\, \vec{E}_2(\omega_2, \vec{k}_2)\\ &\vec{p}_{\mathrm{B,q}}^{(2)}(\omega, \vec{k})\\ &\quad = \mathrm{i}[-\overleftrightarrow{\chi}_{\mathrm{B,q}}^{(2)}(\omega{=}\omega_1{+}\omega_2;\vec{k}, \vec{k}_1, \vec{k}_2){:}\vec{k}\vec{E}_1(\omega_1, \vec{k}_1)\, \vec{E}_2(\omega_2, \vec{k}_2)\\ &\quad + \overleftrightarrow{\chi}_{\mathrm{B,q1}}^{(2)}(\omega{=}\omega_1{+}\omega_2;\vec{k}, \vec{k}_1, \vec{k}_2){:}\vec{k}_1\vec{E}_1(\omega_1, \vec{k}_1)\, \vec{E}_2(\omega_2, \vec{k}_2)\\ &\quad + \overleftrightarrow{\chi}_{\mathrm{B,q2}}^{(2)}(\omega{=}\omega_1{+}\omega_2;\vec{k}, \vec{k}_1, \vec{k}_2){:}\vec{k}_2\vec{E}_1(\omega_1, \vec{k}_1)\, \vec{E}_2(\omega_2, \vec{k}_2)\end{aligned} \tag{8}$$

If we define

$$\vec{p}_{\mathrm{B}}^{(2)}(\omega, \vec{k}) \equiv \overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}(\omega, \vec{k}){:}\vec{E}_1(\omega_1, \vec{k}_1)\vec{E}_2(\omega_2, \vec{k}_2) \tag{9}$$

then we find (with $\overleftrightarrow{\chi}_{\mathrm{d}}^{(2)} \equiv \overleftrightarrow{\chi}_{\mathrm{D}}^{(2)}$)

$$\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}(\omega, \vec{k}) = \overleftrightarrow{\chi}_{\mathrm{d}}^{(2)} + \mathrm{i}[-\overleftrightarrow{\chi}_{\mathrm{B,q}}^{(2)}\cdot\vec{k} + \overleftrightarrow{\chi}_{\mathrm{B,q1}}^{(2)}\cdot\vec{k}_1 + \overleftrightarrow{\chi}_{\mathrm{B,q2}}^{(2)}\cdot\vec{k}_2] \tag{10}$$

In the above derivation, $\omega = \omega_1 + \omega_2$, but we did not specify $\vec{k} = \vec{k}_1 + \vec{k}_2$. We see that $\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}(\omega,\vec{k}{=}\vec{k}_1{+}\vec{k}_2)$ is obviously different from $\overleftrightarrow{\chi}_{\mathrm{B}}^{(2)}(\omega,\vec{k}{\neq}\vec{k}_1{+}\vec{k}_2)$. They would contribute to SFG differently. However, as we shall see below, the difference will be reconciled if contribution from the interfacial layer to SFG is properly taken into account.

To find the interfacial contribution to SFG, we copy the approach and derivation given in refs 20 and 22. The interfacial layer is not infinitesimally thin, but has a finite layer thickness. The fields and the response coefficients should vary smoothly across the interfacial layer from $z = 0^-$ to $z = 0^+$ so that $\vec{E}(\Omega) = \vec{E}(\Omega, z)$, $\varepsilon(\Omega) = \varepsilon(\Omega, z)$, and $\overleftrightarrow{\chi}^{(2)}(\Omega, z)$. We express the field at frequency Ω as

$$\begin{aligned}\vec{E}(\Omega, z) \equiv\ & f_x(\Omega, z)E_x^{\mathrm{II}}(\Omega, z{=}0^+)\hat{x}\\ & + f_y(\Omega, z) \times E_y^{\mathrm{II}}(\Omega, z{=}0^+)\hat{y}\\ & + f_z(\Omega, z)E_z^{\mathrm{II}}(\Omega, z{=}0^+)\hat{z}\end{aligned} \tag{11}$$

with $f_x(\Omega,z) = f_y(\Omega,z) = 1$ and $f_z(\Omega,z) = \varepsilon_z(\Omega,z)/\varepsilon_z^{\mathrm{II}}(\Omega,0^+) = \varepsilon(\Omega,z)/\varepsilon_{\mathrm{II}}(\Omega)$. We can also define a continuously varying bulk nonlinear polarization $\vec{P}_{\mathrm{B}}^{(2)}$ across the interfacial layer. The expression of $\vec{P}_{\mathrm{B}}^{(2)}(\omega,z)$ can be obtained following a similar derivation that leads to $\vec{P}_{\mathrm{B}}^{(2)}$ in eq 8, but because of the rapid variation of the field amplitudes across the interface, we should replace $\mathrm{i}\vec{k}_\alpha\vec{E}_\alpha$ (which comes from the $\nabla\vec{E}_\alpha$ operation) in eq 8 by $\hat{z}(\partial/\partial z)$. We find in the interfacial layer

$$\begin{aligned}\vec{P}_{\mathrm{B}}^{(2)}(\omega, z) =\ & \overleftrightarrow{\chi}_{\mathrm{d}}^{(2)}(\omega, z){:}\vec{E}(\omega_1, z)\, \vec{E}(\omega_2, z)\\ & - \frac{\partial}{\partial z}[\overleftrightarrow{\chi}_{\mathrm{q}}^{(2)}(\omega, z){:}\vec{E}(\omega_1, z)\, \vec{E}(\omega_2, z)\hat{z}]\\ & + \overleftrightarrow{\chi}_{\mathrm{q1}}^{(2)}(\omega, z){:}\left[\frac{\partial}{\partial z}\vec{E}(\omega_1, z)\right]\vec{E}(\omega_2, z)\hat{z}\\ & + \overleftrightarrow{\chi}_{\mathrm{q2}}^{(2)}(\omega, z){:}\vec{E}(\omega_1, z)\left[\frac{\partial}{\partial z}\vec{E}(\omega_2, z)\right]\hat{z}\end{aligned} \tag{12}$$

We then define the surface nonlinear polarization $\vec{P}_{\mathrm{S}}^{(2)}$ and surface nonlinear susceptibility $\overleftrightarrow{\chi}_{\mathrm{S}}^{(2)}$ through the relations

$$\begin{aligned}&\vec{E}^*(\omega)\cdot\vec{P}_{\mathrm{S}}^{(2)} \equiv \int_{\mathrm{int}} \vec{E}^*(\omega, z)\cdot\vec{P}_{\mathrm{B}}^{(2)}(\omega, z)\, \mathrm{d}z\\ &\vec{P}_{\mathrm{S}}^{(2)}(\omega) = \overleftrightarrow{\chi}_{\mathrm{S}}^{(2)}{:}\vec{E}_1(\omega_1)\vec{E}_2(\omega_2) \quad \text{at} \quad z = 0\end{aligned} \tag{13}$$

and obtain

$$\begin{aligned}\chi_{\mathrm{S},ijk}^{(2)} =\ & \int_{\mathrm{int}} \Big\{f_i(\omega, z)\chi_{\mathrm{d},ijk}^{(2)}f_j(\omega_1, z)\, f_k(\omega_2, z)\\ & - \frac{\partial}{\partial z}f_i(\omega, z)\chi_{\mathrm{q},ijkz}^{(2)}f_j(\omega_1, z)\, f_k(\omega_2, z)\\ & + f_i(\omega, z)\chi_{\mathrm{q1},ijkz}^{(2)}\frac{\partial f_j(\omega_1, z)}{\partial z}f_k(\omega_2, z)\\ & + f_i(\omega, z)\chi_{\mathrm{q2},ijkz}^{(2)}f_j(\omega_1, z)\frac{\partial f_k(\omega_2, z)}{\partial z}\Big\}\, \mathrm{d}z\\ & - \chi_{\mathrm{IIq},ijkz}^{(2)}(\omega, z{=}0^+)\end{aligned} \tag{14}$$

Here, $\overleftrightarrow{\chi}_{\mathrm{S}}^{(2)}$ does not depend on $\vec{k}$ since the interfacial response is evaluated at $z = 0$. The electric-quadrupole and magnetic-dipole responses appear through rapid field variation across the interface. They will vanish if the refractive indices of media I and II are matched.[17,30] It is interesting to note that the last term in eq 12 refers to a quantity at $z = 0^+$ in medium II and therefore is obviously a part of the bulk contribution.[20,22] The corresponding term from medium I is absent because we assume medium I has no nonlinearity.

As seen in eq 1, the SF output field arises from an effective surface nonlinear susceptibility (omitting the supersubscript II that denotes quantities in medium II):

$$\overleftrightarrow{\chi}^{(2)}_{\mathrm{S,eff}} = \overleftrightarrow{\chi}^{(2)}_{\mathrm{S}} + \frac{\overleftrightarrow{\chi}^{(2)}_{\mathrm{B}}}{\mathrm{i}\Delta k_z} \tag{15}$$

Since both surface and bulk contributions to SFG always appear together, there have been repeated discussions in the literature on whether the two can be uniquely defined and separately deduced from measurement.[20,24,25,31−35] Here, we show that indeed they can. If we go back to the expression of $\overleftrightarrow{\chi}^{(2)}_{\mathrm{B}}(\omega,\vec{k}\neq\vec{k}_1+\vec{k}_2)$ in eq 10, we can easily show that it can be rewritten as

$$\begin{aligned}\overleftrightarrow{\chi}^{(2)}_{\mathrm{B}}(\omega, \vec{k}\neq\vec{k}_1+\vec{k}_2, \vec{k}_1, \vec{k}_2) &= \overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}} + i\overleftrightarrow{\chi}^{(2)}_{\mathrm{BS}}\Delta k_z\\ \overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}} &= \overleftrightarrow{\chi}^{(2)}_{\mathrm{B}}(\omega, \vec{k}=\vec{k}_1+\vec{k}_2, \vec{k}_1, \vec{k}_2)\\ \overleftrightarrow{\chi}^{(2)}_{\mathrm{BS}} &= \overleftrightarrow{\chi}^{(2)}_{q}\cdot\hat{z}\end{aligned} \tag{16}$$

We can also rewrite $\overleftrightarrow{\chi}^{(2)}_{\mathrm{S}}$ in eq 14, with $\vec{f}(\Omega, z) \equiv f_x(\Omega, z)\hat{x} + f_y(\Omega, z)\hat{y} + f_z(\Omega, z)\hat{z}$, as

$$\begin{aligned}\overleftrightarrow{\chi}^{(2)}_{\mathrm{S}} &= \overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}} - \overleftrightarrow{\chi}^{(2)}_{\mathrm{BS}}\\ \overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}} &= \int_{\mathrm{int}}\Big\{\vec{f}(\omega, z)\cdot\overleftrightarrow{\chi}^{(2)}_{\mathrm{d}}:\vec{f}(\omega_1, z)\vec{f}(\omega_2, z)\\ &\quad - \frac{\partial}{\partial z}\vec{f}_i(\omega, z)\cdot\overleftrightarrow{\chi}^{(2)}_{\mathrm{q}}:\vec{f}(\omega_1, z)\vec{f}(\omega_2, z)\\ &\quad + \vec{f}(\omega, z)\cdot\overleftrightarrow{\chi}^{(2)}_{\mathrm{q1}}:\frac{\partial\vec{f}(\omega_1, z)}{\partial z}\vec{f}(\omega_2, z)\\ &\quad + \vec{f}(\omega, z)\cdot\overleftrightarrow{\chi}^{(2)}_{\mathrm{q2}}:\vec{f}(\omega_1, z)\frac{\partial\vec{f}(\omega_2, z)}{\partial z}\Big\}\,\mathrm{d}z\end{aligned} \tag{17}$$

We then have, with the bulklike term $\overleftrightarrow{\chi}^{(2)}_{\mathrm{BS}}$ redistributed in $\overleftrightarrow{\chi}^{(2)}_{\mathrm{S,eff}}$

$$\overleftrightarrow{\chi}^{(2)}_{\mathrm{S,eff}} = \overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}} + \frac{\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}}{\mathrm{i}\Delta k_z} \tag{18}$$

where $\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}$ is independent of Δk_z. Now that $\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}(\omega)$ is independent of the bulk, it is clearly a true surface property, while $\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}(\omega,\vec{k}=\vec{k}_1+\vec{k}_2)$ following its definition is clearly a true bulk property. We note that $\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}$ and $\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}$ uniquely defined in eqs 16 and 17 are also unique from the microscopic point of view, i.e., independent of the choice of molecular center, as discussed in ref 25.

One can deduce $\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}$ and $\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}$ separately from measurements of forward and backward SFG that yield

$$\begin{aligned}[\overleftrightarrow{\chi}^{(2)}_{\mathrm{S,eff}}]_{\mathrm{R}} &= \overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}} + \frac{\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}}{\mathrm{i}\Delta k_{\mathrm{R},z}}\\ [\overleftrightarrow{\chi}^{(2)}_{\mathrm{S,eff}}]_{\mathrm{T}} &= \overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}} + \frac{\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}}{i\Delta k_{\mathrm{T},z}}\end{aligned} \tag{19}$$

where $\Delta k_{\mathrm{R},z}$ and $\Delta k_{\mathrm{T},z}$ are known from the linear optical properties of the medium. This has been demonstrated in ref 32. For an order-of-magnitude estimate on the relative value of the bulk and surface terms in eq 19, we notice that usually for SF spectroscopy on media with inversion symmetry[22]

$$\begin{aligned}&|\chi^{(2)}_{\mathrm{SS}}| \approx |\overleftrightarrow{\chi}^{(2)}_{\mathrm{d}}|d \approx \left|\frac{\overleftrightarrow{\chi}^{(2)}_{\mathrm{q}}}{a}\right|d\\ &|\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}| \approx |k\overleftrightarrow{\chi}^{(2)}_{\mathrm{q}}|\\ &|\Delta k_{\mathrm{R},z}| \approx |k| \qquad |\Delta k_{T,z}| \approx \beta\end{aligned}$$

where d is the interfacial layer thickness, a is the relevant electron orbit size, and $1/\beta$ is the absorption length. We then find $|\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}/\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}/\Delta k_z)|_{\mathrm{R}} \approx d/a$ and $|\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}/(\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}/\Delta k_z)|_{\mathrm{T}} \approx (\beta/k)(d/a)$. Since d is larger than a, we expect $\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}$ to be larger than $\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}$ for reflected SFG. For allowed vibtational resonances, we often find $\beta/k \approx 10$ and expect $\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}$ to be smaller than $\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}$ for transmitted SFG. In many cases, such as water and silica, the bulk contribution appears to be negligible in the reflected SFG. In general, however, there is no reliable theory that can predict if the bulk contribution is negligible. One then has to rely on measurements of both forward and backward SFG to deduce $\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}$ for an interface.

We note that the above discussion can be readily extended to more general, although less interesting, cases of media with long absorption lengths. All it takes is to replace $\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}$ by $(\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}})/\mathrm{i}\Delta k_z)(\mathrm{e}^{\mathrm{i}\Delta k_z l} - 1)$ in eq 19 and include in $\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}$ the contribution of the other interface at l. With l, $\Delta k_{\mathrm{R},z}$, and $\Delta k_{\mathrm{T},z}$ known, again $\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}$ and $\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}$ can in principle be separately deduced from reflected and transmitted SFG measurements.

We have presented here a detailed description of the basic theory of SFG from an interfacial system. It is seen that there is some ambiguity in defining the nonlinear polarization and susceptibility of a bulk when electric-quadrupole and magnetic-dipole contributions have to be taken into account. However, the directly measurable effective surface nonlinear susceptibility, $\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS,eff}}$, is composed of a true bulk term and a true surface term, and the two can be separately deduced from measurements of forward and backward SFG. The true surface nonlinear susceptibility can then provide unequivocal information about the interfacial structure. Recently, there has been increasing interest in simulating surface SF vibrational spectra to compare with measured ones. However, calculations, most of which use molecular dynamic simulation, generally focus only on the electric-dipole contribution to the surface susceptibility (the $\overleftrightarrow{\chi}^{(2)}_{\mathrm{d}}$ term in $\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}$ of eq 17), while experiments measure directly not $\overleftrightarrow{\chi}^{(2)}_{\mathrm{d}}$ or $\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}$, but $\overleftrightarrow{\chi}^{(2)}_{\mathrm{S,eff}}$. From what we discuss here, it is clear that, to have a fair comparison with experiment, the calculation should include the electric-quadrupole and magnetic-dipole contributions from $\overleftrightarrow{\chi}^{(2)}_{\mathrm{BB}}$ unless they can be proven negligible, or it should compare with the deduced spectra of $\overleftrightarrow{\chi}^{(2)}_{\mathrm{SS}}$. Electric-quadrupole contribution to bulk nonlinearity has recently been formulated and is supposedly ready to be employed in computation.[36]

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Notes

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