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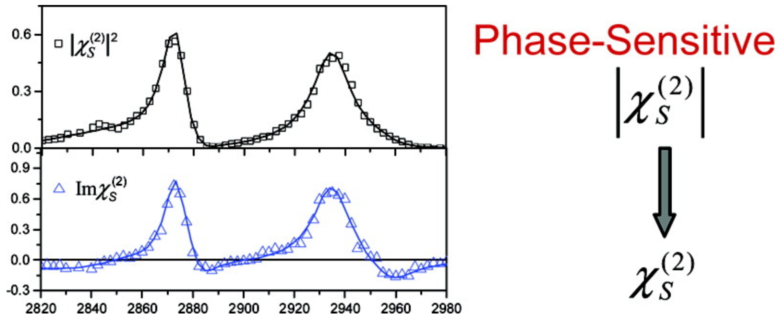

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# Phase-Sensitive Sum-Frequency Vibrational Spectroscopy and Its Application to Studies of Interfacial Alkyl Chains

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Recently, sum-frequency spectroscopy has become an indispensable tool for many interfacial studies because of its high surface specificity. Sum-frequency vibrational spectroscopy (SFVS), in particular, is the only technique available to probe the vibrational structures of a host of different interfaces.[1] As a surface-specific coherent nonlinear optical process, the SFVS output is proportional to the absolute square of the surface response coefficient, $|\chi_S^{(2)}|^2$, which is resonantly enhanced as one of the input frequencies scans over vibrational resonances, thus yielding a surface vibrational spectrum. However, $\chi_S^{(2)}$ is complex in general, and for complete information, we need to know both the amplitude ($|\chi_S^{(2)}|$) and the phase ($\phi$) or real and imaginary parts of $\chi_S^{(2)}$. This was recognized early in the game but has not been generally implemented because it is technically challenging.[2] Recently, a phase-sensitive SFVS scheme was proposed to probe interfaces between centrosymmetric and noncentrosymmetric media.[3] However, it is not applicable to interfaces between centrosymmetric media, many of which are of scientific and technological importance, such as those of liquids and polymers. In this paper, we report the development of a general phase-sensitive SFVS technique that allows spectral measurements of both $|\chi_S^{(2)}|$ and $\phi$ of any interfaces accessible by light. As a demonstration, we applied it to a monolayer of octadecyltrichlorosilane (OTS, $CH_3(CH_2)_{17}SiCl_3$) molecules on fused silica. We showed that, even in this well-investigated case, the result could provide new information owing to the better spectral resolution of the technique.

Sum-frequency generation is a second-order nonlinear optical process in which mixing of two input beams at frequencies $\omega_1$ and $\omega_2$ in a medium generates a coherent output at $\omega = \omega_1 + \omega_2$. In the case of a medium with inversion symmetry, the process is forbidden in the bulk under the electric dipole approximation. The output is then dominated by the surface response and given by $S \propto |\chi_S^{(2)}|^2$.[1] Symmetry-allowed surface vibrations appear as resonances in $\chi_S^{(2)}$. With discrete resonances, we can write

$$\chi_S^{(2)}(\omega_2) = \chi_{NR}^{(2)} + \sum_q \frac{A_q}{\omega_2 - \omega_q + i\Gamma_q} \qquad (1)$$

Here, $\chi_{NR}^{(2)}$ is from nonresonant contribution, $A_q$, $\omega_q$, and $\Gamma_q$ are the strength, resonant frequency, and damping coefficient of the $q$th vibrational mode, respectively. More generally, however, the vibrational modes cannot be considered discrete, but form a band with continuously varying frequencies. Typical examples are media with molecular vibrational frequencies that depend significantly on intermolecular interactions such as water. We then have to write

$$\chi_S^{(2)}(\omega_2) = \chi_{NR}^{(2)} + \int \mathrm{d}\omega_q \frac{A_q}{\omega_2 - \omega_q + i\Gamma_q}\rho(\omega_q) \qquad (2)$$

where $\rho(\omega_q)$ denotes the density of modes at $\omega_q$. Without knowing $\rho(\omega_q)$, it is difficult to deduce detailed resonant structural information from the spectrum of $|\chi_S^{(2)}(\omega_2)|$. This is different if Im $\chi_S^{(2)}$ can be measured. We have

$$\mathrm{Im}\,\chi_S^{(2)}(\omega_2) = -\int \mathrm{d}\omega_q \frac{A_q\Gamma_q}{(\omega_2 - \omega_q)^2 + \Gamma_q^{\ 2}}\rho(\omega_q) \qquad (3)$$

which is analogous to Im[$\epsilon(\omega)$] for linear absorption or emission spectrum, with $\epsilon$ being the optical dielectric constant.

To find Im $\chi_S^{(2)}(\omega_2)$, we need to obtain the phase of $\chi_S^{(2)}(\omega_2)$. This naturally requires an interference method. A simple scheme is described in Figure 1. The two input beams at $\omega_1$ and $\omega_2$ collinearly impinge on the sample surface after passing through a reference SF generator (quartz) and a phase modulator. The SF signal reflected from the sample is given by

$$S_S(\omega_2) = A\{|[|\chi_S^{(2)}(\omega_2)|e^{i\phi(\omega_2)} + a|\chi_R^{(2)}|e^{i\theta(\omega_2)}]|^2 + b^2|\chi_R^{(2)}|^2\} \quad (4)$$

where $A$ is a constant, $a\chi_R^{(2)}$ (with respect to $\chi_S^{(2)}$) is the part of the reference SF field that overlaps and interferes with the SF field ( $\chi_S^{(2)}$) generated from the sample surface, $\theta$ is the relative phase of the reference SF field that can be varied by the phase modulator, and $A(a^2 + b^2)|\chi_R^{(2)}|^2$ is the total reference SF signal. For a given $\omega_2$, varying $\theta(\omega_2)$ produces in $S_S(\omega_2)$ a set of sinusoidal fringes that can be compared with the set of fringes generated by replacing the sample with a reference system, Rs, the nonlinear coefficient of which has a known phase, preferentially zero. The observed fringe shift then yields directly the phase $\phi(\omega_2)$. This is the main technique employed in the past to obtain the phase of a nonlinear response coefficient.[2]

The fringe technique for phase measurement is simple and accurate and is particularly useful when the SF signal is low. It is, however, rather cumbersome for phase measurement over a wide spectral range. The latter can be achieved with a minimum of four spectral scans. First, we measure separately in two scans the spectrum of $A|\chi_S^{(2)}(\omega_2)|^2$ by removing the reference SF generator from the beam path and the spectrum of $A(a^2 + b^2)|\chi_R^{(2)}|^2$ by filtering out the $\omega_2$ input before the sample. Then, we make two scans to yield $S_{S1}(\omega_2)$ and $S_{S2}(\omega_2)$ with the phase of the reference SF field at $\theta(\omega_2)$ and $\theta(\omega_2) + \pi/2$, respectively. Using eq 4, we find

$$\phi(\omega_2) - \theta(\omega_2) = \tan^{-1}\left[\frac{S_{S2} - A|\chi_S^{(2)}|^2 - A(a^2 + b^2)|\chi_R^{(2)}|^2}{S_{S1} - A|\chi_S^{(2)}|^2 - A(a^2 + b^2)|\chi_R^{(2)}|^2}\right] \quad (5)$$

A similar set of measurements with a reference sample of known phase $\phi_{Rs}(\omega_2)$ allows the determination of $\theta(\omega_2)$ and hence $\phi(\omega_2)$.

We have developed the scan technique and applied it to the study of OTS monolayers as a test case. In our experimental arrangement, the input beams, one at 532 nm and the other tunable from 2.5 to

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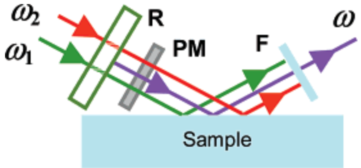

**Figure 1.** Schematics of phase-sensitive sum-frequency vibrational spectrometer. Parallel arrows denote collinear beams. "R", "PM", and "F" stand for reference SF generator, phase modulator, and filter, respectively.

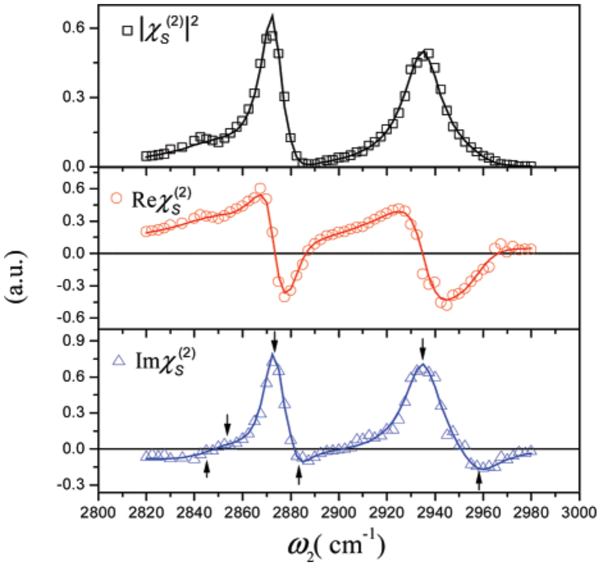

**Figure 2.** Spectra of $|\chi_S^{(2)}|^2$, Re $\chi_S^{(2)}$, and Im $\chi_S^{(2)}$ of an octadecyltrichlorosilane (OTS) monolayer. Solid curves are the fits with eq 1. Arrows in Im $\chi_S^{(2)}$ mark the position of existing vibrational modes.

4 $\mu$m, were derived from a picosecond mode-locked Nd:YAG laser and an associated optical parametric system described elsewhere.[4] The reference SF generator was a *y*-cut crystalline quartz plate, and the phase modulator was a silica plate. The sample studied was an OTS monolayer deposited on a silica substrate, and finally, the reference sample was a *z*-cut crystalline quartz plate. The SF signal reflected from the sample surface was collected by a detector system after proper spectral filtering.

The OTS monolayer system has been well-studied by conventional SFVS.[5] We show that, even so, phase-sensitive SFVS could still provide new information on it. We focus here on the spectra of OTS monolayers in the CH stretch range obtained with S, S and P polarizations (SSP) for waves at $\omega$, $\omega_1$, and $\omega_2$, respectively. They are displayed in Figure 2. The spectrum of $|\chi_S^{(2)}|^2$ is essentially identical to those reported earlier.[5] The spectra of Re $\chi_S^{(2)}$ and Im $\chi_S^{(2)}$ satisfy the Kramers−Kronig relation and vary over positive and negative values. In general, Im $\chi_S^{(2)}$, analogous to absorption or emission spectrum, is more informative. Any deviation of Im $\chi_S^{(2)}$ away from zero indicates the existence of vibrational resonances nearby. The absolute average orientation (up or down) of a moiety can be directly correlated to the sign of its symmetric stretch mode in Im $\chi_S^{(2)}$.

We can use eq 1 to fit simultaneously the experimental spectra of Im $\chi_S^{(2)}$, Re $\chi_S^{(2)}$, and $|\chi_S^{(2)}|^2$, as shown by the solid curves in Figure 2, and identify six unambiguous discrete modes (marked by arrows). The two main peaks at 2873 and 2935 cm$^{-1}$ were previously identified as the symmetric stretch ($r^+$) and the Fermi resonance of the bending mode with $r^+$ of the terminal methyl group.[6] They are both positive in Im $\chi_S^{(2)}$, denoting average orientation of methyl groups pointing away from the substrate. The nearly degenerate antisymmetric stretches ($r^-$) of the methyl group, difficult to detect in $|\chi_S^{(2)}|^2$, appear clearly in Im $\chi_S^{(2)}$ as a weak negative peak at 2958 cm$^{-1}$. The weak, negative feature at 2847 cm$^{-1}$ was attributed to the symmetric stretch ($d^+$) of the methylene groups along the alkyl chain.[6] For a monolayer of all-trans alkyl chains along the surface normal, $d^+$ is usually very weak in SFVS because the methylene planes are flat on the surface with azimuthal isotropy and their arrangement along a chain has near inversion symmetry. Thus the appearance and strength of the $d^+$ mode in SFVS was often taken as a measure of the presence of gauche defects in the chain, although not well-justified.[7] Its negative amplitude in Im $\chi_S^{(2)}$ indicates that, for OTS, it has a net dipole moment pointing toward the substrate. There are two other weak modes not easily seen in the $|\chi_S^{(2)}|^2$ spectrum but discernible in Im $\chi_S^{(2)}$. One is positive at 2853 cm$^{-1}$ (appearing as a shoulder at the low-frequency side of the 2873 cm$^{-1}$ peak) and the other negative at 2883 cm$^{-1}$. On the basis of bulk vibrational spectroscopic studies,[6] they can be identified as the symmetric ($d_\omega^+$) and antisymmetric ($d_\omega^-$) stretch modes of the methylene group next to the terminal methyl group. Their appearance in SFVS indicates that, on average, their molecular plane must be tilted away from the substrate plane.[8] This may be caused by terminal gauche defects in some alkyl chains as they are likely to happen at room temperature. The positive sign of $d_\omega^+$ agrees with the picture that such methylene groups have their symmetric axis point away from the substrate. We note that in the conventional $|\chi_S^{(2)}|^2$ spectra, the overlapping $d^+$ and $d_\omega^+$ modes are hardly distinguishable and could lead to confusion in the analysis.

In summary, we have described a general phase-sensitive SFVS method that allows us to obtain not only the usual intensity spectrum, $|\chi_S^{(2)}(\omega_2)|^2$, but also the spectra of Re $\chi_S^{(2)}(\omega_2)$ and Im $\chi_S^{(2)}(\omega_2)$. The latter provides more direct and detailed information including better resolved spectral features and absolute orientations of different molecular moieties contributing to the spectra. This was demonstrated by applying the technique to an OTS monolayer on silica, showing clearly the additional spectral information obtainable in comparison with conventional SFVS. In particular, we observed the stretch modes of the methylene group adjacent to the terminal methyl group of a monolayer of alkyl chains appearing at different frequencies from those of other methylene groups in the chains.

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**Supporting Information Available:** Fitting parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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