Bulk contribution from isotropic media in surface sum-frequency generation

H. Held,[1,2,*] A. I. Lvovsky,[1,†] X. Wei,[1,‡] and Y. R. Shen[1]

[1]*Department of Physics, University of California, Berkeley, California 94720*

[2]*Department of Integrated Systems Analysis, Potsdam Institute for Climate Impact Research, P.O. Box 60 12 03, D-14412 Potsdam, Germany*

We present systematic conceptual and experimental investigations of the bulk contribution to surface sum-frequency generation (SFG) from an isotropic medium. A practical method for the analysis of spectra obtained in a transmission geometry is presented which allows to estimate the bulk contribution in any future application. A systematic degeneracy due to the molecular nature of the material is found which makes a subtle interpretation of transmission experiments necessary. Practical consequences for the analysis of typical SFG spectra are discussed.

I. INTRODUCTION

Infrared-visible sum-frequency generation (SFG) has been developed into a powerful vibrational spectroscopic technique for studies of surfaces and interfaces.[1] It originates from a second-order nonlinear polarization

$$\mathbf{P}^{(2)}(\omega_s) = \overleftrightarrow{\chi}^{(2)} : \mathbf{E}_1(\omega_1)\mathbf{E}_2(\omega_2) \qquad (1)$$

induced in a medium by two input fields $E_1(\omega_1)$ and $E_2(\omega_2)$, where $\chi^{(2)}$ denotes the nonlinear susceptibility. Being a third-rank tensor, $\chi^{(2)}$ vanishes under the electric-dipole approximation in a centrosymmetric medium, but survives at surfaces or interfaces. This makes SFG highly surface specific in such media.

In a typical surface SFG experiment, two input laser beams with frequencies ω_1 and ω_2 overlap at a surface or interface, and sum-frequency generation in both reflection and transmission directions can be detected (see Fig. 1). Scanning ω_2 over surface vibrational resonances results in a surface vibrational spectrum that provides information about the surface structure.[2]

SFG, however, is not strictly forbidden in a centrosymmetric medium. Beyond the electric-dipole approximation, electric-quadrupole and magnetic-dipole contributions lead to a nonvanishing $\chi^{(2)}$ for the bulk of such a medium. Although it arises from a higher-order mechanism, SFG from the bulk could be comparable to that from the surface because the latter comes from a surface layer of only at most a few monolayers thick. For SFG to be used as a surface probe, it is then important to know whether the bulk contribution to the output is negligible or it can be separated from the surface contribution.

Bloembergen and co-workers[3] worked out the theory of second harmonic generation (SHG) in reflection from an interface and derived explicitly the surface and bulk contributions. Their approach has been adopted and extended in later publications on the topic.[4,5] A most important conclusion from the theory is that part of the bulk contribution is not separable from the surface contribution in real experiments.

These publications form the basis for understanding of the bulk contribution to surface SHG. One would expect that the

results derived for SHG are equally applicable to SFG,[6] but this may not be all true in practical terms especially when SFG occurs near a vibrational resonance. We describe in this paper a systematic analysis of the SFG case.

We find that as in SHG, it is not possible in SFG to separate surface contribution from a certain part of bulk contribution. As we shall discuss later, this is inherent to the well-
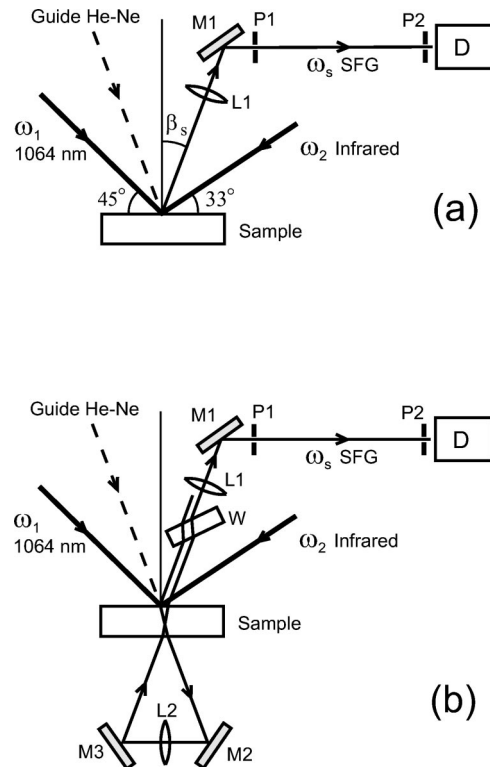

FIG. 1. Experimental setup for measuring reflection and transmission SFG signals. (a) In the reflection geometry, lens $L1$ creates an image of the sample surface on the $LN2$-cooled CCD camera D; iris diaphragms $P1$ and $P2$ are used for alignment and to isolate the SFG signal from omnidirectional optical noise. (b) Transmission signal is directed into the CCD through $P1$ and $P2$ via two mirrors; glass plate M prevents detection of the reflection SFG signal. Switching between the two geometries is done simply by inserting or removing window W.
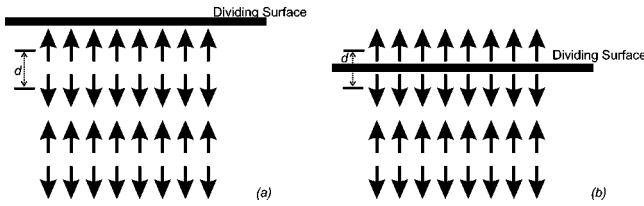
FIG. 2. P_S and P_{BS} cannot be separated [see Eqs. (6) and (7)]. Depending on how the dividing surface (and, accordingly, the molecular reference frame) is defined, part of the total SFG signal will be interpreted either as bulk (a) or as surface signal (b). However, for most liquids such an effect turns out to be marginal (see Sec. V) if atomic groups are chosen as smallest unit. Note that the effect also holds for isotropic materials.

known fact that the magnitude of an electric quadrupole or a magnetic dipole depends on the reference frame chosen if moments of lower order (such as the dipole) are nonzero.[7] In other words, division between the surface contribution and a certain part of the bulk contribution is not unique and depends on how they are defined. Following convention, we define induced dipoles and multipoles with reference to a center properly located within each molecule or atomic group. More specifically, we associate "intrinsic" induced electric dipoles and multipoles with SFG-active atomic groups. The bulk signal resulting from the electric quadrupoles and magnetic dipoles so defined can be expected much weaker than the signal from a polar ordered surface with a strong dipole signal. This expectation is found valid, indeed, for important practical cases. (As the electric quadrupole and the magnetic dipole are of the same order in multipole expansion and can be represented by tensor elements in a unified way, from now on, we refer to both of them just as "quadrupole.") Considering a whole molecule or a bulk set of molecules, however, we can find also the existence of an "extrinsically" induced quadrupole (i.e., electric quadrupole and magnetic dipole) polarization that arises from a distribution of electric dipoles. For a system of randomly distributed individual molecules carrying induced electric dipoles but no quadrupoles, both macroscopic electric dipole and quadrupole polarizations should vanish. If the molecules are correlated to form oppositely oriented pairs, then each pair of molecules carries no electric dipole but a finite quadrupole. Consequently, even if the molecular pairs are randomly distributed, the bulk medium, if described in terms of those pairs as smallest unit and their angular distributions, still possesses a nonvanishing quadrupole polarization. More generally, the larger the clusters are in terms of which bulk and surface are described the larger a quadrupole polarization has to be expected, and, at the same time, the more pronounced the necessity to specify a molecular reference frame would be. An example with a set of well-ordered electric dipoles is shown in Fig. 2, which we will discuss in more detail later in relation to the ambiguity in separation of surface and bulk contributions. The extrinsic electric quadrupole contribution to SHG or SFG, if present, is likely to be more important than the intrinsic one judging from the dimensions of the quadrupoles in the two cases.

While the above discussion is general for SHG and SFG,

we should note that vibrationally resonant SFG usually involves small atomic groups within a molecule, and therefore the physical dimension associated with the "intrinsic" induced electric dipole and multipoles is smaller than that in the SHG case. Especially in case of SFG, this opens the chance for negligible bulk contributions if surface ordering is described in terms of atomic groups.

Comparison between SFG in reflection and in transmission has been used to estimate bulk contribution to SFG.[8] As we shall see later, the deduced quadrupole nonlinear susceptibility for the bulk corresponds to the part of bulk contribution that is separable from the surface contribution. We expect from the abovementioned definition of dipoles and multipoles in terms of atomic groups that all quadrupole nonlinear susceptibility elements are of the same order of magnitude, except that some may vanish for symmetry reason. Therefore, the experimentally deduced bulk quadrupole nonlinear susceptibility would allow us to judge whether the bulk contribution to the observed SFG is negligible or not. If the answer is positive, then SFG is dominated by the surface electric-dipole contribution and can be directly related to the surface structure. An example is SFG in reflection from the air/methanol interface. It was found that the bulk contribution in this case is negligible.[8] We shall give in this paper a detailed description of a systematic scheme for such an evaluation. For better illustration of concepts and easier comparison with experiment, we shall focus on isotropic media although the approach can be readily generalized to media of lower symmetry.

This paper is organized as follows. In Sec. II, we outline the general formalism in terms of macroscopic bulk parameters and identify which of them are directly accessible in transmission experiments. In Sec. III, we illustrate the nonuniqueness in separation of surface and bulk contributions by paradigmatic examples. In Sec. IV, the general bulk theory is specialized on organic liquids and validated by experimental results on the SFG-active CH stretch. Furthermore it follows that the directly accessible bulk parameters are small, in accordance with previous results.[8] The experimental results indicate a degeneracy which we explain as a general property of molecular materials. We then suggest ways how to infer on the remaining (surface-imitating) bulk parameters in Sec. V. We present the most important estimates of the bulk signal for CH bonds and find it negligible in typical situations if the microscopic description is related to the macroscopic through radiating atomic groups rather than whole molecules.

II. THEORY

We discuss in this section a theoretical formalism on surface and bulk contributions to SFG. We first define, as usual, a plane to separate the surface layer from the bulk of a medium. It is a plane close to the surface and yet sufficiently deep into the bulk in a region where the structure is essentially the same as that of the bulk. We consider here a semi-infinite medium with the dividing plane at $z=0$, the microscopically thin surface layer between $0 \leq z \leq 0^+$ and the bulk occupying the half space $z<0$. (This definition of the surface

layer includes the concept of Gibbs' surface. Furthermore, the assumption of a semi-infinite sample does not imply a strong restriction as in a typical application, the infrared laser beam becomes absorbed way before the lower surface of a realistic sample which is finite in the z direction.) The bulk medium is assumed to be isotropic, and therefore the nonvanishing $\chi^{(2)}$ must come from a quadrupole contribution. For the surface layer, because the inversion symmetry is broken, $\chi^{(2)}$ is electric-dipole allowed, and because the layer is very thin, the quadrupole contribution to $\chi^{(2)}$ is negligible.

The bulk nonlinear polarization can be written as[5]

$$P^{(2)}_{Bi}(\omega_s) = i \int_{-\infty}^{0^+} [\chi^{Q1}_{ijlm} E_{1j} E_{2l} k_{1m} + \chi^{Q2}_{ijlm} E_{1j} E_{2l} k_{2m}$$

$$- \chi^{Qs}_{ijlm} E_{1j} E_{2l} k_{sm}] \exp[i(k_{1z} + k_{2z} - k_{sz})] dz. \tag{2}$$

Here, E_{1j}, E_{2l} denote the components of electric field vectors of the visible and the infrared laser beam, k_{1m}, k_{2m}, k_{sm} the components of the wave vectors of the visible, infrared, and sum-frequency field. k_{sm} follows from momentum and energy conservation $k_{sx(y)} = k_{1x(y)} + k_{2x(y)}$, $k_s = k_1 + k_2$, the latter equation referring to the moduli of wave vectors. χ^{Q1}_{ijlm} corresponds to the dipolar polarization induced by a electric dipolar coupling to E_{2l} and the sum frequency field, and a quadrupolar coupling to E_{1j}. The definition of χ^{Q2}_{ijlm} follows in analogy while χ^{Qs}_{ijlm} corresponds to the quadrupolar polarization induced by the dipolar coupling to both E_{1j} and E_{2l} and quadrupolar coupling to the sum frequency field. Often, Eq. (2) is displayed without an integral. Here, for the need to emphasize the relation of microscopic and macroscopic properties, all χ are locally averaged, macroscopic material quadrupole properties, not integrated in the z direction. Note that, finally, Eq. (2) does not contain effects stemming from a change in index of refraction at the surface boundary ("surface quadrupole") as this is a paper about the bulk signal.

For an isotropic medium, each fourth-rank χ tensor has, by symmetry, only three independent nonvanishing tensor elements

$$\chi_{ijij} \equiv \chi_1, \quad \chi_{iijj} \equiv \chi_2, \quad \chi_{ijji} \equiv \chi_3,$$

$$\chi_{iiii} \equiv \chi_1 + \chi_2 + \chi_3. \tag{3}$$

We can then express the modulus of Eq. (2) in the form

$$P^{(2)}_B(\omega_s) = [(\hat{e}_s \cdot \mathbf{E}_2)(\mathbf{X}_1 \cdot \mathbf{E}_1) + (\hat{e}_s \cdot \mathbf{E}_1)(\mathbf{X}_2 \cdot \mathbf{E}_2) + (\mathbf{E}_1 \cdot \mathbf{E}_2)$$

$$\times (\mathbf{X}_3 \cdot \hat{e}_s)]/\Delta k, \tag{4}$$

where $\hat{e}_s$ denotes the direction of $\mathbf{P}^{(2)}(\omega_s)$, $\Delta k \equiv (\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_s) \cdot \hat{z}$ is the phase mismatch of SFG in the bulk being nonzero only in the z direction, and the X's are defined by

$$\mathbf{X}_p \equiv \chi^{Q1}_p \mathbf{k}_1 + \chi^{Q2}_p \mathbf{k}_2 - \chi^{Qs}_p \mathbf{k}_s. \tag{5}$$

There are altogether nine independent EQ nonlinear susceptibility elements associated with $P^{(2)}(\omega_s)$. However, since $\mathbf{E}_i \cdot \mathbf{k}_i = 0$, the elements χ^{Q1}_1, χ^{Q2}_2 and χ^{Qs}_3 never contribute to

$P^{(2)}(\omega_s)$. Thus only six EQ nonlinear susceptibility elements are needed to describe bulk contribution to SFG in an isotropic medium.

It has been shown that the SFG signals in reflection and transmission (see the geometry in Fig. 1) can be described by[5,6,8]

$$S \propto |P^{(2)}_{S,\text{eff}}|^2,$$

$$P^{(2)}_{S,\text{eff}} \equiv P^{(2)}_S + P^{(2)}_B, \tag{6}$$

where $P^{(2)}_S$ is the surface nonlinear polarization. Clearly for SFG, Δk in transmission is much smaller than that in reflection, and therefore Eq. (4) suggests that the bulk contribution is more important for SFG in transmission and less so in reflection. Deduction of bulk and surface contributions separately seems possible from simultaneous measurement of SFG in both transmission and reflection. Indeed, this was the scheme used by Superfine *et al.* to evaluate the importance of bulk contribution in reflected SFG from an air/methanol interface.[8] Equivalent information on bulk parameters can be obtained from experiments utilizing films of varying thickness.[9]

However, the $1/\Delta k$ dependence of $P^{(2)}_B$ is somewhat misleading because $P^{(2)}_B$ contains terms that cannot be separated from $P^{(2)}_S$. This can be seen if we realize that Eq. (4) can be written as

$$P^{(2)}_B = E_1 E_2 (P^{(2)}_{BB}/\Delta k + P^{(2)}_{BS}),$$

$$P^{(2)}_{BB} = d_1(\hat{e}_2 \cdot \hat{e}_s)[\hat{e}_1 \cdot (\mathbf{k}_2 + \mathbf{k}_s)] - d_2(\hat{e}_s \cdot \hat{e}_1)[\hat{e}_2 \cdot (\mathbf{k}_s + \mathbf{k}_1)]$$

$$+ d_3(\hat{e}_1 \cdot \hat{e}_2)[\hat{e}_s \cdot (\mathbf{k}_1 - \mathbf{k}_2)],$$

$$P^{(2)}_{BS} = s_1(\hat{e}_2 \cdot \hat{e}_s)(\hat{e}_1 \cdot \hat{z}) + s_2(\hat{e}_s \cdot \hat{e}_1)(\hat{e}_2 \cdot \hat{z}) + s_3(\hat{e}_1 \cdot \hat{e}_2)(\hat{e}_s \cdot \hat{z}) \tag{7}$$

with

$$d_1 = (\chi^{Q2}_1 - \chi^{Qs}_1)/2,$$

$$d_2 = (\chi^{Qs}_2 - \chi^{Q1}_2)/2,$$

$$d_3 = (\chi^{Q1}_3 - \chi^{Q2}_3)/2,$$

$$s_1 = (\chi^{Q2}_1 + \chi^{Qs}_1)/2,$$

$$s_2 = (\chi^{Qs}_2 + \chi^{Q1}_2)/2,$$

$$s_3 = (\chi^{Q1}_3 + \chi^{Q2}_3)/2. \tag{8}$$

Here, $\hat{e}_i$ is the unit vector representing the direction of the E_i field. It is clear from Eqs. (6) and (7) that the two terms $P^{(2)}_S$ and $P^{(2)}_{BS}$ which add to $P^{(2)}_{S,\text{eff}}$ are not separable. Physically, this is because the division of electric dipole and quadrupole polarizations induced in a medium is not unique, depending on the definition of dipole and quadrupole and the position of the dividing plane (to be discussed further in Sec. III). We can show explicitly with $\mathbf{P}^{(2)}_S = \overleftrightarrow{\chi}^D_S : \mathbf{E}_1 \mathbf{E}_2$ and $\mathbf{P}^{(2)}_{BS}$ in Eq. (7) ($\overleftrightarrow{\chi}^D_S$ being electric-dipole allowed) that[5]

$$P_{Si}^{(2)} + P_{BSi}^{(2)} = [(\chi_{ijl}^D)_S + (\chi_{ijlz}^{Q1} + \chi_{ijlz}^{Q2} + \chi_{ijlz}^{Qs})/2] E_{1j} E_{2l}$$

$$= \int_0^{0^+} \left[\chi_{ijl,\text{local}}^D - \frac{\partial}{\partial z}(\chi_{ijlz}^{Q1} + \chi_{ijlz}^{Q2} \right.$$

$$\left. + \chi_{ijlz}^{Qs})/2 \right] E_{1j} E_{2l} dz. \qquad (9)$$

Here, $\chi_{ijl,\text{local}}^D$ is a tensor local in z which is nonzero only within the surface layer (similar to the bulk tensor derivatives) and whose integration along z reveals the total dipole effect χ_{ijl}^D. To derive Eq. (9), without loss of generality, the unphysical quantities χ_1^{Q1}, χ_2^{Q2}, and χ_s^{Qs} [see remark after Eq. (5)] have been set to zero. It appears here that $(\chi_{ijl}^D)_S$ and $(\chi_{ijlz}^{Q1} + \chi_{ijlz}^{Q2} + \chi_{ijlz}^{Qs})$ play the same role in contributing to the effective surface nonlinear polarization. This further illustrates that, given a nonzero dipole, the magnitude of the quadrupole depends on the reference frame. Here, the dipole is allowed to be reference-frame dependent as well because the medium is semi-infinite. With different definitions of electric dipole and quadrupole polarizations, the magnitudes of $(\chi_{ijl}^D)_S$ and $(\chi_{ijlz}^{Q1} + \chi_{ijlz}^{Q2} + \chi_{ijlz}^{Qs})$ can shift from one to the other, but the sum of the two remains constant. We shall discuss in the next section how we would propose a conventional definition of electric dipole and quadrupole polarizations for vibrationally resonant SFG so that the experimental results are more useful for studying surface structure.

Thus we know that the bulk contribution from s_i in Eq. (8) is intrinsically not separable from the surface contribution. (The same holds for experiments on films with varying thickness as in Briggman *et al.*[9] Two contributions from s_i appear, each being inseparable from the upper and the lower dipole layer, respectively.) However, the quantities d_i in Eq. (8) are different. With each of them being the difference of two χ^{Qi} terms, they are independent of the reference frame and boundary surface chosen to define electric dipole and quadrupole polarizations. As seen from Eqs. (6) and (7), their contribution to SFG is very much enhanced in transmission because of the much smaller phase mismatch. By simultaneous measurements of SFG in transmission and reflection, they can be deduced separately from the surface nonlinear optical coefficients.

III. NONUNIQUENESS IN SEPARATION OF SURFACE AND BULK CONTRIBUTIONS: EXAMPLES AND CONSEQUENCES

We describe here a few examples to elucidate how $\mathbf{P}_S^{(2)}$ and $\mathbf{P}_{BS}^{(2)}$ cannot be separated physically because their definitions are not unique. Consider the case of a medium composed of a regular array (azimuthally isotropic) of small molecules with second-order induced electric dipoles shown in Fig. 2. For simplicity, we assume the corresponding induced quadrupole on each molecule is negligible. This example relates to the formalism of Sec. II in the following way. To define the bulk tensor element, a center for a local reference frame is defined in the middle of two adjacent lines of molecular arrays. In (a) the top two lines are grouped together to form a quadrupole, and so on, in (b) the second and third
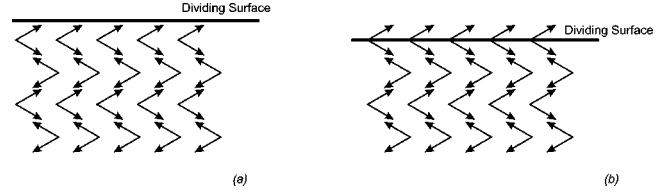

FIG. 3. The same as in Fig. 2, but for more complex entities.

line. The local bulk tensor element $\chi(z)$, being defined as the local average of molecular quadrupoles, is then a delta function with peaks at those centers. We find, depending on the position of the dividing plane, either $P_S^2 = 0$ and $P_{BS}^{(2)} = +Npd/2 = +N_s p/2$ [Fig. 2(a)] or $P_S^{(2)} = N_s p$ and $P_{BS}^{(2)} = -Npd/2 = -N_s p/2$ [Fig. 2(b)]. Here, N and N_s are the bulk and surface densities of molecules, respectively, p is the induced electric dipole on each molecule, and d is the separation between neighboring molecules along z. (For simplicity, further geometric factors such as electric field and wave vectors have been omitted.) In both cases, $P_S^{(2)} + P_{BS}^{(2)} = +N_s p/2$ as it should be. If the induced quadrupole q on each molecule is not negligible, then $P_{BS}^{(2)}$ should contain an additional term Nq. If interaction between molecules is important, there is also an additional electric-dipole contribution in $P_S^{(2)}$ due to broken symmetry at the surface. This example describes fairly well the cases of smectic-A liquid crystal layers and Langmuir-Blodgett films with molecular layers of alternative polar orientations.

A simple modification of the above example is shown in Fig. 3. The same description applies here if the induced electric dipole p is replaced by its z component p_z. It is possible that the two spatially close but oriented at an angle dipoles in Fig. 3 belong to two atomic groups of the same molecule. One can treat the two dipoles either separately or together as a unit. In either case, $P_S^{(2)}$ can be zero or finite depending on the position of the dividing plane.

Both of the above examples assume an ordered array of molecules in the bulk. The electric-dipole $P_S^{(2)}$ could be of the same order of magnitude as the quadrupole $P_{BS}^{(2)}$. Then, the fact that $P_S^{(2)}$ and $P_{BS}^{(2)}$ are not separable means that it is not possible to deduce the pure surface structural information from a SFG measurement. For the latter to be true, we must have in $P_S^{(2)}$ a surface-specific quantity that cannot be shifted to $P_{BS}^{(2)}$ by altering the reference frame or the position of the dividing plane. This is the case when the surface layer has a very different structure and a much stronger polarization than the bulk. For example, in vibrationally resonant SFG, the surface layer may have a different spectrum than the bulk. In the case of a pure liquid or polymer, the surface layer may be much more polar-ordered than the bulk and average of quadrupoles over random orientations effectively reduces the magnitude of $P_{BS}^{(2)}$. For the case of crystals with inseparable surface and bulk SFG spectra, however, one may find $P_S^{(2)}$ and $P_{BS}^{(2)}$ comparable in magnitude. To gain further information on the question whether the true surface response dominates in SFG or not, we need to perturb the surface and see how SFG changes.

What are the practical consequences of the ambiguity in

defining the bulk quadrupole? In fact, two consequences follow. First, if an analysis of the surface structure in terms of angular distribution is published, it needs to be specified to which smallest units (atomic groups, whole molecules, or molecular clusters) and to which microscopic reference frames these angular distributions refer. In previous publications, however, the center of reference was not specified, for good reasons: The analysis referred to atomic groups which are so small that the location of the center of reference within an atomic group does not matter. This is has been numerically confirmed as mentioned in Sec. V. The second consequence is that the bulk parameters s_i cannot be measured and need to be determined from calculations or reasonable order-of-magnitude estimates in relation to the d_i. In Sec. V we outline how to do the latter.

IV. VIBRATIONALLY RESONANT SFG FROM MOLECULAR LIQUIDS

In contrast to s_i, the intrinsic bulk nonlinear susceptibility elements d_i in Eq. (8) can be measured by SFG in transmission and reflection as their contributions to SFG are strongly enhanced in transmission, because of the smaller phase mismatch Δk. Here we discuss the special case of vibrationally resonant SFG in molecular liquids and show that d_i may obey some special relations.

We consider induced quadrupoles of the molecules or atomic groups. If ω_2 is near a vibrational resonance, the nonlinear susceptibility can be written in the form

$$\chi_{ijl}^{(2)} = N \left\langle \left(\frac{\partial \alpha}{\partial q} \right)_{ij} \left(\frac{\partial \mu}{\partial q} \right)_l \right\rangle \Big/ (\omega_2 - \omega_r + i\Gamma_r) \qquad (10)$$

following the Born-Oppenheimer approximation. Here $(\partial \alpha / \partial q)_{ij}$ and $(\partial \mu / \partial q)_l$ are the Raman polarizibility tensor and the infrared dipole derivative of the resonant vibrational mode, respectively, and ω_r and Γ_r are the mode frequency and damping constant, respectively. When the infrared electric-dipole transition is replaced by a quadrupole transition, i.e., $(\partial \mu / \partial q)_l \rightarrow (\partial \mu / \partial q)_{lm}$ (here the new index m acts on the infrared wave vector) one obtains the an expression for χ^{Q2} analogous to Eq. (10). With the replacement $(\partial \alpha / \partial q)_{ij} \rightarrow (\partial \alpha / \partial q)_{ij,m}$, Born-Oppenheimer expressions are obtained also for χ^{Q1} and χ^{Qs}. It is well known that for ω_1 far away from electronic resonance, the Raman polarizability tensor of a molecular system is symmetric to a very good approximation.[10] This is true even if one of the electronic transitions in the Raman process is quadrupular. We expect

$$\chi_{ijl}^{(2)} \cong \chi_{jil}^{(2)},$$

$$\chi_{ijlm}^{Qs} \cong \chi_{jilm}^{Q1},$$

$$\chi_{ijlm}^{Q2} \cong \chi_{jilm}^{Q2}. \qquad (11)$$

We then find from Eqs. (3) and (8) that $|d_1| \approx |d_3|$ and $d_2 \approx 0$. The quantities d_1, d_2, and d_3 can be separately assessed in SFG measurements by the SPS (denoting S, P, and S polarization for the fields at ω_s, ω_1, and ω_2, respec-
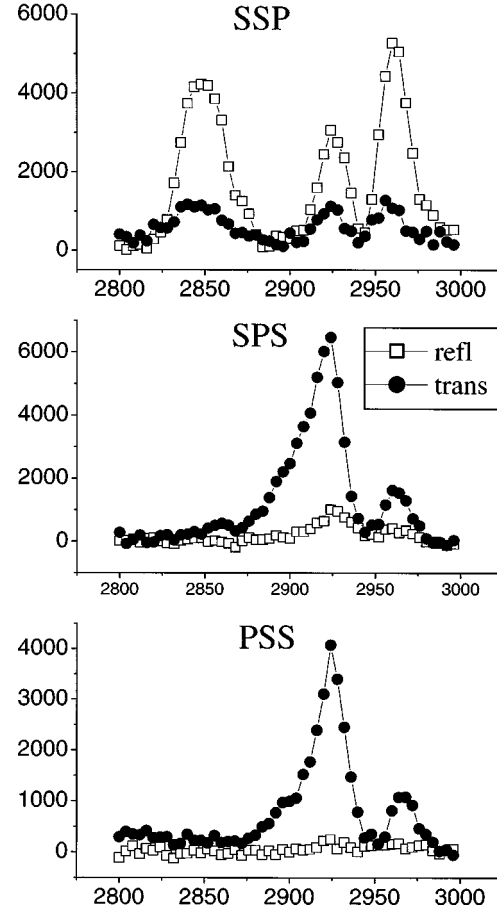

FIG. 4. A set of reflection and transmission SFG spectra obtained from a decane/glass interface. In the *SSP* polarization combination, the transmission spectrum reproduces, with losses, the reflection spectrum—no bulk contribution is present. In the *SPS* and *PSS* combination the transmission spectrum exhibits similar and strong bulk contributions.

tively), *SSP* and *PSS* polarization combinations, respectively. We can therefore conclude that for SFG with the *SSP* polarization combination, the bulk contribution stemming from d_i is negligible (at least as long as the coherence length $l/\Delta k$ is not orders of magnitude larger than for a typical reflection geometry), and with *SPS* and *PSS*, it is about the same. We conclude that a meaningful bulk transmission experiment must include the *PSS* or *SPS* configuration.

The conclusion here has been confirmed by experiment. In Fig. 4, a set of SF vibrational spectra for the decane/silica interface with the three different polarization combinations in shown. (The experimental arrangement has been described elsewhere;[11] key experimental changes with respect to the standard SFG setup, now allowing for transmission measurements, are displayed in Fig. 1.) With the *SSP* polarization combination, it is seen that the spectra in transmission and reflection almost replicate each other. The small difference can be explained by the difference in optical paths and Fresnel coefficients. This indicates that the surface contribution together with a possible surfacelike bulk contribution dominate both transmission and reflection spectra, and hence

$d_2 \approx 0$. The situation is very different with *SPS* and *PSS*. The two transmission spectra are very much alike and are much stronger than the ones from reflection. It indicates that the "amplifiable" bulk contribution $P_{BB}^{(2)}$ [see Eq. (7)] dominates the transmission spectra and $d_1 \approx d_3$. We have obtained similar results for many other liquids: hexane, cyclohexane, and propanol. The same rule also applied to other isotropic media such as polymers.

V. WHEN WOULD THE BULK CONTRIBUTION BE NEGLIGIBLE OR NOT?

The use of SFG as a surface structural probe is questionable unless the bulk quadrupole contribution can be shown to be negligible in comparison with the electric-dipole contribution of a well-ordered surface. In fact, a few cases demonstrating the importance of bulk contribution to SHG reflected from a centrosymmetric medium have been reported in the past.[12] As discussed in Sec. II, it is by no means possible to experimentally separate three out of six bulk parameter combinations, the s_i's, from the surface parameters. This seems to demonstrate the severity of the problem. In most cases, there remains the possibility to obtain further information by modifying the surface structure. However, for many systems with an isotropic bulk, the bulk contribution to SHG and SFG appears to be negligible. We consider such cases in more detail in this section.

The deeper reason why surface structure and the s_i's cannot be separated lies in the ambiguity of dividing a given molecular structure into dipole and quadrupole contributions as discussed in Sec. III. If larger assemblies of atomic groups are treated as smallest unit in terms of which the surface structure is going to be described, then the bulk contribution is not negligible in general (extrinsic quadrupole). Even more this is the case for nonisotropic media such as crystals and liquid crystals in mesophases due to the more ordered molecular arrangement.

Also for an surface description in terms of whole molecules, the extrinsic quadrupole can become important. In the case of rigid molecules, however, this does not hamper the analysis, as the extrinsic quadrupole as a purely geometric effect can be explicitly calculated[5] in the framework of Eq. (10). For example, as the acetone skeleton is well known (Fig. 3 can be interpreted as an assembly of acetone molecules), the extrinsic quadrupole can be calculated from the distance of the SFG-active CH_3 groups from the chosen molecular center in the acetone molecule. This technique is not at the center of the current article and can be circumvented if one chooses the atomic group as the smallest unit with respect to which the surface ordering is being presented. The remaining small ambiguity of where to locate the center of reference within a CH_3 group could numerically be shown to be negligible with respect to a signal from an ordered surface. For that, a molecular model according to Eq. (10) was employed. From now on, we refer to an analysis in terms of atomic groups and ask for the remaining, the intrinsic, quadrupole contribution.

What are typical mechanisms which lead to a negligible intrinsic bulk contribution? Theoretically, there are reasons why $|\chi^{Qi}|$ (and hence $|s_i|$ and $|d_i|$) is small compared to $|\chi_S^D|$ for a molecular system with an isotropic bulk and a polar-oriented surface layer [note that according to Eq. (9), χ^{Qi} and $\chi_S^D = \int \chi_{S,\text{local}}^D dz$ carry the same unit]. Let $\alpha_D^{(2)}$ and $\alpha_Q^{(2)}$ be the electric-dipole and quadrupole hyperpolarizabilities associated with the atomic groups. We have $|\alpha_D^{(2)}| a \sim |\alpha_Q^{(2)}|$ where a is roughly the spread of electronic wavefunctions responsible for the hyperpolarizabilities or the vibrational amplitude (for quadrupole matrix element between vibrational states). With $|\chi_S^D| \sim N_s |\langle \alpha_D^{(2)} \rangle|$, $|\chi^{Qi}| \sim N |\langle \alpha_Q^{(2)} \rangle|$ and $N_s = Nd$, where N and N_s are bulk and surface molecular densities, respectively, and the angular brackets denote the orientational average, we find $|\chi_S^D| \sim N_s |\langle \alpha_D^{(2)} \rangle| = Nd |\langle \alpha_D^{(2)} \rangle| \gg Na |\langle \alpha_D^{(2)} \rangle| \sim N |\langle \alpha_Q^{(2)} \rangle| \sim |\chi^{Qi}|$ if $d \gg a$. This is often the case in vibrationally resonant SFG where the atomic groups probed are smaller than the molecular dimensions. Liquid crystal molecules in the isotropic provide an example.

Apart from this well-known mechanism we note that the orientational average over an isotropic distribution of microscopic quadrupoles can further reduce the bulk quadrupole contribution. From a classical single-bond additivity model, we find as a robust feature that isotropic averaging suppresses the value of χ^{Qi} by one order of magnitude with reference to a bulk of well aligned molecules.

Our measurements on the special case of atomic groups based on the CH stretch have revealed that the bulk quadrupole contributions from d_i's can be neglected (see the results on the decane/silica interface displayed in Fig. 4). To estimate the contribution from the s_i's, we realize from Eq. (8) that barring systematic cancellation such as $d_2 \approx 0$ or accidental cancellation in the remaining d_i, d_i, and s_i should be of the same order of magnitude. We therefore suggest as a general scheme to measure the d_i, to check for $|d_1| \approx |d_3|$ and $|d_2| \approx 0$ (in order to see whether our assumptions of Sec. IV hold for the material under investigation) and to assume $|s_i| \lesssim |d_1|$. Then an upper limit of the bulk contribution can be calculated according to Eq. (7). In general, if the surface molecules form a polar-oriented layer, we can expect the surface contribution to dominate in the reflection geometry. Similar results have been obtained from many other liquid as well as polymer interfaces. In most cases, the bulk contribution is so small that no SFG in reflection would be detected above noise.

Thus, while there is no general theory that can be used to ascertain whether in an isotropic medium the bulk contribution compared to the surface contribution to SFG spectroscopy is negligible or not, we believe we do have a few thumb rules. For vibrational modes associated with small atomic groups in molecules, the bulk contribution from quadrupole hyperbolarizabilities of the atomic groups to reflected SFG is negligible if the atomic groups' structure is not too different from CH_2/CH_3. Oppositely oriented pairs of polar atomic groups also yield only a small quadrupole bulk contribution if the distance between the atomic groups is small compared to the mean distance of molecular layers. In such cases, if the surface contains an oriented layer of polar atomic groups, then the surface contribution should dominate in SFG-VS.

Otherwise, the signal level of SFG-VS would be very low, probably below the detection sensitivity with the current experimental setups. In all these cases, if the atomic groups form a polar-oriented layer at the surface, then the surface contribution to SFG is expected to dominate over the bulk contribution.

Admittedly these are not general rules and can only serve as guidelines. To be certain whether the surface contribution dominates or not, we must resort to further measurements where we modify the surface and see how the SFG spectrum changes.[13] *Ab initio* calculations on the molecular systems involved certainly will also help.

VI. CONCLUSION

A general framework for the analysis of surface versus bulk contributions to vibrationally resonant SFG in isotropic media is presented. Hereby, the surface signal is identified with an electric dipole contribution, the bulk signal with the sum of electric quadrupole and magnetic dipole contributions. For the special, but relevant case of molecular liquids, general rules following from symmetry are derived and experimentally verified. To derive these rules, it was found useful to split the bulk signal into an ''amplifiable'' contribution which is enhanced inversely proportional to the sum frequency phase mismatch, and a surfacelike contribution. While the former is inferred from SFG measurements in transmission and reflection geometry, the latter cannot experimentally be separated from the surface signal. It is shown experimentally that the amplifiable bulk contribution is nearly the same in *SPS* and *PSS* and is negligible in the *SSP* input/output polarization combination. This effect is theoretically argued to hold due to symmetry for any liquid probed well off an electronic resonance. From these findings, an important practical consequence follows. As the surfacelike bulk signal component cannot be measured, the underlying tensor elements need to be inferred from the measurable amplifiable bulk components by an order-of-magnitude argument. When such an order-of-magnitude estimate of the surfacelike bulk contribution for *SPS, PSS*, or even *SSP* is to be performed, experimental knowledge of the amplifiable *SPS/PSS* bulk signal is necessary, as the underlying bulk tensor elements systematically cancel out for the amplifiable *SSP* bulk signal. Examples of molecular models support the validity of this order-of-magnitude inference scheme. Finally it is investigated in which cases the total bulk contribution would ever matter according to the above scheme. Estimates suggest that for SFG-VS involving small atomic groups in molecules, the bulk contribution to SFG from a molecular liquid observed in reflection geometry is negligible, hence, the reflected SFG spectra can be used to provide information about the liquid surface structure. This is likely to be also true for other isotropic media such as polymers. Calculations from molecular dynamics simulation are needed to substantiate the ideas and preliminary results presented in this paper.

ACKNOWLEDGMENTS

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*Email address: held@pik-potsdam.de

†Present address: Fachbereich Physik, Universität Konstanz, D-78464 Konstanz, Germany.

‡Present address: Lucent Technologies Bell Labs, 600 Mountain Ave., Murray Hill, NJ 07974.

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