Surface sum-frequency vibrational spectroscopy of nonpolar media

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Sum-frequency generation spectroscopy is surface specific only if the bulk contribution to the signal is negligible. Negligible bulk contribution is, however, not necessarily true, even for media with inversion symmetry. The inevitable challenge is to find the surface spectrum in the presence of bulk contribution, part of which has been believed to be inseparable from the surface contribution. Here, we show that, for nonpolar media, it is possible to separately deduce surface and bulk spectra from combined phase-sensitive sum-frequency vibrational spectroscopic measurements in reflection and transmission. The study of benzene interfaces is presented as an example.

sum-frequency spectroscopy | surface structure | bulk contribution | electric-quadrupole contribution | nonpolar media

Sum-frequency vibrational spectroscopy (SFVS) has been established as a powerful and versatile tool for studies of surfaces and interfaces of media with inversion symmetry (1–6). It is based on the idea that under the electric-dipole (ED) approximation, the bulk response for SF generation vanishes, but the surface response is necessarily nonvanishing because of the broken inversion symmetry at the surface. However, beyond the ED approximation, the bulk response is generally nonvanishing (7, 8). In using SFVS as a surface probe, one must always worry whether the bulk response is negligible or can be distinguished from the surface response. In many publications on SFVS studies of an interface, however, the bulk response is simply ignored. A few papers have appeared to theoretically and experimentally describe how the surface and bulk responses may or may not be separately deduced from measurement (9–18),^{*,†} but they do not seem to have clarified the situation. The conclusion from a more rigorous theory is that part of the bulk response is intrinsically inseparable from the surface response if surface and bulk resonances are not clearly different (19). However, as we shall show in this paper, separate deduction of surface and bulk spectra is possible for nonpolar media from properly designed reflection and transmission SFVS measurements. Using benzene as a test case, we present, to our knowledge, the first real surface spectrum of a neat liquid. The results also provide guidelines on when bulk contribution may be significant in applications of SFVS to surface studies.

We begin with a brief review on the various physical mechanisms that contribute to SF generation (SFG) from an interfacial system (20). We consider a system formed by two semi-infinite isotropic media. SFG from the system in transmission or reflection measures a corresponding effective surface nonlinear susceptibility $\chi_{s,eff}^{(2)}$, which has contributions from four different physical origins: (i) An ED contribution from the interfacial layer due to broken inversion symmetry. (ii) An electric-quadrupole (EQ) contribution from the rapid field variation at the interface. (iii) An EQ contribution from the bulk. (iv) An EQ contribution from the bulk intrinsically inseparable from the surface ED contribution. To use SFG as an effective surface analytical tool, however, one would like to be able to separate out the ED contribution that directly characterizes the local interfacial structure. Therefore, we must find ways to either separately

measure the other contributions or show that they are negligible in comparison with the ED contribution.

In this paper, we describe a combined theoretical and experimental SFVS study to show that for nonpolar media, the abovementioned different contributions to SF spectra can be separately deduced from measurement, or for polar media, that their relative importance be estimated. With selected beam geometry and polarizations, we can measure the EQ bulk spectra of a medium by transmitted SFVS, although not all of the tensor elements of the bulk nonlinear susceptibility can be accessed. The measured bulk spectra can then be used to evaluate whether the EQ bulk contribution is negligible or not in reflected SFVS. To achieve this, phase-sensitive (PS) SFVS that measures the imaginary part of the nonlinear susceptibility for both SF reflection and transmission is needed. We chose benzene interfaces as a representative case. The bulk contribution of benzene, being a nonpolar liquid, is expected to be strong, whereas the surface contribution from broken inversion symmetry could be weak. Reflected SFVS of the air/benzene interface has been reported by others (21–24), but interpretations of the observed spectra are questionable considering that their reflected SF spectra always contain mixed surface and bulk contributions, thus providing no true surface spectrum.

Significance

Sum-frequency vibrational spectroscopy (SFVS) has been developed into a viable surface analytical tool for media with inversion symmetry. It is considered surface specific because the bulk contribution to the signal vanishes under the electric-dipole approximation. However, there is always the worry that beyond the electric-dipole approximation, the bulk contribution may not be negligible. The problem is particularly acute if the medium under investigation does not have a strongly polar-oriented surface layer. We show here that for nonpolar media with well-separated infrared and Raman modes, it is possible to deduce bulk and surface spectra separately from combined transmission and reflection phase-sensitive SFVS measurements. The work also provides guidelines for evaluation of the importance of bulk contribution to SFVS in general.

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*Eq. 2 is the same as equation 7 in ref. 14 but is expressed in a more transparent form.

[†]Ref. 18 obtains the same expression for the effective surface nonlinear susceptibility in Eq. 1 by assuming that $\chi_{BB}^{(2)}$ is the bulk nonlinear susceptibility, but strictly speaking, this is only true for an infinite medium. For a semi-infinite medium, $\chi_B^{(2)} \equiv \chi_{BB}^{(2)} / (-i\Delta k_z) - \hat{z} \cdot \chi_q^{(2)}$ is the true bulk nonlinear susceptibility.

Theory

For clarity, we first outline the relevant underlying theory for SFVS. The SF outputs in transmission and reflection from an interface of a nonlinear medium measure effective surface nonlinear susceptibilities, $(\vec{\chi}_{S,eff}^{(2)})_T$ and $(\vec{\chi}_{S,eff}^{(2)})_R$, respectively (14, 19, 25)

$$\begin{aligned} \left(\vec{\chi}_{S,eff}^{(2)} \right)_{(T,R)} &\equiv \vec{\chi}_{SS}^{(2)} - \frac{\vec{\chi}_{BB}^{(2)}(\vec{k}_1, \vec{k}_2)}{i\Delta k_{(T,R)z}} \\ \chi_{SS,ijk}^{(2)} &= \chi_{Sd,ijk}^{(2)} + \langle \hat{z} \cdot \vec{\chi}_{qa,ijk}^{(2)} \rangle_{Int} - \hat{z} \cdot \vec{\chi}_{q,ijk}^{(2)} \\ \chi_{BB,ijk}^{(2)}(\vec{k}_1, \vec{k}_2) &= -i(\vec{k}_1 + \vec{k}_2) \cdot \vec{\chi}_{q,ijk}^{(2)} + \vec{\chi}_{q1,ijk}^{(2)} \cdot i\vec{k}_1 + \vec{\chi}_{q2,ijk}^{(2)} \cdot i\vec{k}_2 \\ \Delta \vec{k}_{(T,R)} &= \vec{k}_1 + \vec{k}_2 - \vec{k}_{(T,R)}. \end{aligned} \quad [1]$$

Here, $\vec{\chi}_{BB}^{(2)}$ is the bulk nonlinear susceptibility originating from EQ contribution $\vec{\chi}_{qa}^{(2)}$, and $\vec{\chi}_{SS}^{(2)}$ comprises an ED term $\vec{\chi}_{Sd}^{(2)}$ from the atomically thin interfacial layer, an EQ term $\langle \hat{z} \cdot \vec{\chi}_{qa}^{(2)} \rangle_{Int}$ from field variation in the interfacial layer, and a bulk EQ term $-\hat{z} \cdot \vec{\chi}_{qa}^{(2)}$. It is readily seen from Eq. 1 that $\chi_{BB,ijk}^{(2)}$ and $\chi_{SS,ijk}^{(2)}$ can be deduced from transmitted and reflected SFG measurements with $\Delta k_{Tz} = k_{1z} + k_{2z} - |k_z|$ and $\Delta k_{Rz} = k_{1z} + k_{2z} + |k_z|$, respectively.

For an isotropic medium, $\vec{\chi}_{BB}^{(2)}$ has the explicit expression (14)

$$\begin{aligned} \hat{e} \cdot \vec{\chi}_{BB}^{(2)}(\omega, \vec{k}_1, \vec{k}_2) : \hat{e}_1 \hat{e}_2 &= i \left[(\hat{e} \cdot \vec{k}_1) (\hat{e}_1 \cdot \hat{e}_2) \left(\chi_{q1,i(\bar{j})j}^{(2)} - \chi_{q,i(\bar{j})j}^{(2)} \right) \right. \\ &+ (\hat{e} \cdot \vec{k}_2) (\hat{e}_1 \cdot \hat{e}_2) \left(\chi_{q2,i(\bar{j})j}^{(2)} - \chi_{q,i(\bar{j})j}^{(2)} \right) \\ &+ (\hat{e}_2 \cdot \vec{k}_1) (\hat{e} \cdot \hat{e}_1) \left(\chi_{q1,i(\bar{j})i}^{(2)} - \chi_{q,i(\bar{j})i}^{(2)} \right) \\ &+ (\hat{e}_2 \cdot \vec{k}_2) (\hat{e} \cdot \hat{e}_1) \left(\chi_{q2,i(\bar{j})i}^{(2)} - \chi_{q,i(\bar{j})i}^{(2)} \right) \\ &+ (\hat{e}_1 \cdot \vec{k}_1) (\hat{e} \cdot \hat{e}_2) \left(\chi_{q1,i(\bar{j})i}^{(2)} - \chi_{q,i(\bar{j})i}^{(2)} \right) \\ &\left. + (\hat{e}_1 \cdot \vec{k}_2) (\hat{e} \cdot \hat{e}_2) \left(\chi_{q2,i(\bar{j})i}^{(2)} - \chi_{q,i(\bar{j})i}^{(2)} \right) \right]. \end{aligned} \quad [2]$$

where $\hat{e}$ refers to beam polarization, the subindices $i \neq j$ refer to the orthogonal coordinates in the laboratory, and the bracketed subindices in Eq. 2 denote the coordinates associated with the EQ matrix element in the microscopic expression of a nonlinear susceptibility with discrete resonances

$$\begin{aligned} \vec{\chi}^{(2)}(\omega = \omega_1 + \omega_2) &= \vec{\chi}_{NR}^{(2)} + \sum_v \frac{\vec{A}_v}{\omega_2 - \omega_v + i\Gamma_v} \\ \vec{A}_v &\propto \sum_n \langle g | \vec{M}_\omega | n \rangle \langle n | \vec{M}_{\omega_1} | v \rangle \langle v | \vec{M}_{\omega_2} | g \rangle / (\omega - \omega_{ng}). \end{aligned} \quad [3]$$

For $\chi_{q,i(\bar{j})k}^{(2)}$, $\chi_{q1,i(\bar{j})k}^{(2)}$ and $\chi_{q2,i(\bar{j})k}^{(2)}$, the corresponding EQ matrix elements in $\vec{A}_v$ are $(M_\omega)_{ij}$, $(M_{\omega_1})_{jk}$, and $(M_{\omega_2})_{ki}$.

As seen from Eq. 2, because $\vec{k}(\Omega)$ is necessarily perpendicular to $\hat{e}(\Omega)$ in isotropic medium, only four quantities, $\chi_{q1,i(\bar{j})j}^{(2)} - \chi_{q,i(\bar{j})j}^{(2)}$,

$\chi_{q2,i(\bar{j})j}^{(2)} - \chi_{q,i(\bar{j})j}^{(2)}$, $\chi_{q1,i(\bar{j})i}^{(2)} - \chi_{q,i(\bar{j})i}^{(2)}$, and $\chi_{q2,i(\bar{j})i}^{(2)} - \chi_{q,i(\bar{j})i}^{(2)}$ are accessible by transmitted SFG measurement out of a total of nine independent elements of $\vec{\chi}_{qa}^{(2)}$. These four accessible quantities are further related by $(\chi_{q1,i(\bar{j})j}^{(2)} - \chi_{q,i(\bar{j})j}^{(2)}) - (\chi_{q2,i(\bar{j})j}^{(2)} - \chi_{q,i(\bar{j})j}^{(2)}) = (\chi_{q1,i(\bar{j})j}^{(2)} - \chi_{q,i(\bar{j})j}^{(2)}) - (\chi_{q2,i(\bar{j})j}^{(2)} - \chi_{q,i(\bar{j})j}^{(2)})$ because $(M_\Omega)_{ij} = (M_\Omega)_{ji}$. Even so, transmitted SFG is still able to produce spectra on bulk vibrational resonances. For media composed of symmetric molecules, the vibrational modes are separately IR or Raman active. We expect the resonant part of $\chi_{q1,i(\bar{j})j}^{(2)} = \chi_{q1,i(\bar{j})j}^{(2)}$, $\chi_{q,i(\bar{j})j}^{(2)} = \chi_{q,i(\bar{j})j}^{(2)}$, and $\chi_{q,i(\bar{j})i}^{(2)}$ to be nearly vanishing at IR-inactive resonances [with $(M_\omega)_j = 0$ in Eq. 3], and the resonant part of $\chi_{q2,i(\bar{j})j}^{(2)} = \chi_{q2,i(\bar{j})j}^{(2)}$ to be nearly vanishing at Raman-inactive resonances [with $(M_\omega)_i(M_{\omega_1})_j = 0$]. In general, however, modes can be both IR and Raman active. We then only have $\chi_{q1,i(\bar{j})j}^{(2)} \sim \chi_{q,i(\bar{j})j}^{(2)}$ because the SF output and the visible input frequencies are close. We can expect $\chi_{q2,i(\bar{j})j}^{(2)}$ to be different from $\chi_{q,i(\bar{j})j}^{(2)}$, but of same order of magnitude, and $|\chi_{q2,i(\bar{j})j}^{(2)} - \chi_{q,i(\bar{j})j}^{(2)}|$ provides an estimate on the values of the nonvanishing elements of $\vec{\chi}_{qa}^{(2)}$. Domination of $\vec{\chi}_{Sd}^{(2)}$ in $\vec{\chi}_{SS}^{(2)}$ is a requirement for SFG to be a surface-specific tool.

Results and Discussion

We now describe a SFVS experiment on the air/benzene interface to elucidate the above discussion. This interfacial system has been investigated recently by different groups using SFVS. Benzene molecules are nonpolar, but their CH stretch vibrations can be readily observed by reflected SFVS from the air/benzene interface (21, 24). Allen and coworkers interpreted the observed spectra as originating from the interfacial layer due to broken

Fig. 1. (A) Spectra of $|\chi_{q2,yz(\bar{z}y)}^{(2)} - \chi_{q,i(\bar{z}y)zy}^{(2)}|$ and $\text{Im}(\chi_{q2,yz(\bar{z}y)}^{(2)} - \chi_{q,i(\bar{z}y)zy}^{(2)})$ of benzene liquid. Amplitude and the imaginary part of the SFVS spectra of air/benzene interface in reflection with (B) SSP and (C) SPS polarization, respectively. Blue squares are experimental data and red lines are fitting curves. Spectra of $|\chi_{BB,yyz}^{(2)} / (i\Delta k_{Rz})|$ and $|\chi_{BB,yzy}^{(2)} / (i\Delta k_{Rz})|$ (○) are displayed in B and C for comparison, respectively.

*The EQ nonlinear susceptibility generally consists of two parts: one from EQ polarizability of individual molecules and the other from the phase retardation effect of induced dipoles on spatially distributed molecules. It can, however, be shown that the latter does not contribute to the various terms of $\vec{\chi}_{BB}^{(2)}$ in Eq. 2.

Fig. 2. (A) Spectra of $\text{Im} \chi_{SS,yyz}^{(2)}$ (black), $\text{Im} \chi_{SS,yzy}^{(2)}$ (red), and $- \text{Im} \chi_{q,(\bar{y})zy}^{(2)}$ (blue). (B) The true surface spectrum, $\text{Im} \chi_{S,yyz}^{(2)}$ of the air/benzene interface.

inversion symmetry (21). Tahara and coworkers, by comparing the polarization-dependent SF reflection spectra with the IR and Raman spectra of benzene liquid and gas, assigned some of the observed modes to the bulk and others to the interface (24), but their interpretation does not agree with the prediction of molecular dynamics simulation by the Morita group (23). Therefore, benzene is clearly an interesting case to test our theoretical understanding on surface SFG.

We carried out both transmission and reflection (PS) SFVS measurements on the air/benzene interface. It is known that $\text{Im} \chi^{(2)}$ spectra better characterize resonances. They can be obtained from fitting of the corresponding $|\chi^{(2)}|$ spectra with Eq. 3 and the help of phase-sensitive SFVS measurement (26) at a few selective frequencies (Fig. 1 B and C). Because the spectra comprise only discrete resonances, the fitting is unique and reliable as long as the signs of the resonant amplitudes can be determined from the phase-sensitive measurement. We first focus on measurement of $\chi_{BB}^{(2)}$. We see from Eq. 2 that if SPS polarization (denoting S-, P-, and S-polarized beams at ω , ω_1 , and ω_2 , respectively) is used for transmitted SFG, then because $\hat{e}_2 \perp \hat{e}_1$, only the $i(\hat{e}_1 \cdot \vec{k}_2)(\hat{e} \cdot \hat{e}_2)(\chi_{q2,ij(\bar{y})}^{(2)} - \chi_{q,(\bar{y})ij}^{(2)})$ term in the expression of $\chi_{BB}^{(2)}$ survives. If, in addition, the P-polarized visible input beam is along the surface normal, then $\chi_{SS}^{(2)}$ cannot contribute to SFG, and the transmitted SFG measures solely $(\chi_{q2,ij(\bar{y})}^{(2)} - \chi_{q,(\bar{y})ij}^{(2)})$ of the bulk. Similarly, with SSP polarization and P-polarized IR input normal to the interface, the transmitted SFG measures solely $(\chi_{q1,i(\bar{y})j}^{(2)} - \chi_{q,(\bar{y})ji}^{(2)})$.

The CH stretch spectra of the amplitude and the imaginary part of $(\chi_{q2,yz(\bar{y})}^{(2)} - \chi_{q,(\bar{y})yz}^{(2)})$ of bulk benzene (with z defined along the surface normal and y perpendicular to the incident plane) obtained from our measurement with SPS polarization are displayed in Fig. 1A. The Fresnel factors associated with the nonlinear susceptibilities were removed in the spectral analysis. The spectrum of $|\chi_{q1,y(\bar{y})z}^{(2)} - \chi_{q,(\bar{y})yz}^{(2)}|$ obtained with SSP polarization is about 20 times weaker than $|\chi_{q2,yz(\bar{y})}^{(2)} - \chi_{q,(\bar{y})yz}^{(2)}|$ because ω_1 is close to ω , but ω_2 is not, and therefore from Eq. 2, $\chi_{q1,y(\bar{y})z}^{(2)}$ is close to $\chi_{q,(\bar{y})yz}^{(2)}$, but $\chi_{q2,yz(\bar{y})}^{(2)}$ is not. (Fig. S1). According to Eq. 1, reflection SFVS with SSP and SPS polarizations measure $(\chi_{S,eff}^{(2)})_{R,yyz}$ and $(\chi_{S,eff}^{(2)})_{R,yzy}$, respectively, each of which consists of two terms, $\chi_{SS,ijk}^{(2)}$ and $-\chi_{BB,ijk}^{(2)}/(i\Delta k_{Rz})$. The measured amplitude spectra of $(\chi_{S,eff}^{(2)})_{R,yyz}$ and $(\chi_{S,eff}^{(2)})_{R,yzy}$ together with their imaginary parts are shown in Fig. 1 B and C, respectively. They agree with the spectra reported by others (24). The amplitude

spectra appear much stronger in comparison with those of $|\chi_{BB,yyz}^{(2)}/(i\Delta k_{Rz})|$ and $|\chi_{BB,yzy}^{(2)}/(i\Delta k_{Rz})|$ deduced from $\chi_{BB,yyz}^{(2)}$ and $\chi_{BB,yzy}^{(2)}$ obtained earlier from transmission SFVS. The result indicates that, in both cases, the bulk contribution due to $\chi_{BB}^{(2)}$ is negligibly small. We therefore find $\chi_{S,eff}^{(2)} \cong \chi_{SS}^{(2)}$. However, $\chi_{SS}^{(2)}$ still contains a bulk $-\hat{z} \cdot \vec{\chi}_q^{(2)}$ term that may not be negligible, as we shall see later.

It is possible to separate surface and bulk contributions in $\chi_{SS}^{(2)}$ if their spectra are clearly different or can be distinguished in spectral analysis. In the case of benzene, all spectra in Fig. 1 can be well fitted by five discrete resonances. The detailed fitting parameters are listed in Tables S1–S3. The imaginary spectra without the nonresonant background are obviously more informative. The peaks at 3,036, 3,071, and 3,091 cm⁻¹ are attributed to the IR-active E_{1u} modes and those at 3,049 and 3,062 cm⁻¹ are attributed to the Raman-active E_{2g} and A_{1g} modes (27). From the microscopic expression of $\chi_{qa}^{(2)}$ in Eq. 3, we see that resonant $\chi_q^{(2)}$ and $\chi_{q1}^{(2)}$ should vanish if the resonant mode is IR inactive (Raman active), whereas $\chi_{q2}^{(2)}$ should vanish if the mode is Raman inactive (IR active). Thus, we can allocate the IR-active peaks in $\text{Im}(\chi_{q2,yz(\bar{y})}^{(2)} - \chi_{q,(\bar{y})zy}^{(2)})$ to $- \text{Im} \chi_{q,(\bar{y})zy}^{(2)}$ and the Raman-active peaks to $\text{Im} \chi_{q2,yz(\bar{y})}^{(2)}$.

We know from Eq. 1 that $\chi_{SS,yzy}^{(2)}$ and $\chi_{SS,yyz}^{(2)}$ both contain the term $-\chi_{q,(\bar{y})zy}^{(2)} = -\chi_{q,(\bar{y})yz}^{(2)}$. To see how important the latter is, we plot the spectrum of $- \text{Im} \chi_{q,(\bar{y})zy}^{(2)}$ in Fig. 2A together with the SSP and SPS spectra of $\text{Im} \chi_{SS,yyz}^{(2)} \cong \text{Im}(\chi_{S,eff}^{(2)})_{R,yyz}$ and $\text{Im} \chi_{SS,yzy}^{(2)} \cong \text{Im}(\chi_{S,eff}^{(2)})_{R,yzy}$ from Fig. 1. Apparently, $- \text{Im} \chi_{q,(\bar{y})zy}^{(2)}$ contributes a little in the SSP spectrum but appears dominant in the SPS spectrum. The true surface spectrum of $\text{Im} \chi_{S,yyz}^{(2)} \equiv \text{Im}[\chi_{Sd,yyz}^{(2)} + \langle \hat{z} \cdot \vec{\chi}_{qa,yyz}^{(2)} \rangle_{Int}]$ can be obtained by subtraction of $- \text{Im} \chi_{q,(\bar{y})zy}^{(2)}$ from $\text{Im} \chi_{SS,yyz}^{(2)}$ and is shown in Fig. 2B. Although all CH stretch modes are present, the Raman-active modes at ~3,065 cm⁻¹ are most pronounced. As a surface resonance, it is shifted by 3 cm⁻¹ from the corresponding bulk mode. We could obtain the surface spectrum of $\text{Im} \chi_{S,yzy}^{(2)}$ similarly from Fig. 2A, but it was much weaker than $- \text{Im} \chi_{q,(\bar{y})zy}^{(2)}$. Because the Raman-active mode is a CH stretch in the plane of the benzene molecule, the result suggests that the molecules at the interface are oriented with their planes close to the surface normal.

To see the relative importance of the field gradient contribution $\langle \hat{z} \cdot \vec{\chi}_{qa,yyz}^{(2)} \rangle_{Int}$ against the ED contribution $\chi_{Sd,yyz}^{(2)}$ in $\text{Im} \chi_{S,yyz}^{(2)}$, we measured $\text{Im} \chi_{S,yyz}^{(2)}$ spectra for air/benzene, silica/benzene, and silica/octadecyltrichlorosilane (OTS) monolayer/benzene interfaces. They

Fig. 3. Spectra of $\text{Im} \chi_{S,yyz}^{(2)}$ for different benzene interfaces: air/benzene (black), fused silica/benzene (red), and silica/OTS/benzene (blue).

Fig. 4. Schematics of experimental arrangements for (A) reflected and (B) transmitted SFVS measurements.

are presented in Fig. 3. Because the dielectric constant of benzene is higher than air and silica, the field gradient in all cases should be along the same direction and larger at the air/benzene interface. If $\langle \hat{z} \cdot \vec{\chi}_{qa,yyz}^{(2)} \rangle_{Int}$ dominates in $\text{Im } \chi_{S,yyz}^{(2)}$, the spectral profiles for the three interfaces would be similar, but with different intensities, the one for the air/benzene interface would be most prominent. Instead, the spectra in Fig. 3 exhibit very significant differences. Specifically, for the silica/benzene and silica/OTS/benzene interfaces where the field gradients are comparable, the signs of the Raman-active modes are opposite. Comparison of the spectra with that of the air/benzene interface show different variations for different modes. The IR-active mode at $3,091 \text{ cm}^{-1}$ appears nearly the same for air/benzene and silica/OTS/benzene interfaces. These results indicate that the field gradient contribution is not significant unless the change of $\langle \hat{z} \cdot \vec{\chi}_{qa,yyz}^{(2)} \rangle_{Int}$ is almost canceled by the change of $\text{Im } \chi_{S,yyz}^{(2)}$ in the two cases. These observations suggest that $\chi_{Sd,yyz}^{(2)}$ is likely to have played the dominant role in the spectra and the contribution from $\langle \hat{z} \cdot \vec{\chi}_{qa,yyz}^{(2)} \rangle_{Int}$ is minor, although further verification is needed. That the Raman-active modes are most pronounced in the observed air/benzene spectrum is in agreement with the prediction of Morita and coworkers (23).

We now give a few remarks on media composed of polar molecules. It is still possible to use transmission and reflection SFG to deduce the spectra of $\chi_{SS}^{(2)}$ and $\chi_{BB}^{(2)}$. The $\chi_{BB}^{(2)}$ contribution proportional to $\chi_{q1,y(\bar{y})z}^{(2)} - \chi_{q,\bar{y}(\bar{y})z}^{(2)}$ is often negligible in the reflected SSP spectrum of SFVS because $\chi_{q1,y(\bar{y})z}^{(2)} \sim \chi_{q,\bar{y}(\bar{y})z}^{(2)}$. Without well-separated IR- and Raman-active modes, it is no longer possible to deduce the spectrum of $\chi_{q,\bar{y}(\bar{y})z}^{(2)}$. However, its contribution in $\chi_{SS,yyz}^{(2)}$ is still likely to be not significant for media consisting of relatively small molecules because their $\chi_{q,\bar{y}(\bar{y})z}^{(2)}$ is expected to be roughly the same as or smaller than benzene (22). It is particularly true that the EQ bulk contribution is not important if the interfacial layer comprises polar-oriented molecules that should yield larger $\chi_{Sd,yyz}^{(2)}$. Anticipated difference in bulk and surface spectra can also be used to judge if the bulk contribution in $\chi_{S,yyz}^{(2)}$ is negligible. Perturbing an interface to vary

the field gradient at the interface can help confirm if the EQ contribution to $\chi_{S,yyz}^{(2)}$ is indeed unimportant. Knowing that the reflected SSP spectrum of a medium is dominated by $\chi_{Sd,yyz}^{(2)}$, one can then use it to characterize the interface.

Summary

In summary, we demonstrated that, for interfaces of nonpolar media (with benzene as a representative example), although the EQ bulk contribution to SFVS is generally nonnegligible, surface and bulk SF vibrational spectra can still be separately deduced from properly designed transmission and reflection SFVS measurements and proper spectral analysis, such as the scheme presented here. Separation of surface and bulk SF spectra is generally not possible for polar media. However, if the interface is strongly polar oriented, the reflected SFVS is likely dominated by the ED surface contribution, whereas the relative importance of the EQ bulk contribution can be estimated from the transmitted SFVS measurement. If the interface of a polar medium is not strongly polar oriented, then care must be taken in analyzing the spectra as the EQ contribution to the reflected SFVS may not be negligible. Our study here provides general guidelines for evaluation of possible importance of bulk contribution in broad applications of SFVS as a surface-specific tool.

Materials and Methods

Sample Preparation. Benzene was used as received from Sigma Aldrich (purity > 99.9%). A transparent Petri dish, used as the container for liquid benzene, was first cleaned with concentrated sulfuric acid mixed with nochromix, rinsed with ultrapure water with a resistivity of $18 \text{ M}\Omega\cdot\text{cm}$, and then blown dry with pure N_2 gas. A glass cover was used to prevent benzene from evaporating.

Experimental Setup. The experimental arrangements for reflected and transmitted phase-sensitive SFVS are depicted in Fig. 4 A and B, respectively. The visible pulses at 532 nm (ω_1) and tunable IR pulses (ω_2), generated by a 30-ps Nd:YAG laser system, were used as the inputs. Collinear beam geometry was used in Fig. 4A; the detailed arrangement was described in refs. 26 and 28. Noncollinear beam geometry was used in Fig. 4B. The two input beams were first overlapped with an intersecting angle of 10° on a y-cut quartz wafer that served as a local oscillator to generate a reference SF signal ($\omega = \omega_1 + \omega_2$). The three transmitted beams through the quartz wafer were refocused onto the sample surface by a concave mirror. The SF signal generated in transmission from the sample together with the reference SF signal was detected by a photomultiplier (PMT) after proper filtering. Varying the relative phase between sample and reference SF waves through angle tuning (from -7° to $+7^\circ$) of a 2-mm-thick fused silica plate in the IR beam path generated an interference fringe, from which the phase of the nonlinear susceptibility of the sample was deduced with respect to that of a z-cut quartz. A position-sensitive microscope was used to control the position of sample surface with an accuracy of $1 \mu\text{m}$.

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