Vibrational Spectroscopy of Water at the Vapor/Water Interface

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Using infrared-visible sum-frequency generation we have obtained the OH stretch vibrational spectra of water at the vapor/water interface. From the spectra, we deduce that more than 20% of the surface water molecules have one free OH projecting into the vapor. The spectrum is weakly temperature dependent from 10 to 80 °C. A monolayer of fatty alcohol on water surface terminates the free OH groups and induces an icelike structure in the spectrum.

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Water is certainly the most important liquid on Earth and has been well investigated in the past. Our understanding of its interfacial properties is unfortunately still rather primitive even though it is crucial for the advances of many disciplines of science as well as for the control of many technological processes [1]. This paper concerns the water/vapor interface. The study of pure liquid/vapor interfaces has had a long history [2]. A large amount of theoretical work on the subject already exists in the literature [3]. Experiments, however, have been limited to measurements of thermodynamic quantities such as surface tension and surface electrical potential [4,5]. They can provide only crude information on the molecular orientation at an interface [4,6]. Recently optical second harmonic generation (SHG) and sum-frequency generation (SFG) have been demonstrated to be effective tools to probe various interfaces including pure vapor/liquid interface [7,8]. In a recent publication, Goh *et al.* have used SHG to study the air/water interface [9]. They conclude that the surface water molecules are polar oriented, but their interpretation depends critically on the temperature dependence of the observed SHG signal. As a rule, SFG is a much more powerful technique since it can yield vibrational spectra of surface molecules that allow us to identify species and obtain detailed information on the structure and orientation of particular atomic groups within the molecules. In this paper, using SFG, we present for the first time the OH vibrational spectra of water molecules at a neat water/vapor interface. The results indicate that more than 20% of surface water molecules have a non-hydrogen-bonded OH (free OH bond) pointing out of the liquid and the other OH, hydrogen bonded, pointing into the bulk liquid. The spectra show no strong temperature dependence between 10 and 80 °C. The free OH bonds can be terminated by hydrogen bonding to a monolayer of fatty alcohol floating on water and the spectrum then resembles that of ice. These results provide some very valuable information about the orientation of water molecules at the interfaces.

Infrared-visible SFG as a technique for surface vibrational spectroscopy has been described in earlier publications [7]. It is electric dipole forbidden in a centrosymmetric medium but allowed at an interface where the inversion symmetry is broken. The material parameter that can be deduced from the measurement of SFG is the effective surface nonlinear susceptibility $\chi_S^{(2)}$ $(\omega_{\mathrm{SF}}=\omega_v+\omega_{\mathrm{ir}})$ which can be decomposed into two parts [10],

$$\chi_S^{(2)}=\chi_D+\chi_Q\,, \tag{1}$$

where χ_D is from the electric-dipole contribution of an oriented surface layer and χ_Q is from the electric-quadrupolar contribution from both surface and bulk [10]. We shall show later that χ_Q is negligible in our experiment. Therefore, we will focus on χ_D, which can be written as the sum of a resonant term χ_D^{R} and a nonresonant term χ_D^{NR}:

$$\chi_D=\chi_D^{\mathrm{NR}}+\chi_D^{\mathrm{R}}\,. \tag{2}$$

With ω_{ir} near resonances and ω_v off resonance, χ_D^{R} can be related to the second-order molecular polarizability $\alpha^{(2)}$ as [10]

$$\chi_{D,ijk}^{\mathrm{R}}=N_s\sum_{l,m,n}\langle(\mathbf{i}\cdot\mathbf{l})(\mathbf{j}\cdot\mathbf{m})(\mathbf{k}\cdot\mathbf{n})\rangle\alpha_{lmn}^{(2)}\,, \tag{3a}$$

$$\alpha_{lmn}^{(2)}=\sum_q\frac{A_q}{\omega_q-\omega_{\mathrm{ir}}-i\Gamma_q}\,, \tag{3b}$$

$$A_q=\frac{1}{2\omega_q}\frac{\partial\mu_n}{\partial Q}\frac{\partial\alpha_{lm}^{(1)}}{\partial Q}\,, \tag{3c}$$

where A_q, ω_q, and Γ_q are the strength, frequency, and damping constant of the qth vibrational mode of the molecules, N_s is the surface density of molecules, the angular brackets denote an average over the molecular orientational distribution, and $\partial\mu/\partial Q$ and $\partial\alpha^{(1)}/\partial Q$ are the derivatives of molecular dipole moment and polarizability with respect to the normal mode Q.

The experimental setup for SFG has been described elsewhere [7]. In the present experiment, the laser system produced 0.5 mJ of visible pulse at 0.532 μm (diameter, 700 μm) and 0.2 mJ tunable infrared pulses (diameter 300 μm) tunable from 2700 to 3900 cm^{-1}. The bandwidth of the infrared beam varied from about 8 cm^{-1} around 2900 cm^{-1} to about 45 cm^{-1} at 3700 cm^{-1}. The infrared and visible beams were incident at an angle around 50° and overlapped at the vapor/liquid interface of water in an enclosed temperature controlled cell. Ultrapure water (18 MΩ/cm) obtained from a Millipore filtration system was used. Infrared absorption by the water vapor was kept below 10% by making the beam path in the vapor less than 3 mm. All SFG spectra were normalized to the SFG from a quartz crystal. Around resonances, the signal level from the water surface was about 0.3 photons per pulse, corresponding to $\chi_S^{(2)} \approx 2\times10^{-16}$ esu.

Figure 1(a) shows the SFG spectrum of water at the vapor/water interface for the *ssp* polarization combination (SF output, visible input, and ir input are *s*, *s*, and *p* polarized, respectively). The signal with the other polarization combinations was less than 10% of the *ssp* peak signal and exhibited hardly any discernible resonant features within our experimental uncertainty. The spectrum in Fig. 1(a) can be fitted reasonably well by Eq. (3b) assuming three vibrational resonances around 3200, 3400, and 3700 cm^{-1}. Notice that we assume Lorentzian line shapes for the resonances in Eq. (3b). It has been argued in the literature that the bulk water spectrum (3100–3600 cm^{-1}) is more accurately described by more complicated expressions [11]. However, here, we will discuss only the gross features of the spectrum.

The spectrum shows two main features: a broad band between 3100 and 3500 cm^{-1} and a relative sharp peak at 3690 cm^{-1}. The latter (resolution limited) can be assigned to the stretch mode of free OH [11–13]. The single peak above 3600 cm^{-1} indicates that only one OH of the surface water molecule can be non-hydrogen bonded. If both OH were free two sharp peaks would appear in the spectrum, one antisymmetric lying above 3700 cm^{-1} and the other symmetric around 3600 cm^{-1} [11–13]. The resonances between 3100 and 3500 cm^{-1} are usually attributed to stretch modes of hydrogen-bonded OH.

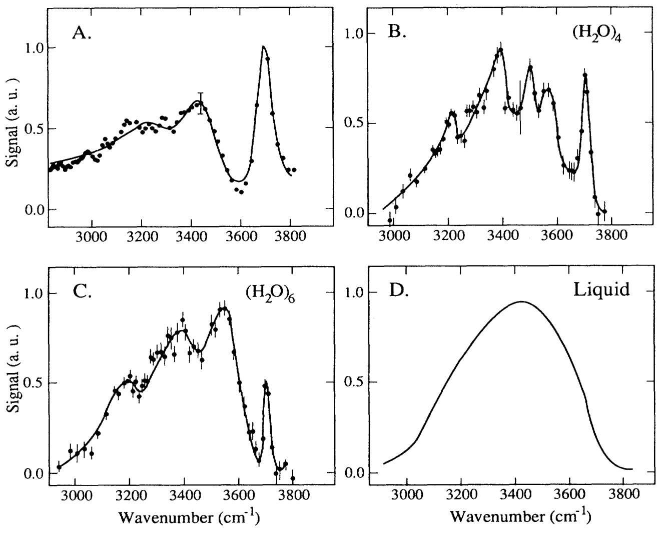

FIG. 1. (a) SFG spectrum of the pure water/vapor interface at 40 °C with polarization combinations *s*, *s*, and *p* for the sum-frequency, visible, and infrared beams, respectively. Solid line is a theoretical fit using Eq. (3). (b),(c) Infrared spectra of water clusters with sizes indicated (from Ref. [12]). (d) Infrared absorption spectrum of liquid water [from E. Whalrafen, J. Chem. Phys. **47**, 114 (1967)].

It is interesting to compare the above SFG spectrum for the water/vapor interface with the infrared absorption spectra for water clusters and liquid [11,12], as presented in Fig. 1. The qualitative resemblance between the surface and the clusters ir spectra is quite striking. Unlike liquid water, they both show a free OH peak at ~3700 cm^{-1} and a broad structured band for bonded OH at lower frequencies. For small clusters, in which the numbers of free and bonded OH in the clusters are not very different, the peak heights of free and bonded OH modes are close. The free OH peak decreases relatively as the cluster size grows and the relative number of free OH decreases. It finally disappears in the liquid case as it should. These features assure that the SFG spectrum in Fig. 1(a) is dominated by the $\chi_D^{(2)}$ contribution from the surface water molecules. This conclusion is further supported by the following observation: The free OH peak in the SFG spectrum disappears while the bonded OH band becomes narrower and peaks towards the low-frequency side, resembling more the ir spectrum of ice, when the water surface is covered by a monolayer of long chain alcohol molecules. This is shown in Fig. 2.

The existence of water molecules with one free OH is actually not so surprising: Water molecules prefer to establish hydrogen bonds with their nearest neighbors in a tetrahedral bonding geometry. At the vapor/liquid interface, they face an environment on the vapor side that no neighboring molecules can be hydrogen bonded to. No

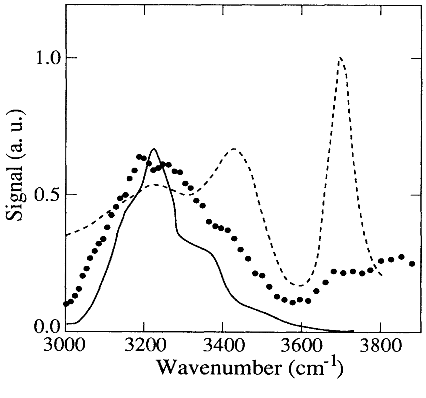

FIG. 2. SFG spectrum (dotted line), with the *ssp* polarization combination, of water surface covered by a stearyl alcohol monolayer compressed to 10 mN/m. For comparison, the SFG spectrum of pure water surface (dashed line) and the infrared absorption spectrum of ice (solid line) [from E. Whallhey and J. E. Bertie, J. Chem. Phys. **46**, 1264 (1967)] are also shown.

matter how a water molecule orients itself at the interface, one hydrogen bond to neighboring molecules is necessarily broken. The situation is similar for water molecules near a hydrophobic solute or wall [14].

We can deduce information about the free OH orientation from the SF spectra. In a simple model for H_2O [11], $\partial\mu/\partial Q$ in Eq. (3) should be along the OH bond and $\partial\alpha^{(1)}/\partial Q$ has cylindrical symmetry with two components, $\alpha_\perp$ and $\alpha_\parallel$, perpendicular and parallel to the OH bond. We then have only two nonvanishing SF polarizabilities $\alpha^{(2)}_{\perp\perp\xi}$ and $\alpha^{(2)}_{\xi\xi\xi}$. Consequently, Eq. (3) yields

$$\chi^{R}_{D,yyz}=\tfrac{1}{2}N_s\alpha[\langle\sin^2\theta\cos\theta\rangle(1-r)+2r\langle\cos\theta\rangle]\,, \tag{4a}$$

$$\chi^{R}_{D,yzy}=\tfrac{1}{2}N_s\alpha[\langle\sin^2\theta\cos\theta\rangle(1-r)]\,, \tag{4b}$$

where $\alpha=\alpha^{(2)}_{\xi\xi\xi}$, $r=\alpha^{(2)}_{\perp\perp\xi}/\alpha^{(2)}_{\xi\xi\xi}=\alpha_\perp/\alpha_\parallel$, N_s is density of free OH at the surface, and θ is the angle between the free OH bond and the surface normal. For free OH, the ratio r has been deduced from Raman scattering to be 0.32 [15]. From the SFG measurements with *ssp* and *sps* polarization combinations we deduce

$$\chi_{D,yzy}/\chi_{D,yyz}\leq 0.3\,. \tag{5}$$

Equation (5) then leads to $\theta\leq 38°$ if a delta function orientational distribution is assumed. The latter assumption may not be valid, but the result here indicates that the OH bond tilts considerably away from the surface plane. We can also estimate the number of free OH bonds on the surface, if the values of $\chi_{s,yzy}$ and α as well as the orientational averages in Eq. (4a) are known. By calibrating the signal at the free OH resonance against the signal from a quartz crystal, we obtained $\chi_{s,yyz}=2.1\times10^{-16}$ esu. From Raman and ir measurements we find, using Eq. (3), $\alpha_{\xi\xi\xi}=2.5\times10^{-30}$ esu [16,17]. The quantity in the square brackets in Eq. (4a) is insensitive to the θ distribution from $\theta=0°$ to 60° and yields a value of $\sim$0.65. Equation (4a) then leads to $N_s=2.7\times10^{14}$ cm^{-2}, corresponding to $\sim$20% of a full water monolayer. This value is a lower bound; we have chosen to use the maximum value of $\alpha_{\xi\xi\xi}$ derived from Raman and ir measurements because of uncertainties in those measurements [18]. The result indicates that considerably more free OH bonds point out of the liquid at the vapor/water interface than is predicted by some molecular dynamics simulations [3,19].

We can fit the spectrum of Fig. 1(a) with three resonant modes in Eqs. (2) and (3) (see Table I). The amplitudes of the bonded OH modes appear to have a 180° phase shift from that of free OH. Since the polarizabilities for the bonded and unbonded OH are most likely of the same sign, this 180° phase difference indicates that the free and bonded OH at the interface are, on average, pointing in opposite directions. With the free OH pointing out of the liquid, the bonded OH must point into the liquid, as one should expect. This picture is consistent with the very small surface potential of water [5], which results from having the permanent dipoles of water molecules lie close to the surface plane. It is interesting to note that a water molecule lying in a vertical plane with its permanent dipole along the surface actually has its free OH bond titled at 38° from the surface normal.

TABLE I. Parameters obtained by fitting the SFG spectrum of Fig. 1(a) with three resonant modes using Eq. (3). $\chi_{NR}=-0.4$.

ω_q (cm^{-1})	Γ_q (cm^{-1})	A_q (a.u.)
3257.5	108.6	24.2
3451.3	101.5	76.4
3682.9	33.3	−38.6

The SFG spectrum of a water surface covered by a full alcohol monolayer in Fig. 2 is also quite interesting. It has recently been shown that such a monolayer on water is able to induce an increase of the icing temperature of the nearby water because the ordered OH groups in the alcohol monolayer closely match those of a hexagonal ice layer in the *a*-*b* plane [20]. The similarity between our spectrum of the vapor/alcohol/water interface and the ir spectrum of ice, shown in Fig. 2, leads us to believe that ice nucleation by the alcohol monolayer can indeed occur: The top layer of water molecules is converted into an icelike structure which provides a seed for ice nucleation.

We have also studied the temperature dependence of the SFG spectrum of the vapor/water interface. As shown in Fig. 3, there is no significant change over the temperature range from 10 to 80 °C. This is consistent with the observed weak temperature dependence of sur-

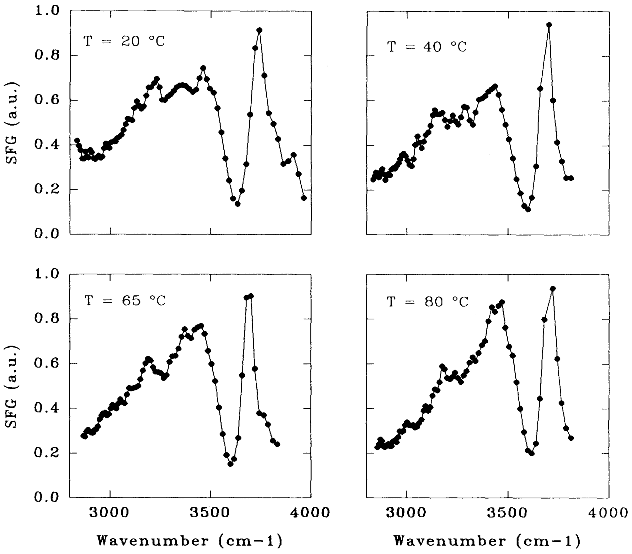

FIG. 3. SFG spectra, with the *ssp* polarization combination, of a pure water/vapor interface at four temperatures.

face tension and surface potential of water [4,6]. The only noticeable change in the spectrum is an increase of the peak around 3400 cm^{-1} at the expense of the peak around 3200 cm^{-1} when the temperature is increased, in agreement with the general trend observed in the ir spectrum of bulk water [11]. This behavior is at variance with the strong temperature dependence of the OH orientation predicted by some molecular dynamic simulations [19]. Our result is also different from that of the SHG measurement on the vapor/water interface reported recently [9], where a substantial change of signal with temperature was observed. We have repeated the experiment and found, within our experimental uncertainty of ±10%, no change in the output signal associated with $\chi^{(2)}_{xzx}$ from 10 to 45 °C while a 50% decrease is expected from the results of Ref. [9].

In conclusion, we have obtained for the first time a vibrational spectrum of water molecules at the vapor/water interface. The spectrum unambiguously identifies the presence of a surface species with one free OH projecting into the vapor. The surface density of this species is estimated to be more than 20% of a full monolayer. In addition the spectrum suggests that a roughly equal number of hydrogen-bonded OH point into the liquid. This picture of the vapor/water interface has been predicted by molecular dynamics simulations and is consistent with the relatively small surface potential of water. We have also found that the SFG spectrum has no strong temperature dependence, and a monolayer of alcohol on water is able to induce an icelike structure at the interface. These results provide very useful information about surface ordering of water molecules and illustrate the promise of SFG as a tool for study of important aqueous interfaces.

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Note added.— We were recently informed by Professor K. Eisenthal that his group had repeated the experiment of SHG from the vapor/water interface (Ref. [9]) and found that as temperature increases from 10 to 80 °C, $\chi^{(2)}_{xzx}$ decreases by less than 10% and $\chi^{(2)}_{zxx}$ decreases by 10%.

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