Nonlinear Optical Studies of the Pure Liquid/Vapor Interface: Vibrational Spectra and Polar Ordering

R. Superfine, J. Y. Huang, and Y. R. Shen
Department of Physics, University of California, Materials and Chemical Sciences Division,
Lawrence Berkeley Laboratory, Berkeley, California 94720
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Using infrared-visible sum-frequency generation we have obtained the vibrational spectra of CH stretches of methanol molecules at the interface between methanol vapor and liquid. This is the first vibrational spectrum ever observed from a neat liquid surface. The measured polarization dependence and phase of the nonlinear susceptibility allow us to conclude that the surface methanol molecules are polar oriented with the CH_3 group pointing away from the liquid with a very broad orientational distribution.

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The surface of a neat liquid is of basic interest to many researchers in different disciplines,[1] but has hardly been explored because of the lack of suitable probes. The standard surface techniques used to study solid surfaces in ultrahigh vacuum are difficult to apply in the liquid case.[2] X-ray total reflection has been employed to investigate the surface structure of a liquid,[3] but little information can be deduced on the molecular orientation at the surface. Recently, optical second-harmonic generation (SHG) and sum-frequency generation (SFG) have been demonstrated to be versatile probes of surfaces and interfaces.[4-10] In particular, they can be used to measure polar orientations of molecules (or an atomic group in the molecules) at various interfaces.[11,12] Thus the techniques should allow us to answer the question of whether at the surface of a neat polar liquid the molecules are polar oriented.[13,14] This is important because the surface properties of the liquid should depend heavily on the polar or nonpolar orientation of the surface molecules. In the nonresonant case, SHG has been applied to the air/water interface for this purpose.[15] In comparison, SFG is a much more powerful technique for such studies since it can detect the vibrational spectrum of the surface molecules. Therefore one can distinguish between various surface species and obtain detailed information on the orientation of particular atomic groups within the molecules. We report here our recent study in this respect on the air/methanol surface using SFG. Methanol was chosen since, similar to water, its properties are dominated by hydrogen bonding, and a theoretical calculation on the surface molecular orientation is available.[16] Our result shows that the surface methanol molecules are polar oriented with CH_3 groups facing away from the liquid, in agreement with the theoretical prediction.

Infrared-visible SFG as a surface vibrational spectroscopic technique has been described in earlier publications.[9,10] The process is allowed in the electric-dipole approximation only in a medium without inversion symmetry. In the case of a molecular liquid, the surface contributes to the SFG spectrum significantly only if the molecules at the surface are polar oriented. The polarization dependence of the SFG spectrum then allows us to deduce the average polar orientation of the surface molecules (or atomic groups in the molecules). This, however, assumes that the quadrupole and bulk contributions to SFG can be neglected or subtracted.[5] Therefore the other important task of our present work is to show that by properly designing the experiments, one can find the relative magnitudes of the various contributions to the observed SFG spectrum. In the methanol case, the spectrum is actually dominated by the polar-oriented surface molecular layer.

Let us begin with a brief discussion of the underlying theory. The material property than can be deduced from the measurement of SFG in reflection from a surface is the effective surface nonlinear susceptibility $\chi_s^{(2)}(\omega_2=\omega_v+\omega_{\rm IR})$ which generally consists of three parts:[5]

$$\chi_s^{(2)}=\chi_D+\chi_I+\chi_{SB}\,, \tag{1}$$

where χ_D is the electric-dipole contribution from the polar-oriented surface layer, χ_I is the electric-quadrupole contribution from the surface region due to the rapid field variation at the interface, and χ_{SB} is the electric-quadrupole contribution originating from the bulk. With the input infrared frequency $\omega_{\rm IR}$ near resonances and the input visible frequency ω_v off resonance, each term in Eq. (1) can be decomposed into a resonant and nonresonant part; for example,

$$\begin{aligned}\chi_D&=\chi_D^{NR}+\chi_D^R\,,\\ \chi_D^R&=\sum_q A_q/(\omega_q-\omega_{\rm IR}-i\Gamma_q)\,.\end{aligned} \tag{2}$$

Here, A_q, ω_q, and Γ_q are the strength, frequency, and damping constant for the qth vibrational mode of the molecules. Note that for the same mode q, the resonant frequency ω_q in χ_D, χ_I, and χ_{SB} may be different. The dispersion of $\chi_s^{(2)}$ vs $\omega_{\rm IR}$ is reflected in the SFG spectrum.

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We are particularly interested in the electric-dipole term χ_D, as it carries information about the polar orientation of the surface molecules. We can write

$$(\chi_D)_{ijk} = N_s s_i(\omega_a) s_j(\omega_b) s_k(\omega_c) \times \sum_{l,m,n} \langle (\hat{\mathbf{i}}\cdot\hat{l})(\hat{\mathbf{j}}\cdot\hat{\mathbf{m}})(\hat{\mathbf{k}}\cdot\hat{\mathbf{n}})\rangle \alpha^{(2)}_{lmn} , \qquad (3)$$

where N_s is the surface density of the polar-oriented molecules at the surface, $s_i(\omega_a) = E_z(z=0,\omega_a)/D_z(z=0,\omega_a)$ for $i=z$ and is equal to unity for $i=x$ or y, $\alpha^{(2)}$ is the second-order nonlinear polarizability, and the angular brackets denote an average over the orientational distribution. In our SFG experiment on methanol, the CH_3 stretch modes are probed. As a simple model for the molecular polarizability we assume that the CH_3 group of methanol has C_{3v} symmetry, and the second-order polarizability of each CH bond can be characterized by a single component $\alpha^{(2)}_{\xi\xi\xi}$ along the bond. We then find, for future analysis of molecular orientation, the following explicit expressions for two elements of χ_D:

$$(\chi_D^R)_{yyz} = N_s \varepsilon(\omega_{\mathrm{IR}})^{-1} \alpha^{(2)}_{\xi\xi\xi} (0.275\langle\cos\theta\rangle + 0.165\langle\cos^3\theta\rangle) ,$$

$$(\chi_D^R)_{yzy} = N_s \varepsilon(\omega_v)^{-1} \alpha^{(2)}_{\xi\xi\xi} (-0.165\langle\cos\theta\rangle + 0.165\langle\cos^3\theta\rangle) ,$$

$$\alpha^{(2)}_{\xi\xi\xi} = a_{\mathrm{CH}}/(\omega_{\mathrm{CH}} - \omega_{\mathrm{IR}} - i\Gamma) , \qquad (4)$$

where $\varepsilon(\omega_{\mathrm{IR}})$ and $\varepsilon(\omega_v)$ are the dielectric constants of methanol at the infrared and visible frequencies, respectively, $\hat{\mathbf{z}}$ is taken as the surface normal, and θ is the angle between the symmetric axis of the CH_3 group and the surface normal. In order to deduce χ_D from $\chi_s^{(2)}$, we must also know χ_I and χ_{SB}. One can show from a crude estimate that $|\chi_D|$ for a polar-oriented monolayer should be significantly larger than $|\chi_I| \sim |\chi_{SB}|$ (knowing that the quadrupole bulk contribution comes from the electric quadrupole polarizability of the molecules).[5] Nonetheless, we shall discuss later how experimentally we can conclude that the yyz and yzy components of χ_I and χ_{SB} are negligible.

The experimental setup has been described in detail elsewhere.[10] In the present experiment, the 1-mJ visible pulse at 0.532 μm and the 0.15-mJ infrared pulse tunable about 3.3 μm with a pulse width of ~20 ps and a repetition rate of 10 Hz were directed and overlapped at the vapor/liquid interface of methanol in a Teflon trough enclosed in a cell. The absorption of the incident infrared beam in the methanol vapor was kept well below 5% by making the beam path in the vapor less than 2 mm. All measurements were performed at room temperature. The frequency of the IR beam was calibrated to within ±1.5 cm^{-1} with a polystyrene reference and all spectra were normalized to the SFG spectrum from a quartz crystal. The SF signal from $(\chi_s^{(2)})_{yyz}$ at the CH_3 symmetric stretch frequency was about 50 photons per pulse, corresponding to $|(\chi_s^{(2)})_{yyz}| = 3.5\times10^{-16}$ esu.

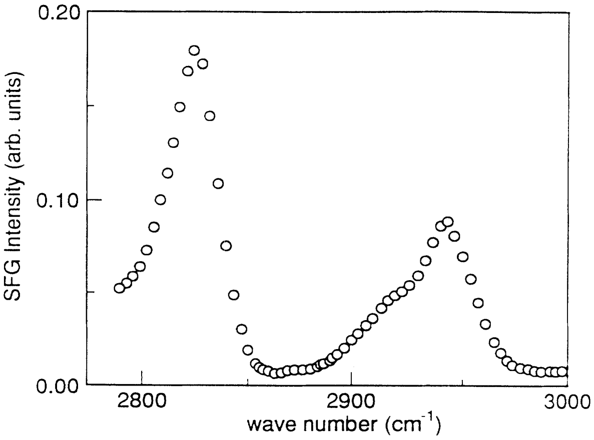

FIG. 1. SFG spectrum obtained from the liquid/vapor interface of pure methanol. The beam polarizations are s, s, and p for the sum frequency, visible (0.532 μm), and infrared beams, respectively.

Figure 1 shows the SFG spectrum from the air/methanol liquid interface for the ssp- (SF output, visible input, and IR input are s, s, and p polarized, respectively) polarization combination. The signal from the sps polarization combination was at the noise level $(\chi_s^{(2)})_{yzy} < 0.5\times10^{-16}$ esu. A fit of the ssp spectrum to Eq. (2) gives vibrational resonances at 2832, 2925, and 2951 cm^{-1}. The 2832 cm^{-1} comes from the symmetric (ν_s) CH_3 stretch.[17] The peaks at 2925 and 2951 cm^{-1} have been assigned in Raman-scattering studies to two Fermi resonances of the CH_3 ν_s mode with overtones of the CH_3 bending modes.[18] The spectrum in Fig. 1 is at least partly due to χ_D of an oriented surface layer because the same measurement at a glass/methanol liquid interface yielded hardly detectable SFG spectra. We now want to show that the observed spectrum is actually dominated by χ_D.

The bulk contribution to the effective surface susceptibility χ_{SB} has, in fact, two separate parts. One arises from the true electric quadrupole contribution from the bulk χ_{SB1}, while the other χ_{SB2} is a bulklike surface contribution originating from the difference between the quadrupole nonlinear susceptibilities of the two sides of the interface.[5] The absence of the reflected SFG from the glass/methanol liquid interface indicates that the contribution from χ_{SB} is small ($|\chi_{SB}| < 8\times10^{-17}$ esu). If SFG in transmission through a methanol cell is measured, then the χ_{SB1} contribution is expected to dominate because of the associated long coherent length for SFG (~15 μm as compared to ~330 Å for SFG in reflection). This should allow us to find χ_{SB1}. In Fig. 2, we present the ssp SFG spectrum of the CH_3 ν_s mode from such a measurement. The double humps instead of a single resonant peak for the CH_3 ν_s mode can be understood by taking into account the strong resonant IR absorption. A fit to this spectrum yields $|\chi_{SB1}|_{yyz} = 7\times10^{-19}$ esu at resonance. We, therefore, have $|\chi_{SB1}|_{yyz}/|\chi_s^{(2)}|_{yyz} \sim 0.02$. For the sps-polarization combination,

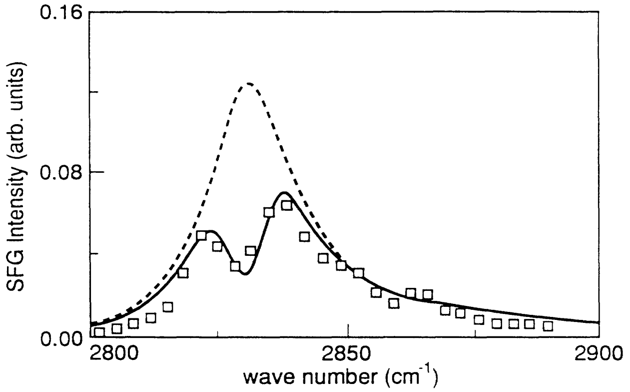

FIG. 2. SFG spectrum for pure methanol obtained in transmission geometry. The solid line is a fit to the data for a single resonant peak including the effect of absorption of the infrared beam in the bulk liquid. The dotted line is obtained from a similar calculation without taking into account the IR absorption.

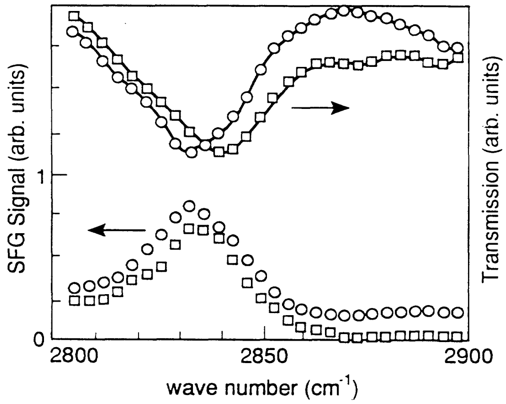

FIG. 3. Comparison of the bulk IR absorption spectra (top) with the reflected surface SFG spectra for pure methanol (circles) and for a 1:1 water/methanol solution (squares). All spectra are normalized and the two SFG spectra are shifted vertically from each other for clarity.

the lack of a detectable SF signal in transmission in our experiment gives $|\chi_{SB1}|_{yzy} < 3\times10^{-20}$ esu.

To further convince ourselves that the χ_{SB} contribution is negligible in reflected SFG from methanol, we conducted the following experiment. It is known that the resonant frequency of the CH$_3$ ν_s mode of bulk methanol shifts $+7$ cm^{-1} upon dilution of the methanol to a 1:1 aqueous solution.[18,19] We have confirmed the result by taking the IR-absorption spectra of pure and mixed methanol in a separate detection arm simultaneously with the SFG measurement. As shown in Fig. 3, while the IR-absorption spectra do exhibit the shift, the SFG spectra remain essentially unchanged. This clearly indicates that the SFG spectra are dominated by the surface. A fit to the SFG spectra gives $|(\chi_{SB})_{yyz}| < 8\%|(\chi_s)_{yyz}|$ or $|(\chi_{SB})_{yyz}| < 2.7\times10^{-17}$ esu at the resonant peak.

The χ_I term comes from the electric quadrupole contribution due to the rapid variation of the input fields at the interface. We could estimate its magnitude by measuring SFG from the methanol molecules adsorbed at various liquid/glass interfaces with different dielectric constant ratios.[5] However, methanol does not adsorb strongly on glass. Instead, we used methoxy (CH$_3$O) in our experiment for the estimate, and found that in the CH$_3$ stretch frequency region, $|(\chi_I)_{yyz}| < 10\%|(\chi_s)_{yyz}| \sim 3.4\times10^{-17}$ esu and $|(\chi_I)_{yzy}| < 5\times10^{-17}$ esu.

From the above results, we can then establish the fact that $|(\chi_D)_{yyz}|$ from a polar-oriented methanol molecular layer at the air/methanol interface actually dominates the SFG spectrum in Fig. 1. It is the first vibrational spectra ever recorded from a neat liquid surface. The lack of signal for the *sps*-polarization combination sets the limit that $|(\chi_D)_{yzy}| < 0.8\times10^{-16}$ esu.

It is interesting and important to know whether the polar-oriented surface methanol molecules have their CH$_3$ groups facing up or down. This information can be obtained from the sign of χ_s for methanol relative to that of a methoxy monolayer adsorbed on glass.[12] The latter is known to have the CH$_3$ groups pointing away from the glass. By measuring the phases of χ_s in the two cases, we found that the two χ_s at resonance have the same sign, and therefore the surface methanol molecules, on average, must be oriented with the CH$_3$ groups projecting out of the liquid. This is consistent with the theoretical prediction: The methanol molecules are oriented to maximize the number of hydrogen bonds among them at the interface.[13,16]

From the measured values of $(\chi_D)_{yyz} = 3.5\times10^{-16}$ esu and $(\chi_D)_{yzy} = (0\pm0.8)\times10^{-16}$ esu, we can find $\langle\cos\theta\rangle$ and $\langle\cos^3\theta\rangle$ from Eq. (4) if N_s and $\alpha^R_{\xi\xi\xi}$ are known. Then with the assumption of a Gaussian distribution for θ, the average tilt angle θ_0 and the width of the distribution $\Delta\theta$ can be determined. We take $N_s = \rho^{2/3}$, where ρ is the methanol liquid density, and obtain $\alpha_{\xi\xi\xi}$ from Eq. (4) by assuming that $a_{\rm CH}$ for methanol is the same as the one for the terminal CH$_3$ group of a fatty acid molecule and, therefore, can be deduced from the SFG measurement of a fully packed monolayer of fatty acid on water.[10] Because the result of the analysis is very sensitive to the uncertainty in the data, the uncertainties in the values of θ_0 and $\Delta\theta$ are large. We can only conclude that our data are consistent with a range of values between $(\theta_0 = 0, \Delta\theta = 110°)$ and $(\theta_0 = 60°, \Delta\theta = 70°)$. Undoubtedly, the orientational distribution is very broad. This is consistent with the turbulent nature of the air/liquid interface, and was predicted by the recent molecular-dynamics calculation.[16]

In conclusion, we have shown that SFG allows us to measure the surface vibrational spectrum of a neat polar liquid and determine the polar orientation of the surface molecules. No other technique has the same capability. We have found that at the pure methanol liquid/vapor interface, the methanol molecules are oriented with their CH_3 groups facing up and with a very broad orientational distribution.

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