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ABSTRACT

The basic theory of sum-frequency generation (SFG) is revisited. A rigorous derivation showing that linear optical transmission and reflection at an interface result from the interference of the incident wave and induced radiation wave in a medium is presented. The derivation is extended to SFG in a medium with a finite interface layer to see how SFG evolves. Detailed description on interface vs bulk and electric dipole (ED) vs electric quadrupole (EQ) contribution to SFG are provided with essentially no model dependence, putting the theory of SFG on a solid ground and removing possible existing confusions. Electric-quadrupole contributions to SFG from the interface and bulk are discussed. It is seen that there is a relevant bulk EQ contribution intrinsically inseparable in measurement from the interface ED contribution but plays a major role among all EQ contributions; its importance relative to the ED part can only be judged by referring to the established reference cases.

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I. INTRODUCTION

Second-harmonic and sum-frequency generation (SHG/SFG) spectroscopy has become a powerful surface analytical tool for surface studies in many disciplines.[1–8] It is based on the simple idea that optical responses of a surface and bulk of a medium follow different selection rules. In particular, for media with inversion symmetry, SHG/SFG is electric-dipole (ED) forbidden in the bulk, but at a surface or interface, the symmetry is naturally broken. This leads to strong suppression of the process in the bulk, leaving it to stand out at the surface. The underlying theory for SHG/SFG as a surface probe was worked out in early days[9] and has been reformulated over the years and adopted to analyze experimental results.[10–16] However, there are always confusions on a number of issues: What is the proper way to describe an interfacial layer as the division between the surface and the bulk of a medium is generally vague? Should it be treated as a thin dielectric layer with a specific refractive index? What are the appropriate Fresnel coefficients to be used to relate measured nonlinear susceptibilities with the intrinsic ones? Is the electric-dipole (ED)-forbidden, but electric-quadrupole (EQ)-allowed, bulk contribution to SHG/SFG negligible or not? Is the EQ contribution to SHG/SFG from the interfacial layer more important?

When can the interface ED contribution to SHG/SFG be considered dominant over all EQ contributions?

The confusions arise because of our lack of detailed microscopic understanding of the process. In this paper, we revisit the basic theory for surface SFG (with SHG taken as a special case of SFG), starting from the microscopic origin of wave transmission, reflection, and mixing. It is known physically that such processes are all results of radiation from polarization induced in media by incoming waves and interference between the incoming and induced radiation waves. Fearn *et al.*[17,18] showed that because of interference, an optical wave normally incident on an abrupt interface between air and a semi-infinite medium is transformed into transmitted and reflected waves right at the interface with the well-known Fresnel coefficients; that is, there is no finite transition region around the interface to establish transmission and reflection. We extend their derivation to the general cases of linear transmission and reflection of S- and P-polarized inputs at an oblique incidence angle, as well as SFG from a semi-infinite medium, with a finite interface layer between two media. For simplicity, we limit our discussion to isotropic and cubic media. The derivation provides a realistic model-independent description of SFG from the surface and bulk and allows us to put the theory of SFG on a firm basis. While many

steps of the derivations and the final results are not very different from what already exist in the literature, the previous loose ends are tightened up in the description. In particular, we now have a microscopic understanding on how SFG develops in a medium and are able to remove a great deal of confusions regarding surface vs bulk contributions and ED vs EQ contributions to SFG.

In the following, we start, in Sec. II, by presenting a rigorous derivation illustrating that linear transmission and reflection of optical waves are the result of interference between the incident and induced radiation waves and occur right at the interface with the proper Fresnel coefficients. We then review, in Sec. III, the theory of SFG as a result of radiation induced nonlinearly in a medium by two input waves and show how it develops in the medium. Our particular interest is on bulk media with inversion symmetry such that electric quadrupole nonlinearity is solely responsible for SFG in the bulk. Section IV describes the surface contribution to SFG from an interface layer defined by a range of significant variation of the optical dielectric constant. In general, both the electric dipole (ED) and electric quadrupole (EQ) nonlinearities of the interface layer could be important, and their contributions to SFG are larger than the nominal bulk EQ contribution. In Sec. V, different surface and bulk contributions to SFG are compared. It is seen that while the nominal bulk EQ contribution can be made negligible in the experiment, the surface nonlinear susceptibility measured always contains an effective bulk EQ contribution that is intrinsically inseparable from the interfacial ED contribution but is a major part of the overall EQ contribution. We then discuss how, in practice, we can use established cases as references to see whether SFG as a probe for various interfacial systems is surface specific or not. Finally, Sec. VI summarizes the discussion and gives a perspective on SF spectroscopy. In the Appendix, we show that surface contribution and nominal EQ bulk contribution to SFG can be separately deduced from measurements.

II. LINEAR TRANSMISSION AND REFLECTION AT A PLANE INTERFACE

To lay the ground work for a microscopic theory of SFG, we present here a derivation, following Fearn $et\ al.$,[17] that shows linear transmission and reflection at an interface result from interference between the incident wave and the induced radiation wave in a medium. From elementary electrodynamics,[19] it is known that the radiation field, $\vec{E}_R(\omega, \vec{k}, \vec{r}, z')$, with wave vector $\vec{k}$ and frequency ω, observed at position $\vec{r}$ from a polarization sheet of $\vec{P}(\omega, \vec{k}_s, z')\Delta z'$ $= |\vec{P}|\Delta z' e^{i\vec{k}_s \cdot \vec{r}' - i\omega t}$ at z' in a uniform medium ($z' > 0$), is given by

$$\vec{E}_R(\omega, \vec{k}, \vec{r}, z') = \frac{i2\pi\omega^2}{c^2 k_z} i\vec{k} \times \left[i\vec{k} \times \vec{P}(\omega, \vec{k}_s, z')\Delta z' e^{i\vec{k} \cdot (\vec{r} - z'\hat{z})} \right]. \quad (1)$$

(note that $\vec{k} \neq \vec{k}_s$). The field observed at $\vec{r}$ from the whole stack of polarization sheets in a semi-infinite medium ($z > 0$) is

$$\vec{E}_p(\omega, \vec{r}) = \int_0^\infty \vec{E}_R(\omega, \vec{r}, z')dz'$$

$$= \int_0^\infty \frac{i2\pi\omega^2}{c^2 k_z} i\vec{k} \times [i\vec{k} \times \vec{P}(\omega, \vec{k}_s, z')]e^{i\vec{k} \cdot (\vec{r} - z'\hat{z})} dz'. \quad (2)$$

When a wave, $\vec{E}_i^I(\omega, \vec{k}^I, z)$, from medium I is incident at an angle θ_I on an abrupt interface ($z = 0$) between media I and II with dielectric constants $\varepsilon_I(\omega)$ and $\varepsilon_{II}(\omega)$, respectively,[Fig. 1(a)] the transmitted field in medium II, $\vec{E}_t^{II}(\omega, \vec{k}^{II}, z)$, induces a linear polarization $\vec{P}(\omega, \vec{k}^{II}, z) = \frac{1}{4\pi}(\varepsilon_{II}^{(1)} - \varepsilon_{II}^{(1)})\vec{E}(\omega, \vec{k}^{II}, z)$ in medium II, with $\varepsilon_I(\omega)$ of medium I serving as the reference background. The transmitted field in medium II should be the sum of the incident field and induced radiation field from $\vec{P}(\omega, \vec{k}^{II}, z)$, with medium I as the background, and has the mathematical expression

$$\vec{E}_t^{II}(\omega, z) = \vec{\mathcal{E}}_t^{II}(\omega)e^{ik_z^{II}z}e^{i(k_x x - \omega t)}$$

$$= \vec{E}_i^I(\omega, z) + \vec{E}_p(\omega, z),$$

$$\vec{E}_i^I(\omega, z) = \vec{\mathcal{E}}_i^I(\omega)e^{ik_z^I z}e^{i(k_x x - \omega t)},$$

$$E_p(\omega, z) = \int_0^\infty \frac{i2\pi\omega^2}{c^2 k_z^I} i\hat{k}$$

$$\times [i\hat{k} \times (\varepsilon_{II} - \varepsilon_I)\vec{\mathcal{E}}_t^{II}(\omega)e^{ik_z^{II}z'}]e^{ik_z^I|z-z'|}e^{i(k_x x - \omega t)} dz'. \quad (3)$$

FIG. 1. (a) Beam geometry for linear transmission and reflection at an interface ($z = 0^-$ to 0^+) between two media, I and II, with optical dielectric constants ε_I and ε_{II}, respectively. (b) Beam geometry for sum-frequency generation at the interface described in (a), but medium II is nonlinearly active with nonlinear susceptibility $\overleftrightarrow{\chi}_B^{(2)}$. The input beams at ω_1 and ω_2 have wave vectors $\vec{k}_1^{II}$ and $\vec{k}_2^{II}$ in medium II, respectively, and the SF outputs in transmission and reflection have wave vectors $\vec{k}_3^{II}$ in medium II and $\vec{k}_3^I$ in medium I.

For an S-polarized input, we have $\vec{E}_i^I(\omega,z)$ along $\hat{y}$ and

$$E_{p,y}(\omega,z) = \frac{ik^I(\varepsilon_{II}-\varepsilon_I)}{2\varepsilon_I\cos\theta_I}\left[e^{ik_z^I z}\int_0^z \varepsilon_{t,y}^{II}(\omega)e^{i(k_z^{II}-k_z^I)z'}\,dz' + e^{-ik_z^I z}\int_z^\infty \varepsilon_{t,y}^{II}(\omega)e^{i(k_z^{II}+k_z^I)z'}\,dz'\right]e^{i(k_x x-\omega t)}$$

$$= \frac{ik^I(\varepsilon_{II}-\varepsilon_I)}{2\varepsilon_I\cos\theta_I}\left[\frac{1}{i(k_z^{II}-k_z^I)}(e^{ik_z^{II}z}-e^{ik_z^I z}) - \frac{1}{i(k_z^{II}+k_z^I)}e^{ik_z^{II}z}\right]\varepsilon_{t,y}^{II}(\omega)e^{i(k_x x-\omega t)}$$

$$= \frac{k^I(\varepsilon_{II}-\varepsilon_I)}{2\varepsilon_I\cos\theta_I}\left[\frac{-1}{(k_z^{II}-k_z^I)}e^{ik_z^I z} + \frac{2k_z^I}{(k_z^{II})^2-(k_z^I)^2}e^{ik_z^{II}z}\right]\varepsilon_{t,y}^{II}(\omega)e^{i(k_x x-\omega t)}. \tag{4}$$

We then find from Eq. (3)

$$E_{t,y}^{II}(\omega,z) = \varepsilon_{t,y}^{II}(\omega)e^{ik_z^{II}z'}e^{i(k_x x-\omega t)}$$

$$= \left[\varepsilon_{i,y}^I(\omega) - \frac{k^I(\varepsilon_{II}-\varepsilon_I)}{2\varepsilon_I\cos\theta_I}\frac{1}{(k_z^{II}-k_z^I)}\varepsilon_{t,y}^{II}(\omega)\right]e^{ik_z^I z}e^{i(k_x x-\omega t)}$$

$$+ \frac{k^I(\varepsilon_{II}-\varepsilon_I)}{2\varepsilon_I\cos\theta_I}\frac{2k_z^I}{(k_z^{II})^2-(k_z^I)^2}\varepsilon_{t,y}^{II}(\omega)e^{ik_z^{II}z}e^{i(k_x x-\omega t)}. \tag{5}$$

For the above equation to be valid, we must have[17]

$$\frac{k^I(\varepsilon_{II}-\varepsilon_I)}{2\varepsilon_I\cos\theta_I}\frac{2k_z^I}{(k_z^{II})^2-(k_z^I)^2} = 1,$$

$$\varepsilon_{i,y}^I(\omega) - \frac{k^I(\varepsilon_{II}-\varepsilon_I)}{2\varepsilon_I\cos\theta_I}\frac{1}{(k_z^{II}-k_z^I)}\varepsilon_{t,y}^{II}(\omega) = 0. \tag{6}$$

With medium I serving as the known background with $k^I = \omega n_I/c$ given, the first equation of Eq. (6) leads to $k^{II} = \omega n_{II}/c$, and the second yields $\varepsilon_{t,y}^{II}(\omega) = F_{t,y}^{I-II}\varepsilon_{i,y}^I(\omega)$, with $F_{t,y}^{I-II} = [2k_z^I/(k_z^I+k_z^{II})] = 2n_I\cos\theta_I/(n_I\cos\theta_I+n_{II}\cos\theta_{II})$ that can be identified as the transmission Fresnel coefficient. Both are familiar results we should have expected. The field of the reflected wave into medium I is from all induced radiation in medium II,

$$E_{r,y}(\omega,z<0) = E_{p,y}(\omega,z<0) = \int_0^\infty \frac{i2\pi\omega^2}{c^2 k_z^I}(\varepsilon_{II}-\varepsilon_I)\varepsilon_{t,y}^{II}(\omega)e^{ik_z^{II}z'}e^{ik_z^I|z-z'|}e^{i(k_x x-\omega t)}\,dz'$$

$$= \frac{ik^I(\varepsilon_{II}-\varepsilon_I)}{2\varepsilon_I\cos\theta_I}\left[e^{-ik_z^I z}\int_0^\infty \frac{-2k_z^I}{k_z^I+k_z^{II}}\varepsilon_{i,y}^I(\omega)e^{i(k_z^{II}+k_z^I)z'}\,dz'\right]e^{i(k_x x-\omega t)}$$

$$= \left(\frac{k_z^I-k_z^{II}}{k_z^I+k_z^{II}}\right)\varepsilon_{i,y}^I(\omega)e^{-ik_z^I z}e^{i(k_x x-\omega t)} = F_{r,y}^{I-II}\varepsilon_{i,y}^I(\omega)e^{-ik_z^I z}e^{i(k_x x-\omega t)}, \tag{7}$$

$$F_{r,y}^{I-II} = \frac{k_z^I-k_z^{II}}{k_z^I+k_z^{II}} = \frac{n_I\cos\theta_I-n_{II}\cos\theta_{II}}{n_I\cos\theta_I+n_{II}\cos\theta_{II}},$$

which is again expected for Fresnel reflection with $F_{r,y}^{I-II}$ being the reflection Fresnel coefficient. An important finding of the above derivation is that $\varepsilon_{t,y}^{II}(\omega)$ is independent of z for $z>0$. This indicates that Fresnel transmission and reflection must have occurred right at the sharp boundary due to interference between

the incident field and the induced radiation field in the $(z>0)$ region.

The same is true for a P-polarized wave incident on the sharp interface [Fig. 1(a)]. Following a similar derivation of Eqs. (2)–(7) for the S-polarized wave, we have for the field perpendicular to $\hat{k}^I$ in

the x–y plane

$$i\hat{k}^I \times [i\hat{k}^I \times \vec{E}_{t,P}^{II}(\omega,z)] = -\hat{k}^I \times [\hat{k}^I \times \vec{\varepsilon}_{t,P}^{II}(\omega)]e^{ik_z^{II}z'}e^{i(k_x x - \omega t)} = \vec{E}_i^I(\omega,z) + \vec{E}_P(\omega,z),$$

$$\vec{E}_i^I(\omega,z) = \vec{\varepsilon}_i^I(\omega)e^{ik_z^I z}e^{i(k_x x - \omega t)},$$

$$\vec{E}_P(\omega,z) = \int_0^\infty \frac{i2\pi\omega^2}{c^2 k_z^I} i\hat{k}^I \times [i\hat{k}^I \times (\varepsilon_{II} - \varepsilon_I)\vec{\varepsilon}_{t,P}^{II}(\omega)e^{ik_z^{II}z}]e^{ik_z^I|z-z'|}e^{i(k_x x - \omega t)}dz'$$

$$= -\frac{ik^I(\varepsilon_{II} - \varepsilon_I)}{2\varepsilon_I \cos\theta_I}\Big[e^{ik_z^I z}\int_0^z \hat{k}^I \times (\hat{k}^I \times \vec{\varepsilon}_{t,P}^{II}(\omega))e^{i(k_z^{II}-k_z^I)z'}dz' + e^{-ik_z^I z}\int_z^\infty \hat{k}^I \times (\hat{k}^I \times \vec{\varepsilon}_{t,P}^{II}(\omega))e^{i(k_z^{II}+k_z^I)z'}dz'\Big]e^{i(k_x x - \omega t)}$$

$$= -\frac{k^I(\varepsilon_{II} - \varepsilon_I)}{2\varepsilon_I \cos\theta_I}\Big[\frac{-1}{(k_z^{II}-k_z^I)}e^{ik_z^I z} + \frac{2k_z^I}{(k_z^{II})^2 - (k_z^I)^2}e^{ik_z^{II}z}\Big]\hat{k}^I \times (\hat{k}^I \times \vec{\varepsilon}_{t,P}^{II}(\omega))e^{i(k_x x - \omega t)}.$$

$$(8)$$

For the above equation to be valid, we must have $\frac{k^I(\varepsilon_{II}-\varepsilon_I)}{2\varepsilon_I \cos\theta_I}\frac{2k_z^I}{(k_z^{II})^2-(k_z^I)^2}$

$= 1$ that leads to $k^{II} = \omega n_{II}/c$ and

$$\vec{\varepsilon}_{i,P}^I(\omega) - \frac{k^I(\varepsilon_{II}-\varepsilon_I)}{2\varepsilon_I \cos\theta_I}\frac{1}{(k_z^{II}-k_z^I)}\cos(\theta_I - \theta_{II})\vec{\varepsilon}_{t,P}^{II}(\omega) = 0$$

that yields

$$\vec{\varepsilon}_{t,P}^{II}(\omega) = F_{t,P}^{I-II}\vec{\varepsilon}_{i,P}^I(\omega),$$

$$F_{t,P}^{I-II} = \frac{2\sin\theta_{II}\cos\theta_I}{\sin(\theta_I+\theta_{II})\cos(\theta_I-\theta_{II})} = \frac{2n_I\cos\theta_I}{n_I\cos\theta_{II}+n_{II}\cos\theta_I}.$$

$$(9)$$

The field of the reflected P-polarized wave is obtained from

$$\vec{E}_{r,P}(\omega,z) = \int_0^\infty \frac{i2\pi\omega^2}{c^2 k_z^I} i\hat{k}^I \times [i\hat{k}^I \times \chi_{II}^{(1)}\vec{\varepsilon}_{t,P}^{II}(\omega)e^{ik_z^{II}z'}]e^{ik_z^I(z'-z)}e^{i(k_x x - \omega t)}dz'$$

$$= -\frac{ik^I(\varepsilon_{II}-\varepsilon_I)}{2\varepsilon_I \cos\theta_I}\Big[e^{-ik_z^I z}\int_0^\infty \hat{k}^I \times (\hat{k}^I \times \vec{\varepsilon}_{t,P}^{II}(\omega))e^{i(k_z^{II}+k_z^I)z'}dz'e^{i(k_x x - \omega t)}\Big]$$

$$= -\frac{k^I(\varepsilon_{II}-\varepsilon_I)}{2\varepsilon_I \cos\theta_I}\Big[\frac{1}{(k_z^{II}+k_z^I)}\cos(\theta_I+\theta_{II})\frac{2\sin\theta_{II}\cos\theta_I}{\sin(\theta_I+\theta_{II})\cos(\theta_I-\theta_{II})}\vec{\varepsilon}_{i,P}^I(\omega)e^{-ik_z^I z}\Big]e^{i(k_x x - \omega t)}$$

$$= F_{r,p}^{I-II}\vec{\varepsilon}_{i,P}^I(\omega)e^{-ik_z^I z}e^{i(k_x x - \omega t)},$$

$$F_{r,p}^{I-II} = -\frac{\sin(\theta_{II}-\theta_I)\cos(\theta_I+\theta_{II})}{\sin(\theta_I+\theta_{II})\cos(\theta_I-\theta_{II})} = \frac{n_I\cos\theta_{II}-n_{II}\cos\theta_I}{n_I\cos\theta_{II}+n_{II}\cos\theta_I}.$$

$$(10)$$

Again, these are familiar results but indicate that Fresnel transmission and reflection occur right at the sharp boundary.

In reality, an interface can never be abrupt. The above description needs to be revised by considering an interface layer with a finite layer thickness, characterized by a structural change over a few monolayers between two media. The structural difference between the surface and the bulk of a medium is in their atomic arrangement and electronic distribution. The division between the surface and the bulk is generally vague since the transition from the bulk

to surface cannot be sharp. A dividing plane between the surface and the bulk is usually defined vaguely as the plane where the interface and neighboring bulk no longer have appreciable differences in their structures and properties. Such a definition obviously depends on the interrogating tool. For example, to probe an interface, x-ray scattering, photoemission spectroscopy, scanning microscopy, and ellipsometry all probe different structural properties and therefore deal with somewhat different interface layers. In our case of optical studies, naturally, we must focus on differences in optical

responses of the surface and bulk that arise from their structural difference.

A significant structural difference of an interface layer from the bulk media usually extends over 1–3 monolayers. The corresponding optical responses likely extend over 3–5 monolayers. On the molecular basis, the linear optical dielectric constant, $\varepsilon = 1 + 4\pi \overleftrightarrow{\chi}^{(1)} = 1 + 4\pi N \langle \overleftrightarrow{\alpha}^{(1)} \rangle$, comes from the orientation-averaged molecular polarizability, $\langle \overleftrightarrow{\alpha}^{(1)} \rangle$, where N is the molecular density and $\overleftrightarrow{\alpha}^{(1)}$ is defined to have molecular interactions with neighbors, including microscopic local field correction, taken into account. Because of changes in molecular density and arrangement, ε should vary across an interface but is expected to be of short range because of short-range molecular interactions. For an interface layer of 1–3 monolayers with a significant structural difference from neighboring bulk media, ε (or refractive index n) is expected to vary over ~5 monolayers from >90% of the bulk value (ε_{I} or n_{I}) on the one side to >90% of the bulk value ($\varepsilon_{\mathrm{II}}$ or n_{II}) on the other side. Measurements on ~1-nm thin film dielectrics also indicate that their refractive index is close to 90% of their bulk value.

Thus, for optical studies, we define the interface layer as a layer from $z = 0^-$ to $z = 0^+$, in which ε is appreciably different from that of neighboring bulks. The precise locations of 0^- and 0^+ are not important because the results do not depend on them as we shall see. With the finite interface layer, Eq. (2) for the induced radiation field becomes

$$\vec{E}_p(\omega, \vec{r}) = \left(\int_{0^-}^{0^+} dz' + \int_{0^+}^{\infty} dz' \right) \frac{2\pi\omega^2}{ic^2 k_z} \hat{k}$$

$$\times [\hat{k} \times \vec{P}(\omega, \vec{k}_s, z')] e^{i\vec{k}\cdot(\vec{r}-z'\hat{z})} e^{-i\omega t} dz'. \quad (11)$$

For linear transmission and reflection, the radiation field from the induced $\vec{P}$ in the few monolayers of the interface layer is clearly negligible in comparison with the total induced radiation field from medium II, and the earlier derivation for Fresnel transmission and reflection should still apply for $\vec{E}_t(z > 0^+)$ and $\vec{E}_r(z < 0^-)$, i.e., Fresnel transmission occurs at $z = 0^+$ and Fresnel reflection at $z = 0^-$. The exact location of 0^+ and 0^- is clearly not important. The field inside the interface layer is somewhat more complex. The sudden change in $\vec{E}$ (and $\vec{B}$) across an abrupt interface should now become a continuous variation across the finite interface layer. There are two propagating fields in the interface layer, one forward and one backward. The forward transmitted wave amplitude continuously changes from $\vec{\varepsilon}_i^I$ at $z = 0^-$ to $\vec{\varepsilon}_t^{II}$ at $z = 0^+$, and the incident angle θ_I changes to the exit angle θ_{II}. The backward reflected wave amplitude continuously changes from $\vec{\varepsilon}_r^{II} = 0$ with reflection angle θ_{II} at $z = 0^+$ to $\vec{\varepsilon}_r^I$ with reflection angle θ_I at $z = 0^-$. The total field varies in accordance with variation of $\varepsilon(z)$ in the interface layer following the field continuity rules: the field component along x or y is constant in the layer, i.e., $E_{x,y} = (E_t + E_r)_{x,y} = (E_i^I + E_r^I)_{x,y} = (E_t^{II})_{x,y}$ independent of z, and the displacement current component along z is constant, leading to $E_z(z)\varepsilon(z) = (E_t + E_r)_z \varepsilon(z) = (E_i^I + E_r^I)_z \varepsilon_I = (E_t^{II})_z \varepsilon_{II}$.

III. SUM-FREQUENCY GENERATION FROM BULK

Sum-frequency generation is a result of radiation from nonlinearly induced polarization in a medium, and the microscopic theory for the process follows a similar derivation presented in Sec. II for linear optics. As sketched in Fig. 1(b), two input waves $\vec{E}_1^I = \vec{\varepsilon}_1^I e^{i\vec{k}_1^I \cdot \vec{r} - i\omega_1 t}$ and $\vec{E}_2^I = \vec{\varepsilon}_2^I e^{i\vec{k}_2^I \cdot \vec{r} - i\omega_2 t}$ are incident from medium I. The transmitted fields induce a second-order nonlinear polarization in medium II and the interface layer, $\vec{P}^{(2)}(\omega_3, \vec{k}_s, z) = \overleftrightarrow{\chi}^{(2)}(\omega_3, \vec{k}_s, z) : \vec{E}_1(z, \omega_1)\vec{E}_2(z, \omega_2)$, at the sum frequency $\omega_3 = \omega_1 + \omega_2$ and wave vector $\vec{k}_s^{II} = \vec{k}_1^{II} + \vec{k}_2^{II}$. Coherent radiation from the stack of polarization sheets, $P^{(2)}(\omega_3, \vec{k}_s, z)\Delta z$, from $z = 0^-$ to ∞ leads to SFG in both the transmitted and reflected directions. In the multipole expansion form, the nonlinear polarization $\vec{P}^{(2)}(\omega_3, \vec{k})$ induced by $\vec{E}_1$ and $\vec{E}_2$ in a medium can be written as[1,3]

$$\vec{P}^{(2)}(\omega_3, z) = \overleftrightarrow{\chi}_d^{(2)}(z) : \vec{E}_1(\omega_1, z)\vec{E}_2(\omega_2, z)$$

$$+ \overleftrightarrow{\chi}_{q1}^{(2)}(z) : \nabla\vec{E}_1(\omega_1, z)\vec{E}_2(\omega_2, z)$$

$$+ \overleftrightarrow{\chi}_{q2}^{(2)}(z) : \vec{E}_1(\omega_1, z)\nabla\vec{E}_2(\omega_2, z)$$

$$- \nabla \cdot [\overleftrightarrow{\chi}_q^{(2)}(z) : \vec{E}_1(\omega_1, z)\vec{E}_2(\omega_2, z)] \quad (12)$$

up to the electric-quadrupole (including magnetic-dipole) terms. Here, $\overleftrightarrow{\chi}_d^{(2)}(z)$ and $\overleftrightarrow{\chi}_{qi}^{(2)}(z)$ denote electric-dipole (ED) and electro-quadrupole (EQ) nonlinear susceptibilities, respectively, with the former being a rank-3 tensor and the latter being a rank-4 tensor. On the molecular basis, $\overleftrightarrow{\chi}^{(2)}{}'$s are related to nonlinear molecular polarizabilities $\overleftrightarrow{\alpha}^{(2)}$ by $\overleftrightarrow{\chi}^{(2)} = N\langle \overleftrightarrow{\alpha}^{(2)} \rangle$; again, $\overleftrightarrow{\alpha}^{(2)}$ is defined to have neighboring molecular interactions taken into account.

We consider first the ideal case of an abrupt interface between media I and II. If $\overleftrightarrow{\chi}_d^{(2)} \equiv \overleftrightarrow{\chi}_{BD}^{(2)}$ of bulk medium II is nonvanishing, then in comparison, the bulk $\overleftrightarrow{\chi}_{qi}^{(2)}$ is negligible, and so is the nonlinearity of the interface layer. Following the derivation in Eqs. (2)–(4) with $\vec{P}^{(2)}(\omega_3, z) = \overleftrightarrow{\chi}_{BD}^{(2)} : \vec{E}_1(\omega_1, z)\vec{E}_2(\omega_2, z)$ replacing $\vec{P}$ and having $\vec{k}_3^{II} \perp \vec{E}^{II}(\omega_3) \propto \vec{P}^{(2)}(\omega_3)$ so that $\hat{k}_3^{II} \times [\hat{k}_3^{II} \times \vec{P}^{(2)}(\omega_3)] = -\vec{P}^{(2)}(\omega_3)$, we find the SF field generated at z in medium II to be

$$\vec{E}_B^{II}(\omega_3, z) = \frac{i2\pi\omega_3^2}{c^2 k_{3z}^{II}} \overleftrightarrow{\chi}_{BD}^{(2)} : \vec{\varepsilon}_1^{II}\vec{\varepsilon}_2^{II} e^{i(k_{3x}x - \omega_3 t)} \left[\int_0^z e^{i(k_{1z}^{II} + k_{2z}^{II})z'} e^{ik_{3z}^{II}(z-z')} dz' \right.$$

$$\left. + \int_z^\infty e^{i(k_{1z}^{II} + k_{2z}^{II})z'} e^{ik_{3z}^{II}(z'-z)} dz' \right]$$

$$= \frac{i2\pi\omega_3^2}{c^2 k_{3z}^{II}} \overleftrightarrow{\chi}_{BD}^{(2)} : \vec{\varepsilon}_1^{II}\vec{\varepsilon}_2^{II} e^{i(k_{3x}x - \omega_3 t)} \left[\frac{e^{i(k_{1z}^{II} + k_{2z}^{II})z} - e^{ik_{3z}^{II}z}}{i(k_{1z}^{II} + k_{2z}^{II} - k_{3z}^{II})} \right.$$

$$\left. - \frac{e^{i(k_{1z}^{II} + k_{2z}^{II})z}}{i(k_{1z}^{II} + k_{2z}^{II} + k_{3z}^{II})} \right], \quad (13)$$

which shows that due to interference, the SF field variation with z in medium II is, unlike the linear transmission and reflection case, quite complicated. However, at sufficiently large z such that

practically unavoidable phase fluctuations of the input fields would make $\exp\left[i\left(k_{1z}^{II} + k_{2z}^{II}\right)z\right]$ vanish, we still obtain the usual expression for SFG in transmission or in the forward direction as

$$\vec{E}_{Bt}^{II}(\omega_3, z) = \frac{i2\pi\omega_3^2}{c^2 k_{3z}^{II}} \overleftrightarrow{\chi}_{BD}^{(2)} : \vec{\boldsymbol{\varepsilon}}_1^{II} \vec{\boldsymbol{\varepsilon}}_2^{II} \frac{-e^{i(k_{3z}^{II}z + k_{3x}^{II}x - \omega_3 t)}}{i(k_{1z}^{II} + k_{2z}^{II} - k_{3z}^{II})}. \quad (14)$$

At $z = 0$, we have the expression for SFG in the reflection direction as

$$\vec{E}_{Br}^{II}(\omega_3, z = 0) = \frac{i2\pi\omega_3^2}{c^2 k_{3z}^{II}} \overleftrightarrow{\chi}_{BD}^{(2)} : \vec{\boldsymbol{\varepsilon}}_1^{II} \vec{\boldsymbol{\varepsilon}}_2^{II} \frac{-e^{i(k_{3x}^{II}x - \omega_3 t)}}{i(k_{1z}^{II} + k_{2z}^{II} + k_{3z}^{II})}. \quad (15)$$

We can recognize that $\vec{E}_{Br}^{II}(\omega_3, z = 0)$ is associated with the SF wave in the reflected direction from the expression of $\vec{E}_{Bt}^{II}(\omega_3, z)$ at small z,

$$\vec{E}_B^{II}\left(\omega_3, z \ll \frac{1}{k^{II}}\right)$$

$$\simeq \frac{i2\pi\omega_3^2}{c^2 k_{3z}^{II}} \overleftrightarrow{\chi}_{BD}^{(2)} : \vec{\boldsymbol{\varepsilon}}_1^{II} \vec{\boldsymbol{\varepsilon}}_2^{II} e^{i(k_{3x}x - \omega_3 t)} \left[1 - \frac{1 + i(k_{1z}^{II} + k_{2z}^{II})z}{i(k_{1z}^{II} + k_{2z}^{II} + k_{3z}^{II})}\right]$$

$$\simeq \frac{i2\pi\omega_3^2}{c^2 k_{3z}^{II}} \frac{-\overleftrightarrow{\chi}_{BD}^{(2)}}{i(k_{1z}^{II} + k_{2z}^{II} + k_{3z}^{II})} : \vec{\boldsymbol{\varepsilon}}_1^{II} \vec{\boldsymbol{\varepsilon}}_2^{II} e^{i(-k_{3z}^{II}z + k_{3x}x - \omega_3 t)}. \quad (16)$$

This SF wave in the reflection direction in medium II can be regarded as an incident wave onto medium I, and as described in Sec. II, the transmitted SF field into medium I should be given by

$$\vec{E}_B^I(\omega_3, z < 0^-) = \overleftrightarrow{F}^{II-I} \cdot \vec{E}_B^{II}(\omega_3, 0^+)e^{-ik_{3z}^I z + i(k_x x - \omega_3 t)}$$

$$= (k_{3z}^{II}/k_{3z}^I)\overleftrightarrow{F}^{I-II} \cdot \vec{E}_B^{II}(\omega_3, 0^+)e^{-i(k_{3z}^I z - k_x x + \omega_3 t)}. \quad (17)$$

We note that there is a reflected SF field at the interface back into medium II that should be superimposed on $\vec{E}_{Bt}^{II}(\omega_3, z)$ in medium II to form the total forward propagating SF wave.

For media with inversion symmetry, $\overleftrightarrow{\chi}_{BD}^{(2)} = 0$, SFG now comes from the bulk EQ contribution. We can find $\vec{E}_B^{II}(\omega_3, z)$ by simply replacing $\overleftrightarrow{\chi}_{BD}^{(2)}$ in Eq. (13) by the EQ bulk nonlinear susceptibility

$$\overleftrightarrow{\chi}_{BBQ}^{(2)} \equiv \overleftrightarrow{\chi}_{q1}^{(2)} \cdot i\vec{k}_1^{II} + \overleftrightarrow{\chi}_{q2}^{(2)} \cdot i\vec{k}_2^{II} - i(\vec{k}_1^{II} + \vec{k}_2^{II}) \cdot \overleftrightarrow{\chi}_{q3}^{(2)}, \quad (18)$$

which is obtained from Eq. (12) by writing $\vec{P}^{(2)}(\omega_3)$ with $\overleftrightarrow{\chi}_d^{(2)} = 0$ as $\overleftrightarrow{\chi}_{BBQ}^{(2)} : \vec{E}_1(\omega_1)\vec{E}_2(\omega_2)$ after the ∇ operation on $\vec{E}_1(\omega_1)$ and $\vec{E}_2(\omega_2)$. However, as we shall see later, the interfacial part of Eq. (11) for the SF field will produce an additional EQ term that is effectively a bulk contribution, which is generally non-negligible and actually inseparable from the interfacial ED contribution because of ambiguity in dividing ED and EQ terms in the multipole expansion.[9,10,13]

IV. SUM-FREQUENCY GENERATION FROM INTERFACE LAYER

We now consider contribution from a finite interface layer to SFG when $\overleftrightarrow{\chi}_{BD}^{(2)} = 0$. For the derivation, we still have the induced polarization given by Eq. (12). As described in Sec. II, we define the interface layer as the region where the dielectric constant varies significantly, say, from 90% of ε_I to 90% of ε_{II} over a few monolayers. Accordingly, the z components of the three fields, satisfying the relation $E_z(\omega_i, z)\varepsilon(\omega_i, z) = E_z^I(\omega_i)_z\varepsilon_I(\omega_i) = E_z^{II}(\omega_i)_z\varepsilon_{II}(\omega_i)$, vary significantly and very rapidly across the interface, greatly enhancing the EQ interfacial contribution to SFG, but their phase variation with z is negligible. We focus on reflected SFG here and define[3] $f_\alpha(\omega_j, z) \equiv E_\alpha(\omega_j, z)/E_{0,\alpha}^{II}(\omega_j)$ with $E_{0,\alpha}^{II} \equiv E_\alpha^{II}(\omega_j, z = 0^+)$ and $\alpha = x$, y, or z and use the notations $\vec{f}\vec{E}_0^{II} \equiv \hat{x}f_x E_{0,x}^{II} + \hat{y}f_y E_{0,y}^{II} + \hat{z}f_z E_{0,z}^{II}$ and $\nabla\left(\vec{f}\vec{E}_0^{II}\right) \equiv (\nabla f_x)\hat{x}E_{0,x}^{II} + (\nabla f_y)\hat{y}E_{0,y}^{II} + (\nabla f_z)\hat{z}E_{0,z}^{II}$. Because only E_z varies with z, we have $f_x = f_y = 1$. The backward propagating SF field at $\vec{r}$ in medium I generated from the interfacial layer (z = 0^- to 0^+) can be written as

$$\vec{E}_{Sr}^I(\omega_3) \equiv \frac{i2\pi\omega_3^2}{c^2 k_{3z}^{II}} \overleftrightarrow{F}^{II-I} \cdot \int_{0^-}^{0^+} \vec{f}(\omega_3, z') \cdot \vec{P}^{(2)}(\omega_3, \vec{k}_s, z')e^{i\vec{k}_3^I \cdot \vec{r} - i\omega_3 t}dz' = \frac{i2\pi\omega_3^2}{c^2 k_{3z}^{II}} \overleftrightarrow{F}^{II-I} \cdot [\overleftrightarrow{\chi}_{SD}^{(2)} + \overleftrightarrow{\chi}_{SSQ}^{(2)}]\vec{E}_{10}^{II}(\omega_1)\vec{E}_{20}^{II}(\omega_2)e^{i\vec{k}_3^I \cdot \vec{r} - i\omega_3 t},$$

$$\overleftrightarrow{\chi}_{SD}^{(2)} = \int_{0^-}^{0^+} \vec{f}(\omega_3, z') \cdot \overleftrightarrow{\chi}_d^{(2)}(z') : \vec{f}(\omega_1, z')\vec{f}(\omega_2, z')dz', \quad (19)$$

$$\overleftrightarrow{\chi}_{SSQ}^{(2)} = \int_{0^-}^{0^+} \vec{f}(\omega_3, z') \cdot \{\overleftrightarrow{\chi}_{q1}^{(2)}(z') : \nabla\vec{f}(\omega_1, z')\vec{f}(\omega_2, z') + \overleftrightarrow{\chi}_{q2}^{(2)}(z') : \vec{f}(\omega_1, z')\nabla\vec{f}(\omega_2, z')] - \nabla \cdot [\overleftrightarrow{\chi}_{q3}^{(2)}(z') : \vec{f}(\omega_1, z')\vec{f}(\omega_2, z')]\}dz'.$$

The Fresnel coefficient $\overleftrightarrow{F}^{II-I}$ appears on conversion of the field to $\vec{E}_{Sr}^I(\omega_3)$ in medium I, as in the case of Eq. (17). The last term in the integral of Eq. (19) can be transformed as

$$-\int_{0^-}^{0^+} \vec{f}(\omega_3, z')\nabla \cdot [\overleftrightarrow{\chi}_{q3}^{(2)}(z') : \vec{f}(\omega_1, z')\vec{f}(\omega_2, z')]dz' = -\int_{0^-}^{0^+} \nabla \cdot [\vec{f}(\omega_3, z') \cdot \overleftrightarrow{\chi}_{q3}^{(2)}(z') : \vec{f}(\omega_1, z')\vec{f}(\omega_2, z')]dz'$$

$$+ \int_{0^-}^{0^+} \nabla\vec{f}(\omega_3, z') : \overleftrightarrow{\chi}_{q3}^{(2)}(z') : \vec{f}(\omega_1, z')\vec{f}(\omega_2, z')]dz',$$

in which the first integral can be performed to yield $-\hat{z} \cdot \overset{\leftrightarrow}{\chi}_{q3}^{(2)}(0^+)$ because $\vec{f}(0^+) = 1$ and $\overset{\leftrightarrow}{\chi}_{q3}^{(2)}(0^-) = 0$. We show here that this term appears rigorously and naturally from the derivation, but in the literature, its presence seems to have caused much confusion and is often ignored. Actually, this is a term that cannot be theoretically and experimentally separated from $\overset{\leftrightarrow}{\chi}_{SD}^{(2)}$ because the division of the ED and EQ terms in the multipole expansion is not unique as we shall explain in Sec. V, but it is a major part of the overall EQ contributions. We can see in the above derivation that even if the interface is composed of an adsorbed molecular layer on a substrate, the $-\hat{z} \cdot \overset{\leftrightarrow}{\chi}_{q3}^{(2)}(0^+)$ term still appears but describes an EQ bulk contribution of the substrate. In this respect, it is truly an effective bulk contribution. The SF field of Eq. (19) now becomes

$$\vec{E}_{Sr}^{I}(\omega_3) = \frac{i2\pi\omega_3^2}{c^2 k_{3z}^{II}} \overset{\leftrightarrow}{F}^{II-I} \cdot \left[\overset{\leftrightarrow}{\chi}_{SD}^{(2)} - \hat{z} \cdot \overset{\leftrightarrow}{\chi}_{q3}^{(2)}(0^+) + \overset{\leftrightarrow}{\chi}_{SQ}^{(2)}\right]$$

$$\times \vec{E}_{10}^{II}(\omega_1)\vec{E}_{20}^{II}(\omega_2)e^{i\vec{k}_3^I \cdot \vec{r} - i\omega_3 t},$$

$$\overset{\leftrightarrow}{\chi}_{SQ}^{(2)} = \int_{0^-}^{0^+} \left[\overset{\leftrightarrow}{\chi}_{q1}^{(2)}(z') : \nabla\vec{f}(\omega_1, z')\vec{f}(\omega_2, z')\right. \tag{20}$$

$$+ \overset{\leftrightarrow}{\chi}_{q2}^{(2)}(z') : \vec{f}(\omega_1, z')\nabla\vec{f}(\omega_2, z') + \nabla\vec{f}(\omega_3, z')$$

$$\left. \times \overset{\leftrightarrow}{\chi}_{q3}^{(2)}(z') : \vec{f}(\omega_1, z')\vec{f}(\omega_2, z')\right]dz'.$$

The total reflected SF field is

$$\vec{E}_r^I(\omega_3) = \vec{E}_{Sr}^I(\omega_3) + \vec{E}_{Br}^I(\omega_3), \tag{21}$$

with $\vec{E}_{Sr}^I(\omega_3)$ given by Eq. (20) and $\vec{E}_{Br}^I(\omega_3)$ by Eqs. (16) and (17) with $\overset{\leftrightarrow}{\chi}_{BD}^{(2)}$ replaced by $\overset{\leftrightarrow}{\chi}_{BQQ}^{(2)}$.

Several interesting points come out of this derivation. First, $-\hat{z} \cdot \overset{\leftrightarrow}{\chi}_{q3}^{(2)}(0^+)$ appears independent of the interface layer and acts like a bulk contribution from medium II. Second, inclusion of this term into the EQ bulk contribution of medium II changes $\frac{\overset{\leftrightarrow}{\chi}_{BBQ}^{(2)}}{-i\Delta k_z^{II}}$ in Eq. (14) to $\frac{\overset{\leftrightarrow}{\chi}_{BQ}^{(2)}}{-i\Delta k_z^{II}} \equiv \frac{\overset{\leftrightarrow}{\chi}_{BBQ}^{(2)}}{-i\Delta k_z^{II}} - \hat{z} \cdot \overset{\leftrightarrow}{\chi}_{q3}^{(2)}$, with $\Delta k_z^{II} \equiv k_{1z}^{II} + k_{2z}^{II} + k_{3z}^{II}$ and

$$\overset{\leftrightarrow}{\chi}_{BQ}^{(2)} \equiv \left[\overset{\leftrightarrow}{\chi}_{q1}^{(2)} \cdot i\vec{k}_1^{II} + \overset{\leftrightarrow}{\chi}_{q2}^{(2)} \cdot i\vec{k}_2^{II} - i\vec{k}_3^{II} \cdot \overset{\leftrightarrow}{\chi}_{q3}^{(2)}\right]. \tag{22}$$

Both Eq. (20) for the interface layer and Eq. (22) for the bulk show that the three fields involved in SFG play equivalent roles as they should in a three-wave mixing process. Finally, in the expression of the SF output, all fields have reference to their values at $z = 0^+$ in medium II through the definition of $\vec{f}$. To express the SF field in the reflected direction in medium I in terms of the input fields in medium I, we can use the Fresnel coefficients for transmission from I to II to transform the fields in medium II to the counterparts in medium I. Variation of the fields in the interface layer is taken care by $\vec{f}$ instead of modifying the Fresnel coefficients.

We summarize the results here. The SF field generated in the reflected direction into medium I is given by

$$\vec{E}_3^I(\omega_3, z < 0) = \frac{i2\pi\omega_3^2}{c^2 k_{3z}^I} \overset{\leftrightarrow}{X}_{S,eff}^{(2)} : \vec{\varepsilon}_1^I(\omega_1)\vec{\varepsilon}_2^I(\omega_2)e^{-ik_{3z}^I z + ik_{3x} x - i\omega_3 t},$$

$$\overset{\leftrightarrow}{X}_{S,eff}^{(2)} \equiv \overset{\leftrightarrow}{F}^{I-II}(\omega_3) : \overset{\leftrightarrow}{\chi}_{S,eff}^{(2)} : \overset{\leftrightarrow}{F}^{I-II}(\omega_1)\overset{\leftrightarrow}{F}^{I-II}(\omega_2) = \overset{\leftrightarrow}{F}^{I-II}(\omega_3) : \left[\overset{\leftrightarrow}{\chi}_S^{(2)} - \frac{\overset{\leftrightarrow}{\chi}_{BQ}^{(2)}}{i\Delta k_z^{II}}\right] : \overset{\leftrightarrow}{F}^{I-II}(\omega_1)\overset{\leftrightarrow}{F}^{I-II}(\omega_2) = \overset{\leftrightarrow}{X}_S^{(2)} - \frac{\overset{\leftrightarrow}{X}_B^{(2)}}{i\Delta k_z^{II}},$$

$$\overset{\leftrightarrow}{\chi}_S^{(2)} = \overset{\leftrightarrow}{\chi}_{SD}^{(2)} + \overset{\leftrightarrow}{\chi}_{SQ}^{(2)},$$

$$\overset{\leftrightarrow}{\chi}_{SD}^{(2)} = \int_{0^-}^{0^+} \vec{f}(\omega_3, z) \cdot \overset{\leftrightarrow}{\chi}_d^{(2)}(z) : \vec{f}(\omega_1, z)\vec{f}(\omega_2, z)dz, \tag{23}$$

$$\overset{\leftrightarrow}{\chi}_{SQ}^{(2)} = \int_{0^-}^{0^+} \left[\vec{f}(\omega_3, z) \cdot \overset{\leftrightarrow}{\chi}_{q1}^{(2)}(z) : \nabla\vec{f}(\omega_1, z)\vec{f}(\omega_2, z) + \vec{f}(\omega_3, z) \cdot \overset{\leftrightarrow}{\chi}_{q2}^{(2)}(z) : \vec{f}(\omega_1, z)\nabla\vec{f}(\omega_2, z) + \nabla\vec{f}(\omega_3, z) \cdot \overset{\leftrightarrow}{\chi}_{q3}^{(2)}(z) : \vec{f}(\omega_1, z)\vec{f}(\omega_2, z)\right]dz,$$

$$\overset{\leftrightarrow}{\chi}_{BQ}^{(2)} \equiv \overset{\leftrightarrow}{\chi}_{q1}^{(2)} \cdot i\vec{k}_1^{II} + \overset{\leftrightarrow}{\chi}_{q2}^{(2)} \cdot i\vec{k}_2^{II} - i\vec{k}_3^{II} \cdot \overset{\leftrightarrow}{\chi}_{q3}^{(2)},$$

$$F_{xx}^{I-II} \frac{2\varepsilon_I k_z^{II}}{\varepsilon_{II} k_z^I + \varepsilon_I k_z^{II}}, F_{yy}^{I-II} = \frac{2k_z^I}{k_z^I + k_z^{II}}, F_{zz}^{I-II} = \frac{2\varepsilon_I k_z^I}{\varepsilon_{II} k_z^I + \varepsilon_I k_z^{II}}.$$

With $I_i = (n_i c/2\pi)|\vec{E}_i^I(\omega_i)|^2$, the intensity of the reflected SFG takes the form

$$I(\omega_3) = \left(\frac{8\pi^3 n^I \omega_3^4}{n_1^I n_2^I c^3 (k_z^I)^2}\right)|\hat{e} \cdot \overset{\leftrightarrow}{X}_{S,eff}^{(2)} : \hat{e}_1 \hat{e}_2|^2 I_1(\omega_1) I_2(\omega_2). \tag{24}$$

A note of caution is in order here. Because $\overset{\leftrightarrow}{\chi}_{SD}^{(2)}$ is from ED monolayers that likely occupy only a fraction of the interface layer and usually situate toward medium I, we have $\overset{\leftrightarrow}{\chi}_d^{(2)}(z)$ in the integral of $\overset{\leftrightarrow}{\chi}_{SD}^{(2)}$ significant only in a narrow range close to $z = 0^-$ with associated

$\vec{f}(\omega_i, z)$ close to $\vec{f}(\omega_i, z = 0^-)$. This effectively reduces the Fresnel coefficients on $\overset{\leftrightarrow}{\chi}_{SD}^{(2)}$ as suggested earlier in the three-layer model of SFG from an interface.[20]

V. COMPARISON OF ELECTRIC QUADRUPOLE BULK CONTRIBUTION WITH ELECTRIC DIPOLE AND QUADRUPOLE CONTRIBUTIONS TO SUM FREQUENCY GENERATION

We discuss here the relative importance of the EQ contributions, $\overset{\leftrightarrow}{\chi}_{SQ}^{(2)}$ and $\overset{\leftrightarrow}{\chi}_{BQ}^{(2)}$, with respect to $\overset{\leftrightarrow}{\chi}_{SD}^{(2)}$ in SFG and also what can be separately measured and what cannot. For SFG to be a surface spectroscopy tool, we are interested in extracting $\overset{\leftrightarrow}{\chi}_{SD}^{(2)}$ from measurement, particularly, because current theoretical calculations to simulate surface SFG spectra are limited to $\overset{\leftrightarrow}{\chi}_{SD}^{(2)}$. In many cases, $\overset{\leftrightarrow}{\chi}_{SD}^{(2)}$ can, indeed, be distinguished from $\overset{\leftrightarrow}{\chi}_{SQ}^{(2)}$ and $\overset{\leftrightarrow}{\chi}_{BQ}^{(2)}$ in the measurement. For example, $\overset{\leftrightarrow}{\chi}_{SD}^{(2)}$ may have its characteristic spectrum clearly different from $\overset{\leftrightarrow}{\chi}_{SQ}^{(2)}$ and $\overset{\leftrightarrow}{\chi}_{BQ}^{(2)}$, or the interface layer is known to possess highly ordered, strongly polar monolayers of molecules. In many other cases, however, the spectra of $\overset{\leftrightarrow}{\chi}_{SD}^{(2)}$ and $\overset{\leftrightarrow}{\chi}_{SQ}^{(2)}/\overset{\leftrightarrow}{\chi}_{BQ}^{(2)}$ are not distinguishable especially if they come from the same molecular subgroup, and $\overset{\leftrightarrow}{\chi}_{SQ}^{(2)}/\overset{\leftrightarrow}{\chi}_{BQ}^{(2)}$ may not be negligible although many reports in the literature simply assumed they were. In the following, we provide some physical argument and detailed description for estimation of $\overset{\leftrightarrow}{\chi}_{SQ}^{(2)}$ and $\overset{\leftrightarrow}{\chi}_{BQ}^{(2)}$ in comparison with $\overset{\leftrightarrow}{\chi}_{SD}^{(2)}$, considering that all of them originate from the same molecular subgroup.

We realize that $\overset{\leftrightarrow}{\chi}_{S,eff}^{(2)} = \overset{\leftrightarrow}{\chi}_{SD}^{(2)} + \overset{\leftrightarrow}{\chi}_{SQ}^{(2)} - \overset{\leftrightarrow}{\chi}_{BQ}^{(2)}/i\Delta k_z^{II}$ is the quantity usually measured in the SFG experiment with known Fresnel coefficients, but its expression in Eq. (18) can be rewritten as

$$\overset{\leftrightarrow}{\chi}_{S,eff}^{(2)} = \overset{\leftrightarrow}{\chi}_{SS}^{(2)} + \overset{\leftrightarrow}{\chi}_{BBQ}^{(2)}/i\Delta k_z^{II},$$

$$\overset{\leftrightarrow}{\chi}_{SS}^{(2)} = \overset{\leftrightarrow}{\chi}_{SD}^{(2)} + \overset{\leftrightarrow}{\chi}_{SQ}^{(2)} - \hat{z} \cdot \overset{\leftrightarrow}{\chi}_{q3}^{(2)}, \qquad (25)$$

$$\overset{\leftrightarrow}{\chi}_{BBQ}^{(2)} = \overset{\leftrightarrow}{\chi}_{BQ}^{(2)} + \hat{z} \cdot \overset{\leftrightarrow}{\chi}_{q3}^{(2)} = \overset{\leftrightarrow}{\chi}_{q1}^{(2)} \cdot i\vec{k}_1^{II} + \overset{\leftrightarrow}{\chi}_{q2}^{(2)} \cdot i\vec{k}_2^{II} - i(\vec{k}_1^{II} + \vec{k}_2^{II}) \cdot \overset{\leftrightarrow}{\chi}_{q3}^{(2)}$$

such that $\overset{\leftrightarrow}{\chi}_{SS}^{(2)}$ is independent of wave vectors, but $\overset{\leftrightarrow}{\chi}_{BBQ}^{(2)}$ is not. Thus, measurement with two different sets of $\vec{k}_1^{II}$ and $\vec{k}_2^{II}$ allows separate deduction of $\overset{\leftrightarrow}{\chi}_{SS}^{(2)}$ and $\overset{\leftrightarrow}{\chi}_{BBQ}^{(2)}$. In the Appendix, it is shown that with different beam polarization combinations, differences of some tensor elements of $\overset{\leftrightarrow}{\chi}_{qi}^{(2)}$ in $\overset{\leftrightarrow}{\chi}_{BBQ}^{(2)}$, namely, $\chi_{q1,\alpha(\bar{\beta}\alpha)\beta}^{(2)} - \chi_{q3,(\bar{\alpha}\beta)\beta\alpha}^{(2)}$, $\chi_{q2,\alpha\beta(\bar{\beta}\alpha)}^{(2)} - \chi_{q3,(\bar{\alpha}\beta)\beta\alpha}^{(2)}$, and $\chi_{q1,\alpha(\bar{\beta}\alpha)\beta}^{(2)} - \chi_{q2,\alpha\beta(\bar{\alpha}\beta)}^{(2)}$ in an explicit tensorial notation, can be extracted from measurement to provide estimated values for $\overset{\leftrightarrow}{\chi}_{qi}^{(2)}$, but $\overset{\leftrightarrow}{\chi}_{BBQ}^{(2)}$ can always be made small compared to $\overset{\leftrightarrow}{\chi}_{qi}^{(2)}$ by setting the angle between $\vec{k}_1^{II}$ and $\vec{k}_2^{II}$ small (vanished if $\vec{k}_1^{II}$ and $\vec{k}_2^{II}$ are parallel).[15] We can therefore neglect $\overset{\leftrightarrow}{\chi}_{BBQ}^{(2)}$ in our consideration and focus on $\overset{\leftrightarrow}{\chi}_{S,eff}^{(2)} = \overset{\leftrightarrow}{\chi}_{SS}^{(2)}$.

We are now left with a comparison between the ED and EQ contributions in $\overset{\leftrightarrow}{\chi}_{SS}^{(2)}$. We first compare $\overset{\leftrightarrow}{\chi}_{SQ}^{(2)}$ with $\chi_{SD}^{(2)}$ in $\overset{\leftrightarrow}{\chi}_{SS}^{(2)}$. We can simplify the expression of $\overset{\leftrightarrow}{\chi}_{SQ}^{(2)}$ in Eq. (20), knowing that only the spatial variation of f_z with z is nonvanishing ($\nabla\vec{f} = \hat{z}\partial f_z/\partial z$). In an explicit tensorial notation, the only nonvanishing EQ terms in $\overset{\leftrightarrow}{\chi}_{SQ}^{(2)}$ are those of $\chi_{q1,\alpha(\bar{z}z)\alpha}^{(2)}, \chi_{q2,\alpha\alpha(\bar{z}z)}^{(2)}$, and $\chi_{q3,(\bar{z}z)\alpha\alpha}^{(2)}$, where the bracketed $\bar{z}z$ in the subindices denote the EQ field component and its gradient along z. With $f_z(\omega_i, z) \equiv E_z(\omega_i, z)/E_{0,z}^{II}(\omega_i) = \varepsilon_{II}(\omega_i)/\varepsilon(\omega_i, z)$ and $\partial f_z(\omega_i)/\partial z = -[\varepsilon_{II}(\omega_i)/\varepsilon^2(\omega_i, z)]\partial\varepsilon(\omega_i)/\partial z$, each of the three nonvanishing $\overset{\leftrightarrow}{\chi}_{qi}^{(2)}$ terms can be expressed in terms of $\varepsilon(\omega_i, z)$. We have, for example,

$$\int_{0^-}^{0^+} f_y(\omega_3)\chi_{q1,y(\bar{z}z)y}^{(2)}(z)\frac{\partial f_z(\omega_1)}{\partial z}f_y(\omega_2)dz$$
$$= \int_{0^-}^{0^+} \chi_{q1,y(\bar{z}z)y}^{(2)}(z)\frac{-\varepsilon_{II}(\omega_1)}{\varepsilon^2(\omega_1, z)}\frac{\partial\varepsilon}{\partial z}dz.$$

If we assume that $\chi_{q1,y(\bar{z}z)y}^{(2)}(z)$ has a similar z dependence across the interface layer as $\varepsilon(\omega_i, z)$ [or $\chi^{(1)}(\omega, z)$], i.e.,

$$\chi_{q1,y(\bar{z}z)y}^{(2)}(z) = \chi_{q1,y(\bar{z}z)y}^{(2)}(0^+)$$
$$\times \{1 - [\varepsilon_{II}(\omega_1) - \varepsilon(\omega_1, z)]/[\varepsilon_{II}(\omega_1) - \varepsilon_I(\omega_1)]\},$$

we find

$$\int_{0^-}^{0^+} \chi_{q1,y(\bar{z}z)y}^{(2)}(z)\frac{-\varepsilon_{II}(\omega_1)}{\varepsilon^2(\omega_1, z)}\frac{\partial\varepsilon}{\partial z}dz$$
$$= \chi_{q1,y(\bar{z}z)y}^{(2)}(0^+)\varepsilon_{II}(\omega_1)\left[\frac{\varepsilon_I - \varepsilon_{II}}{\varepsilon_I\varepsilon_{II}} + \frac{1}{\varepsilon_I} + \frac{\log(\varepsilon_{II}/\varepsilon_I)}{\varepsilon_I - \varepsilon_{II}}\right]. \quad (26)$$

The first term comes from field variation, or $f_z(\omega_i, z)$, with z, and the next two terms come from additional spatial variation of $\chi_{q1,y(\bar{z}z)y}^{(2)}(z)$ with z. We should note that the choice of 0^- and 0^+ to define the interface layer is not critical and does not depend on any specific model. As long as the span from 0^- to 0^+ covers nearly the whole range in which optical responses vary significantly due to structure variation, the final result is the same.

For $\varepsilon_I = 1$ and $\varepsilon_{II} = 2.7$, we obtain from Eq. (26)

$$\int_{0^-}^{0^+} f_x(\omega_3)\chi_{q1,y(\bar{z}z)y}^{(2)}(z)\frac{\partial f_z(\omega_1)}{\partial z}f_y(\omega_2)dz = -0.6\chi_{q1,y(\bar{z}z)y}^{(2)}(0^+).$$

A larger difference between ε_I and ε_{II} leads to a larger negative value as expected. On the other hand, this quantity vanishes if $\varepsilon_I = \varepsilon_{II}$ as the field gradient disappears. Similarly, we obtain $\int_{0^-}^{0^+} f_y(\omega_3)\chi_{q2,yy(\bar{z}z)}^{(2)}(z)f_y(\omega_1)\frac{\partial f_z(\omega_2)}{\partial z}dz = -0.6\chi_{q2,yy(\bar{z}z)}^{(2)}(0^+)$ and $\int_{0^-}^{0^+} \frac{\partial f_z(\omega_3)}{\partial z}\chi_{q3,(\bar{z}z)yy}^{(2)}(z)f_y(\omega_1)f_y(\omega_2)dz = -0.6\chi_{q3,(\bar{z}z)yy}^{(2)}(0^+)$.

The expression of $\chi_{SS}^{(2)}$ for the SSP polarization combination as a representative case is

$$(\chi_{SS}^{(2)})_{SSP} = \chi_{SD,yyz}^{(2)} + \chi_{SQ,yy(\bar{z}z)}^{(2)} - \chi_{q3,(\bar{z}y)yz}^{(2)}$$
$$= \chi_{SD,yyz}^{(2)} - 0.6\chi_{q2,yy(\bar{z}z)}^{(2)} - \chi_{q3,(\bar{z}y)yz}^{(2)}. \quad (27)$$

We expect $|\chi_{q2}^{(2)}| < |\chi_{q3}^{(2)}|$ from their microscopic expression. Therefore, to see if $\chi_{SD}^{(2)}$ dominates over the EQ contribution $\chi_{SQ}^{(2)}$ and $\chi_{q3}^{(2)}$ in $\chi_{SS}^{(2)}$, we only need to compare $\chi_{SD}^{(2)}$ with $\chi_{q3}^{(2)}$.

It turns out that $\chi_{SD}^{(2)}$ and $\chi_{q3}^{(2)}$ actually are not separable both theoretically and experimentally, as has been pointed out repeatedly in the literature.[9,10] This is because division of ED and EQ terms in the multipole expansion is intrinsically not unique and depends, for example, on the position of the molecular center chosen on molecules.[13] A group of molecules appearing to have only EQ polarization with a particular choice of molecular center may appear to have partly EQ polarization and partly ED polarization when the center is shifted. Here, we make the division of $\chi_{SD}^{(2)}$ and $\chi_{q3}^{(2)}$ unique by defining $\chi_{SD}^{(2)}$ as solely from molecular layers with polar orientation and $\chi_{qi}^{(2)}$ (with $\left\langle \alpha_d^{(2)} \right\rangle = 0$) from regions with centro-symmetric molecular orientation distribution and $\chi_d^{(2)} = 0$, but $\chi_{SD}^{(2)}$ and $\chi_{q3}^{(2)}$ are still inseparable in measurement. To see if $\chi_{SD}^{(2)}$ dominates over $\chi_{q3}^{(2)}$, we have to resort to other means to get an estimate on $\chi_{q3}^{(2)}$. As described in the Appendix, we can separately measure, for example, $\chi_{q2,\alpha\beta(\tilde{\beta}\alpha)}^{(2)} - \chi_{q3,(\tilde{\alpha}\beta)\beta\alpha}^{(2)}$, and knowing that all $\chi_{qi}^{(2)}$ elements are likely to have the same order of magnitude, we assert $|\chi_{q3,(\tilde{\alpha}\beta)\beta\alpha}^{(2)}| \sim |\chi_{q1,\alpha(\tilde{\beta}\alpha)\beta}^{(2)} - \chi_{q3,(\tilde{\alpha}\beta)\beta\alpha}^{(2)}|$. It is also seen in the Appendix that we are not able to measure individual elements of $\chi_{qi}^{(2)}$; this is again because of ambiguity in defining EQ susceptibilities: values of individual $\chi_{qi}^{(2)}$ elements would change if the assigned molecular center is shifted, but the difference of two $\chi_{qi}^{(2)}$ elements would not.[13]

Because $\chi_{SD}^{(2)}$ and $\chi_{q3}^{(2)}$ are characteristic of molecules and, for different materials, molecular arrangements are different, we can only provide a qualitative description in comparing them. Generally, $\chi_{qi}^{(2)}$ arises from two sources, one from molecular arrangement and the other from electronic response of individual molecules. It has been shown that the former vanishes if the molecular arrangement has inversion symmetry.[1] Thus, for isotropic or cubic media, both $\chi_{SD}^{(2)}$ and $\chi_{q3}^{(2)}$ are directly related to their respective ED and EQ molecular polarizabilities, $\overset{\leftrightarrow}{\chi}_{SD}^{(2)} = \int_{0^-}^{0^+} N\overset{\leftrightarrow}{\alpha}_d^{(2)} dz = N\overset{\leftrightarrow}{\alpha}_d^{(2)} \eta_d Ml$ and $\hat{z} \cdot \overset{\leftrightarrow}{\chi}_{q3}^{(2)} = N\hat{z} \cdot \left\langle \overset{\leftrightarrow}{\alpha}_{q3}^{(2)} \right\rangle = N\hat{z} \cdot \overset{\leftrightarrow}{\alpha}_{q3}^{(2)} \eta_q$, where l is the thickness of a monolayer, M is the effective number of ED monolayers, $\left\langle \overset{\leftrightarrow}{\alpha}_d^{(2)} \right\rangle \equiv \eta_d \overset{\leftrightarrow}{\alpha}_d^{(2)}$, and $\left\langle \overset{\leftrightarrow}{\alpha}_{q3}^{(2)} \right\rangle \equiv \eta_q \overset{\leftrightarrow}{\alpha}_{q3}^{(2)}$. (Because $\overset{\leftrightarrow}{\alpha}_d^{(2)}$ refers to polarizability per molecule and NMl is the surface molecular density in an effective layer of thickness of Ml in which $\left\langle \overset{\leftrightarrow}{\alpha}_d^{(2)} \right\rangle$ is significantly different from zero, we have $\overset{\leftrightarrow}{\chi}_{SD}^{(2)} = NMl\left\langle \overset{\leftrightarrow}{\alpha}_d^{(2)} \right\rangle$). By defining $a \equiv \hat{z} \cdot \overset{\leftrightarrow}{\alpha}_{q3}^{(2)} / \overset{\leftrightarrow}{\alpha}_d^{(2)}$, we have $\chi_{SD}^{(2)}/\chi_{q3}^{(2)} = Ml\eta_d/a\eta_q$. We expect $\eta_d/\eta_q \gg 1$ if the surface layer is highly ordered in orientation, but the bulk is random. As an example, consider an isotropic material with oriented polar end groups of molecules in the interface layer. We assume, for simplicity, that $\overset{\leftrightarrow}{\alpha}_d^{(2)}$ is dominated by $\alpha_{d,\zeta\zeta\zeta}^{(2)}$ and $\overset{\leftrightarrow}{\alpha}_{q3}^{(2)}$ by $\alpha_{q3,\zeta\zeta\zeta\zeta}^{(2)}$ in the molecular coordinates of (ξ, η, ζ). With θ being the

angle between $\hat{\zeta}$ and $\hat{z}$, we have

$$\eta_d = \frac{\left\langle \alpha_d^{(2)} \right\rangle_{d,zzz}}{\alpha_{d,\zeta\zeta\zeta}^{(2)}} = \left\langle (\hat{z} \cdot \hat{\zeta})(\hat{z} \cdot \hat{\zeta})(\hat{z} \cdot \hat{\zeta}) \right\rangle_d = \left\langle \cos^3\theta \right\rangle_d,$$

$$\eta_q = \frac{\left\langle \alpha_{q3}^{(2)} \right\rangle_{q,(\hat{z}z)zz}}{\alpha_{q,\zeta\zeta\zeta\zeta}^{(2)}} = \left\langle (\hat{z} \cdot \hat{\zeta})(\hat{z} \cdot \hat{\zeta})(\hat{z} \cdot \hat{\zeta})(\hat{z} \cdot \hat{\zeta}) \right\rangle_q = \left\langle \sin^2\theta \cos^2\theta \right\rangle_q.$$

We find $\eta_q = 2/15$ for an isotropic orientation distribution and $\eta_d = 1$ and ~0.9 for an ED layer of molecules, respectively, with a $\delta(\theta = 0)$ orientation distribution and with a uniform distribution of $\hat{\zeta}$ about $\hat{z}$ from $\theta = 0$ to $\pi/6$. In such cases, we would expect $\chi_{SD}^{(2)}/\chi_{q3}^{(2)} = Ml\eta_d/a\eta_q \gg 1$ if $Ml/a > 1$. Usually, $M = 1$ or 2, l is somewhat larger than the size of the molecule, and a is a characteristic size of the molecular subgroup. For the same molecular subgroup on different molecules of different sizes, $\chi_{SD}^{(2)}/\chi_{q3}^{(2)}$ is expected to be larger for larger molecules. Unfortunately, there is no general way to evaluate a for various types of molecular subgroups. We have to resort to practical experience for a comparison of $|\chi_{SD}^{(2)}|$ and $|\chi_{q3}^{(2)}|$.

For SF vibrational spectroscopy, we can use the dangling OH stretch of the vapor/ice interface and CH_3 and CH_2 stretches of a monolayer of hydrocarbons as references. For the SSP-SFG process, for example, the former has $|\chi_{SD}^{(2)}| = 1 \times 10^{-21}$ m^2/V^2, and the latter has $|\chi_{SD}^{(2)}| = (2-3) \times 10^{-21}$ m^2/V^2.[21,22] Other stretch modes of small molecular groups such as CO_x, NO_x, and NH_x have roughly the same value of $|\chi_{SD}^{(2)}|$. For molecular groups with weaker polarity and broader orientation distribution, $|\chi_{SD}^{(2)}|$ is smaller. In contrast, $|\chi_{SQ}^{(2)}|$ for OH stretches (of water)[23] and CH_x stretches[22] are ~1.1×10^{-22} m^2/V^2 and ~$(1.5-3) \times 10^{-22}$ m^2/V^2, respectively. Nonresonant $|\chi_{qi}^{(2)}|$ values of small molecules with all frequencies in the near IR or visible are about ~1×10^{-22} m^2/V^2.[24] For molecular groups with larger electron orbits, $|\chi_{qi}^{(2)}|$ is expected to be larger although $|\chi_{SD}^{(2)}|$ may also increase. Overall, on materials with weak $\overset{\leftrightarrow}{\alpha}_d^{(2)}$ (weaker than that of the dangling OH stretch), small η_d (larger spread of polar orientation), more delocalized electron orbits, and molecular subgroups comparable in size to the whole molecule, we need to be cautious that $\chi_{SD}^{(2)}$ may not dominate over $\chi_{q3}^{(2)}$ in $\chi_{SS}^{(2)}$ or $\chi_{S,eff}^{(2)}$. Evaluation of $\chi_{q3}^{(2)}$ or employment of other approaches to assure surface specificity of reflected SFG is advised.

VI. SUMMARY AND PERSPECTIVE

A rigorous microscopic calculation is presented to show that linear optical transmission and reflection result from interference between the incoming wave and the induced electric-dipole radiation wave in transmitting through a semi-infinite medium, and the Fresnel formulas apply right at the interface. The derivation is extended to sum-frequency generation in a semi-infinite nonlinear optical medium with a finite interface layer. It describes how SFG evolves in the medium and puts the basic theory of SFG on a more solid ground. Electric-quadrupole (including magnetic-dipole) contribution to SFG that could be important in media with inversion

symmetry is properly formulated and thoroughly discussed. It can be decomposed into two parts, one depending on the wave vectors of the inputs and the other not. The former, belonging to the bulk medium, is adjustable by input beam geometry to allow separate determination of surface and bulk nonlinear susceptibilities of SFG. It can be made negligible compared with the latter. The latter, consisting of an EQ contribution from the interface layer and an effective bulk EQ contribution, appears together with the surface electric dipole contribution in the effective surface nonlinear susceptibility to be measured. The interface layer is naturally defined by the region where the optical dielectric constant varies appreciably, but a precise definition of the region is not needed. The interface EQ contribution to SFG can be described in terms of variation of the optical dielectric constant across the interface. Because of the high field gradient along the surface normal, it is comparable to or larger than the bulk EQ contribution. The interface ED contribution, usually from 1 to 2 monolayers, may or may not be significantly larger than the EQ contribution.

In comparing various contributions to SFG, it is seen that the bulk EQ contribution can be made negligible, but there is still an effective EQ term intrinsically inseparable from the surface ED contribution in measurement. This term can be considered as representative of all EQ contributions since it has a value comparable to or larger than other EQ contributions. For SFG to be ED surface-specific, we only need to see if this term is dominated over by the surface ED contribution. Unfortunately, for this comparison, there are no general rules one can refer to. We have to resort to established cases as references, such as dangling OH and terminal CH_x stretch modes on surfaces in SF vibrational spectroscopy that are known to be surface-specific. SFG on a material with a polar-oriented interface layer specified by similar molecular polarity, polar orientation distribution, and size of molecules or subgroups of molecules is likely to be surface-specific.

Now that we have a clear picture of the basic theory of SFG, we can make a few general remarks. We are interested in employing SFG as a surface tool, and the most disturbing problem often encountered is that the SF signal contains a part arising from non-surface-specific EQ contribution of the participating medium. While the EQ contribution could be discriminated from the surface ED contribution in many cases, it could not in many other cases. Its negligence without justification could lead to erroneous interpretation of experimental results and cause confusion and controversy. The OH stretching spectra of ice interfaces and the OH bending mode of vapor/water interfaces are good examples. In this respect, molecular dynamics simulations considering only the surface ED contribution cannot help.[25] One would hope that in the future, such simulations could be extended to provide information about whether EQ contribution is negligible or not.

SF spectroscopy has already been established as a surface-specific tool in many applications without the need of worrying about complication caused by EQ contribution. We discuss here only cases that may suffer from non-negligible EQ contribution. The obvious cases are interfaces of neat liquids and solids, when their surface and bulk spectra are not clearly distinguishable. To be sure that a SF spectrum is dominated by interfacial ED contribution, one would have to be able to estimate the EQ contribution separately by transmission SFG or resort to other means such as perturbing the interface and see if the observed spectrum drastically changes.

Application of SFG to probe buried interfaces is particularly vulnerable to possible EQ contribution because the input beams unavoidably have a long interaction length in the bulk medium to generate an unwanted SF signal. A special beam or sample arrangement is required to avoid the problem. For example, in the polymer case, a reflected SF spectrum from a polymer/metal interface can be identified to be from the interface if it does not vary with the thickness of the polymer film on the metal.[26]

As a surface analytic tool, SFG also faces similar ambiguity in dividing the surface and bulk as other surface techniques. However, as we have seen, in comparison with x-ray diffraction and scanning tunneling microcopy, SFG enjoys the advantage of essentially no dependence on surface/bulk division and model fitting in the data analysis. The basic theory described in this paper applies equally to both the surface SF electronic and surface SF vibrational spectroscopies, providing information on surface molecular and electronic structures, respectively. So far, the reported surface SF electronic spectroscopy work has been relatively rare presumably because current researchers are less interested in surface electronic functions of materials. The situation, however, may change as interfacial electronic properties of condensed matter, such as surface topological effects and surface-induced superconductivity, have recently attracted more attention. On crystalline solids whose electronic and phonon properties are described in terms of band structure and band states, their optical transitions and responses are generally characterized by $\vec{k}$ dependent optical constants. In such cases, the EQ contribution is naturally taken into consideration by the linear dependence of the optical constants on $\vec{k}$. Details on how it affects surface nonlinearity still need to be worked out.

Surface SF spectroscopy has been proven to be an effective and versatile tool for probing adsorbates at all types of interfaces accessible by light, often without the need to worry about complication from EQ contribution. SF spectroscopic studies on functions and properties of adsorbed molecular contaminants, macromolecules, and biomolecules at various interfaces, *in situ* probing of electronic and optoelectronic device interfaces during operation, and surface reactions of adsorbates in different environments are clearly areas ready to be explored more in depth. Difficulties that impede advances in these areas are probably related to the complexity of experimental setup, assignment of spectral features, and absence of the algorithm for the spectral analysis, all of which hopefully could be improved in the near future. A unique feature of SF vibrational spectroscopy is its ability to provide information about polar orientation of surface molecules or molecular subgroups through measurement of ratios of their surface ED nonlinear susceptibility elements. This has not been covered in our discussion. We should, however, remark that usually less than two such ratios are measured by different polarization combinations of SFG, permitting determination of only two parameters in an orientation distribution function. This deficiency indicates that accurate measurement of the ratios cannot be of much help to provide more information on orientation although how to measure the ratios accurately has been an issue addressed by a number of reports in the literature.

A major advancement of surface SF spectroscopy probably would come from further improvement of SFG techniques, such as extension of the spectral range to mid-IR and THz, construction of portable experimental setups, and enhancement of detection

sensitivity. What we advertise here is that conformation of the spectral analysis and interpretation to the basic theory by researchers in the field are also crucial.

APPENDIX: NONVANISHING NONLINEAR SUSCEPTIBILITY ELEMENTS EXTRACTABLE FROM SFG MEASUREMENTS WITH VARIOUS BEAM POLARIZATION COMBINATIONS

Consider the SFG process described in Fig. 1. If medium II is isotropic or cubic, the nonvanishing surface nonlinear susceptibility elements of $\overset{\leftrightarrow(2)}{\chi}_{SS}$ due to structural symmetry are $(\chi^{(2)}_{SS,z\alpha\alpha}, \chi^{(2)}_{SS,\alpha z\alpha}, \chi^{(2)}_{SS,\alpha\alpha z}, \chi^{(2)}_{SS,zzz})$ given here in an explicit tensorial notation with the Cartesian coordinates. Each $\overset{\leftrightarrow(2)}{\chi}_{qi}$ tensor in the bulk EQ nonlinear susceptibility $\overset{\leftrightarrow(2)}{\chi}_{BBQ}$ of Eq. (22) has only two independent, nonvanishing elements,

$$\chi^{(2)}_{q1,\alpha(\bar{\beta}\alpha)\beta} = \chi^{(2)}_{q1,\alpha(\bar{\alpha}\beta)\beta}, \ \chi^{(2)}_{q1,\alpha(\bar{\beta}\beta)\alpha}, \ \text{and} \ \chi^{(2)}_{q1,\alpha(\bar{\alpha}\alpha)\alpha} = \chi^{(2)}_{q1,\alpha(\bar{\beta}\alpha)\beta} + \chi^{(2)}_{q1,\alpha(\bar{\alpha}\beta)\beta} + \chi^{(2)}_{q1,\alpha(\bar{\beta}\beta)\alpha},$$

$$\chi^{(2)}_{q2,\alpha\beta(\bar{\alpha}\beta)} = \chi^{(2)}_{q2,\alpha\beta(\bar{\beta}\alpha)}, \ \chi^{(2)}_{q2,\alpha\alpha(\bar{\beta}\beta)}, \ \text{and} \ \chi^{(2)}_{q1,\alpha(\bar{\alpha}\alpha)\alpha} = \chi^{(2)}_{q2,\alpha\beta(\bar{\alpha}\beta)} + \chi^{(2)}_{q2,\alpha\beta(\bar{\beta}\alpha)} + \chi^{(2)}_{q2,\alpha\alpha(\bar{\beta}\beta)},$$

$$\chi^{(2)}_{q3,(\bar{\alpha}\beta)\beta\alpha} = \chi^{(2)}_{q3,(\bar{\beta}\alpha)\alpha\beta}, \ \chi^{(2)}_{q3,(\bar{\alpha}\alpha)\beta\beta}, \ \text{and} \ \chi^{(2)}_{q3,(\bar{\alpha}\beta)\alpha\beta} = \chi^{(2)}_{q3,(\bar{\beta}\alpha)\beta\alpha} + \chi^{(2)}_{q3,(\bar{\beta}\alpha)\alpha\beta} + \chi^{(2)}_{q3,(\bar{\alpha}\alpha)\beta\beta},$$

with $\alpha = x, y,$ or z and $\alpha \neq \beta$. Here, the bracketed sub-indices indicate the EQ field component with the subindex under a bar referring to the direction of the associated wave vector component. The surface nonlinear susceptibility measured in SFG is, from Eq. (25),

$$(\chi^{(2)}_{S,eff})_{\alpha\beta\gamma} \equiv (\chi^{(2)}_{SS})_{\alpha\beta\gamma} - \frac{(\chi^{(2)}_{BBQ})_{\alpha\beta\gamma}}{i\Delta k^{II}_z}. \tag{A1}$$

For SSP polarization combination with $\vec{k}^{II}_2$ in the x–z plane, we have[15]

$$(\chi^{(2)}_{S,eff})_{SSP} = (\chi^{(2)}_{SS})_{yyz} - \frac{(\chi^{(2)}_{BBQ})_{yyz}(\hat{P} \cdot \hat{z}) + (\chi^{(2)}_{BBQ})_{yyx}(\hat{P} \cdot \hat{x})}{i\Delta k^{II}_z},$$

$$(\chi^{(2)}_{BBQ})_{yyz} = \chi^{(2)}_{q1,y(\bar{z}y)z}(ik^{II}_{1,z}) + \chi^{(2)}_{q2,yy(\bar{z}z)}(ik^{II}_{2,z}) - i(k^{II}_{1,z} + k^{II}_{2,z})\chi^{(2)}_{q3,(\bar{z}y)yz},$$

$$(\chi^{(2)}_{BBQ})_{yyx} = \chi^{(2)}_{q1,y(\bar{x}y)z}(ik^{II}_{1,x}) + \chi^{(2)}_{q2,yy(\bar{x}x)}(ik^{II}_{2,x}) - i(k^{II}_{1,x} + k^{II}_{2,x})\chi^{(2)}_{q3,(\bar{x}y)yx}. \tag{A2}$$

With $k^{II}_{2,x}/k^{II}_{2,z} = \sin\theta^{II}_2/\cos\theta^{II}_2, \hat{P} \cdot \hat{x} = \cos\theta^{II}_2,$ and $\hat{P} \cdot \hat{z} = -\sin\theta^{II}_2,$ we find

$$(\chi^{(2)}_{S,eff})_{SSP} = (\chi^{(2)}_{SS})_{yyz} + \frac{k^{II}_{2,x}\cos\theta^{II}_2}{k^{II}_{2,z}\Delta k^{II}_z}\Big[(\chi^{(2)}_{q1,y(\bar{z}y)z} - \chi^{(2)}_{q3,(\bar{z}y)yz})k^{II}_{1,z}$$

$$+ (\chi^{(2)}_{q2,yy(\bar{z}z)} - \chi^{(2)}_{q3,(\bar{z}y)yz})k^{II}_{2,z}\Big] - \frac{\cos\theta^{II}_2}{\Delta k^{II}_z}$$

$$\times \Big[(\chi^{(2)}_{q1,y(\bar{x}y)x} - \chi^{(2)}_{q3,(\bar{x}y)yx})k^{II}_{1,x} + (\chi^{(2)}_{q2,yy(\bar{x}x)} - \chi^{(2)}_{q3,(\bar{x}y)yx})k^{II}_{2,x}\Big]$$

$$= (\chi^{(2)}_{SS})_{yyz} + \frac{\cos\theta^{II}_2}{k^{II}_{2,z}\Delta k^{II}_z}(\chi^{(2)}_{q1,\alpha(\bar{\beta}\alpha)\beta} - \chi^{(2)}_{q3,(\bar{\alpha}\beta)\beta\alpha})(\vec{k}^{II}_1 \times \vec{k}^{II}_2) \cdot \hat{y}. \tag{A3}$$

The above equation shows that if $\vec{k}^{II}_1 \| \vec{k}^{II}_2$, then the $\chi^{(2)}_{BBQ}$ part vanishes, and $\left(\chi^{(2)}_{S,eff}\right)_{SSP} = \left(\chi^{(2)}_{SS}\right)_{yyz}$. On the other hand, if $k^{II}_{2,x} = 0$, then $\left(\chi^{(2)}_{SS}\right)_{yyz} = 0$, and $\left(\chi^{(2)}_{S,eff}\right)_{SSP} = -\left(\chi^{(2)}_{BBQ}\right)_{ijk}/i\Delta k^{II}_z$

$\propto \left(\chi^{(2)}_{q1,\alpha(\bar{\beta}\alpha)\beta} - \chi^{(2)}_{q3,(\bar{\alpha}\beta)\beta\alpha}\right)$. Similarly, for SPS and PSS polarization combinations, we can show

$$(\chi^{(2)}_{S,eff})_{SPS} = (\chi^{(2)}_{SS})_{yzy} + \frac{\cos\theta^{II}_1}{k^{II}_{1,z}\Delta k^{II}_z}(\chi^{(2)}_{q2,\alpha\beta(\bar{\alpha}\beta)} - \chi^{(2)}_{q3,(\bar{\beta}\alpha)\beta\alpha})(\vec{k}^{II}_2 \times \vec{k}^{II}_1) \cdot \hat{y},$$

$$(\chi^{(2)}_{S,eff})_{PSS} = (\chi^{(2)}_{SS})_{zyy} + \frac{\cos\theta^{II}_3}{(k^{II}_{1,z} + k^{II}_{2,z})\Delta k^{II}_z}(\chi^{(2)}_{q1,\alpha(\bar{\beta}\alpha)\beta} - \chi^{(2)}_{q2,\alpha\beta(\bar{\alpha}\beta)})$$

$$\times [\vec{k}^{II}_2 \times (\vec{k}^{II}_1 + \vec{k}^{II}_2) \cdot \hat{y}]. \tag{A4}$$

Again, if $\vec{k}^{II}_1 \| \vec{k}^{II}_2$, we have $(\chi^{(2)}_{S,eff})_{SPS} = (\chi^{(2)}_{SS})_{yzy}$, and $\left(\chi^{(2)}_{S,eff}\right)_{PSS} = \left(\chi^{(2)}_{SS}\right)_{zyy}$. If we set $k^{II}_{1,x} = 0$ and $k^{II}_{3,x} = 0$ for SPS and PSS polarization combinations, respectively, we can measure $\left(\chi^{(2)}_{q2,\alpha\beta(\bar{\alpha}\beta)} - \chi^{(2)}_{q3,(\bar{\alpha}\beta)\beta\alpha}\right)$ and $\left(\chi^{(2)}_{q1,\alpha(\bar{\beta}\alpha)\beta} - \chi^{(2)}_{q2,\alpha\beta(\bar{\alpha}\beta)}\right)$. Note that for individual $\chi^{(2)}_{qi}$ elements, we can only determine their values to a common arbitrary constant. This is because of intrinsic ambiguity in dividing ED and EQ terms in the multipole expansion, as discussed in Sec. V.

The description here shows that $(\chi^{(2)}_{SS})_{yyz}, (\chi^{(2)}_{SS})_{yzy}, (\chi^{(2)}_{SS})_{zyy}, (\chi^{(2)}_{q1,\alpha(\bar{\beta}\alpha)\beta} - \chi^{(2)}_{q3,(\bar{\alpha}\beta)\beta\alpha}), (\chi^{(2)}_{q2,\alpha\beta(\bar{\alpha}\beta)} - \chi^{(2)}_{q3,(\bar{\alpha}\beta)\beta\alpha}),$ and $(\chi^{(2)}_{q1,\alpha(\bar{\beta}\alpha)\beta} - \chi^{(2)}_{q2,\alpha\beta(\bar{\alpha}\beta)})$ can be separately measured. In principle, it is also possible to deduce from measurement $(\chi^{(2)}_{SS})_{zzz}$ and other differences of $\overset{\leftrightarrow(2)}{\chi}_{qi}$ tensor elements, for example, $(\chi^{(2)}_{qi,\alpha(\bar{\alpha}\alpha)\alpha} - \chi^{(2)}_{qj,(\bar{\alpha}\alpha)\alpha\alpha})$, using sets of selected $\vec{k}^{II}_i$ with PPP polarization combination, but the procedure is much more complicated. Since we are not really interested in $\overset{\leftrightarrow(2)}{\chi}_{BBQ}$ for characterization of materials, we will not go into more detailed discussion. By keeping the angle between $\vec{k}^{II}_1$ and $\vec{k}^{II}_2$ small, we can make $-(\chi^{(2)}_{BBQ})_{\alpha\beta\gamma}/i\Delta k^{II}_z$ negligible in comparison with $(\chi^{(2)}_{SS})_{\alpha\beta\gamma}$, especially in reflected SFG because of the large Δk^{II}_z. In transmitted SFG with $|\Delta k^{II}_z| \ll |k^{II}_{iz}|$, the signal from $-(\chi^{(2)}_{BBQ})_{\alpha\beta\gamma}/i\Delta k^{II}_z$ can be strong as long as the angle between $\vec{k}^{II}_1$ and $\vec{k}^{II}_2$ is not small. For

media of hexagonal symmetry, the above results are approximately valid if optical responses parallel and perpendicular to the uni-axis are not very different.

The $\overset{\leftrightarrow}{\chi}{}^{(2)}_{qi}$ tensor elements for a molecular group are likely of the same order of magnitude. This is particularly true for SF vibrational spectroscopy with ω_2 near vibrational resonance and $\omega_1 \sim \omega_3$. From the microscopic expression of EQ nonlinear susceptibility, we expect $\chi^{(2)}_{q1,\alpha(\tilde{\beta}\alpha)\beta} \sim \chi^{(2)}_{q3,(\tilde{\alpha}\beta)\beta\alpha}$, but $|\chi^{(2)}_{q2,\alpha\beta(\tilde{\alpha}\beta)}| < |\chi^{(2)}_{q3,(\tilde{\alpha}\beta)\beta\alpha}|$ because the EQ electronic orbit of $\chi^{(2)}_{q2,\alpha\beta(\tilde{\alpha}\beta)}$ is connected to the ground electronic state and that of $\chi^{(2)}_{q1,\alpha(\tilde{\beta}\alpha)\beta}$ and $\chi^{(2)}_{q3,(\tilde{\alpha}\beta)\beta\alpha}$ to the excited states.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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