LETTERS TO THE EDITOR

The Letters to the Editor section is divided into four categories entitled Communications, Notes, Comments, and Errata. Communications are limited to three and one half journal pages, and Notes, Comments, and Errata are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 1997 issue.

COMMUNICATIONS

Probing the intermolecular hydrogen bonding of water molecules at the CCl₄/water interface in the presence of charged soluble surfactant

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The molecular structure and hydrogen bonding of water molecules at the CCl₄/water interface in the presence of a charged soluble surfactant has been explored in this study using vibrational sum frequency generation. By examining OH stretching modes that are highly sensitive to the local hydrogen bonding environment it is found that water molecules at the CCl₄/water interface both in the presence and absence of a charged soluble surfactant are predominantly in a tetrahedral arrangement much like the structure of ice. Isotopic dilution studies have been employed to further characterize this icelike interfacial structure. A blueshift of approximately 120 cm^{-1} of the icelike OH stretching mode is observed upon dilution with D_2O. The first vibrational spectra of the OH stretching mode from uncoupled HOD molecules at the CCl₄/water interface is also reported. © *1997 American Institute of Physics.* [S0021-9606(97)03346-1]

The interactions between water and charged amphiphiles at surfaces can play a dominant role in many processes including micellization, stabilization of membranes, and protein activity.[1–5] At an oil/water interface an amphiphile alters the hydrogen bonding of water at the junction, resulting in a lowering of the interfacial tension. How these changes in hydrogen bonding with surfactant adsorption are manifested in the nonlinear vibrational spectroscopy of interfacial water at the CCl_4/H_2O interface is the focus of this paper.

Total internal reflection sum frequency generation (TIR-VSFG) is employed here in a unique set of experiments which characterize in detail the hydrogen bonding between interfacial water molecules at the liquid/liquid interface in the presence of a simple charged soluble surfactant. The combination of the surface sensitivity of VSFG and the enhancement afforded by operating in a total internal reflection geometry makes TIR-VSFG a powerful tool in studies such as these. The spectroscopy of the OH stretching modes of interfacial water molecules has been used in this study as a diagnostic of interfacial water structure and hydrogen bonding. These modes are particularly sensitive to the hydrogen bonding environment of water molecules as shown by numerous IR and Raman studies of bulk water.[6,7] For bulk water, these studies have shown that water molecules partition into icelike and waterlike structures. We report that at the CCl₄/water interface both in the presence and in the absence of surfactant, nearly all interfacial molecules are in a tetrahedral arrangement much like the structure of ice with little or no evidence for a waterlike structure.

Further explorations of the icelike character of the interfacial water molecules in the presence of surfactants is obtained through isotopic dilution experiments. Isotopic dilution studies in which the OH stretching vibrations are

progressively decoupled by additions of D_2O have been invaluable in studies of hydrogen bonding in bulk water[8] and ice[9] but this is the first study in which such experiments have been applied to liquid surfaces. The shift in energy observed in the icelike O–H peak with uncoupling of the OH symmetric stretching vibration has provided us with a quantitative means of comparing the hydrogen bonding at this interface with that measured for bulk ice and supercooled liquid water. Through isotopic dilution studies we have also obtained the first vibrational spectra of the uncoupled OH stretching mode from HOD molecules at the CCl₄/water interface. This mode has been shown to be an excellent indicator of the local hydrogen bonding environment in bulk studies.[10]

Figure 1 shows the VSFG spectra from the CCl₄/water interface with the aqueous phase having a bulk sodium dodecyl sulfate (SDS) concentration of 1.0 mM. All spectra presented were obtained under S_{sfg}, S_{vis}, P_{ir} polarization conditions which picks out vibrational modes with components of the transition dipole moment perpendicular to the plane of the interface. The series of spectra were taken with various mixtures of H_2O and D_2O ranging from a mole fraction of 1.00 to 0.10. The mole fraction of H_2O, D_2O, and HOD were calculated by assuming complete isotopic exchange.[10] The presence of SDS at the interface is evidenced by the C–H stretching modes of the alkyl chain and is also verified by interfacial tension measurements. Because these modes have been examined in detail in previous studies[3,11] from this laboratory under higher spectral resolution, further discussion is not warranted here. The shoulder in the spectra near 3000 cm^{-1} has not been studied in any detail here but could be due to the OH stretch from water molecules that are hydrogen bonded to the charged sulfate head group with the large redshift presumably a result of the strong hydrogen
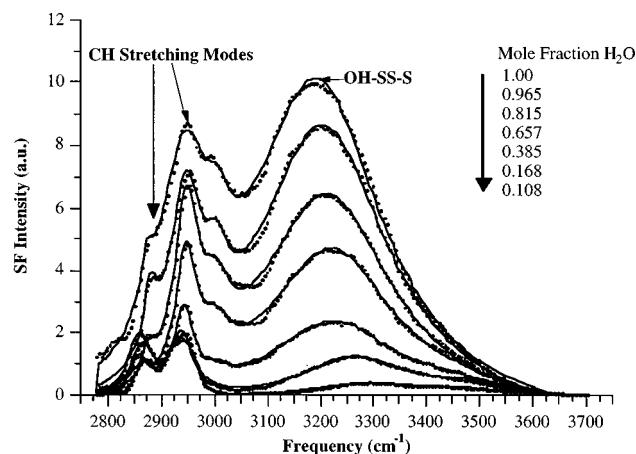

FIG. 1. VSFG spectra from the CCl_4/H_2O interface with 1.0 mM SDS in the aqueous phase as a function of mole fraction of H_2O under S-sf, S-vis, P-ir polarization conditions. Solid lines are a spectral fit to the data.

bond. The solid lines in Fig. 1 are a spectral fit to the data from which we are able to extract peak intensities, positions, bandwidths, and integrated areas.

Focusing on the spectrum in Fig. 1 corresponding to SDS in 100% H_2O, the dominant feature in the OH stretching spectral region is centered around 3200 cm^{-1}. We attribute the observed peak at 3200 cm^{-1} to the OH–SS–S mode, which corresponds to the in-phase coupled symmetric stretch from water molecules that have complete tetrahedral coordination much like the structure of ice. In contrast, for SDS at the air/water interface the VSFG spectrum shows two peaks,[11] one corresponding to the OH–SS–S mode and an additional peak located between 3400 and 3450 cm^{-1}, which is attributed to water molecules that have incomplete tetrahedral coordination and a more waterlike structure. These two peaks are commonly referred to as the ''icelike'' and ''waterlike'' modes with the icelike mode corresponding to a higher degree of hydrogen bond order and the waterlike mode to a lower degree of hydrogen bond order.[5,8] From the dominance of the icelike mode in the VSFG spectra from SDS at the CCl_4/H_2O interface we infer that the prevailing structure of the interfacial water molecules in the presence of a charged surfactant is a tetrahedral arrangement much like the structure of ice. As will be described in a later publication,[12] relative to the neat CCl_4/H_2O interface, the addition of surfactant results in increased intensity in the icelike mode due to electrostatic field induced orientation of water molecules in the double-layer region.

Another OH mode often observed in bulk and surface water studies[5] but not observed here is located at approximately 3680 cm^{-1} and is attributed to the free OH stretch from water molecules that have hydrogen atoms not participating in hydrogen bonding. The laser system employed limits our ability to detect this mode.[13] The redshift of the peak position of the OH stretching modes with increased intermolecular hydrogen bonding as is seen in the three aforementioned modes has been thoroughly examined.[7,14] The shift occurs because hydrogen bonding actually ''steals'' bond strength from the OH bond and thus stronger hydrogen

bonds result in weaker OH covalent bonds and vibrational modes at lower energy. A comparison of the peak positions with the degree of hydrogen bonding illustrates the well-known trend that the peak position of the OH stretching mode is redshifted with increasing hydrogen bonding. Accompanying the redshift of the peak frequency with increased hydrogen bonding is a large increase in the bandwidth of the OH stretch. This increase in the bandwidth results from dynamic dipole–dipole coupling between neighboring water molecules which produces a distribution of low and high frequency stretching modes.[7,14,15] The nature of this distribution also has an effect on the position of the peak frequency of the OH stretching mode. Deconvolution of these two effects, hydrogen bonding and intermolecular coupling, on the energetics of the OH stretching peaks in the vibrational spectra is difficult and generally requires the study of HOD in H_2O or D_2O, which eliminates the intermolecular coupling effect. However, the extent of hydrogen bonding can be inferred through a comparison of the relative number of water molecules contributing to the icelike and waterlike modes. This comparison is possible since the icelike mode is indicative of more complete hydrogen bonding than the waterlike mode.

Our observation that at the CCl_4/water interface the icelike mode dominates the OH stretching spectral region provides direct evidence that there is more complete hydrogen bonding between neighboring water molecules at the interface than in the bulk. This observation is a consequence of the hydrophobic effect which causes the interfacial water molecules to rearrange into a tetrahedral structure thus maximizing the intermolecular hydrogen bonding in the presence of a nonpolar solute such as CCl_4.[1,12,16] We are probing specifically the asymmetric interfacial region which for an ionic strength of 1.0 mM corresponds to at most 30 water layers (see Ref. 12), thus one might expect CCl_4 to be present in this region. In the bulk aqueous phase the water molecules are not influenced by the presence of a nonpolar molecule and the waterlike peak accompanies the icelike peak. At the *neat* CCl_4/water interface we also find that the icelike mode dominates the VSFG spectrum.[17] The similarity of the water structure at the CCl_4/water interface both in the presence and in the absence of a charged soluble surfactant further allows us to infer that the presence of the surfactant and counter ions in the aqueous phase does not disrupt to any measurable degree the hydrogen bond ordering of the interfacial water molecules.

Further information about the interfacial water hydrogen bonding structure can be extracted from the spectra of the isotopic mixtures shown in Figs. 1 and 2 where the latter corresponds to spectra from the lowest H_2O concentrations depicted on an expanded scale for clarity. Numerous IR and Raman studies of H_2O/D_2O mixtures have been conducted in the past to gain a better understanding of the structure of water in both bulk liquid water and bulk ice.[6,7,9] As D_2O (H_2O) is added to H_2O (D_2O) the intermolecular coupling between the OH (OD) oscillators decreases as a result of the difference in hydrogen bonding between H_2O and D_2O and the difference in energy of the OH and OD stretches.
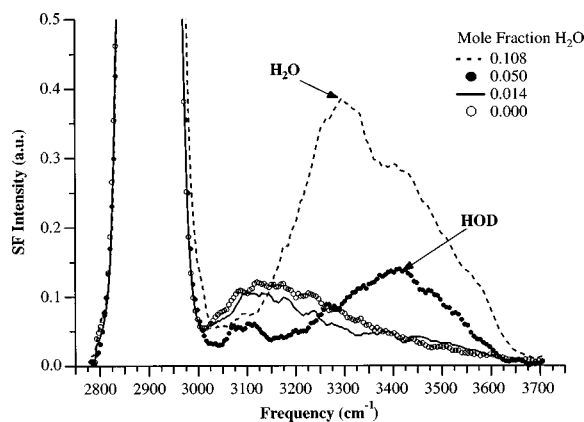
FIG. 2. VSFG spectra from the CCl_4/H_2O interface with 1.0 mM SDS in the aqueous phase for low mole fractions of H_2O under S-sf, S-vis, P-ir polarization conditions.

FIG. 3. Plot of the peak position of the OH–SS–S mode from the spectral data fits as a function of the mole fraction of H_2O.

The intermolecular decoupling as D_2O (H_2O) is added to H_2O (D_2O) manifests itself in the IR and Raman spectra as a blueshift in the spectral position of the OH (OD) stretching vibrations. This blueshift occurs as the mole fraction of H_2O (D_2O) is decreased and results from the decreased intermolecular coupling of the OH oscillators. Experiments conducted on cubic and amorphous ice[9] as well as supercooled liquid water[15] have shown a blueshift in the OH–SS–S peak of approximately 100–120 cm^{-1} as the mole fraction of H_2O varies from 1.00 to 0.01.

Close inspection of the spectra in Fig. 1 shows a similar blueshift of the OH–SS–S peak position with decreasing H_2O mole fraction. The peak position goes from 3200 cm^{-1} at a mole fraction of 1.00 to 3320 cm^{-1} at a mole fraction of 0.05. The blueshift in the peak frequency of the OH–SS–S with decreasing H_2O mole fraction is a result of the intermolecular decoupling of the OH oscillators by the addition of OD oscillators as previously mentioned. The magnitude of the blueshift that we observe for the CCl_4/H_2O–SDS system is approximately the same, 120 cm^{-1}, as has been observed for both bulk amorphous ice and cubic ice[9] as well as supercooled water at −5 °C.[15] This similarity provides further support that the interfacial water molecules are in an icelike arrangement with a high degree of hydrogen bond order and a tetrahedral structure. Figure 3 shows the peak frequency of the OH–SS–S stretch obtained from the fits to the spectral data plotted as a function of the mole fraction of H_2O. From Fig. 3 we see that the peak frequency of the OH–SS–S mode blueshifts in nominally a linear fashion with decreasing H_2O mole fraction over the range from 1.0 to 0.2. Beyond a mole fraction of 0.2 the slope of the frequency shift with decreased H_2O becomes significantly steeper. This observation is most likely due to the increased HOD component present at the interface interfering with the fitting of the spectra to the uncoupled OH stretch from H_2O .

Figure 2 shows the VSFG spectra from the lowest mole fraction H_2O solutions studied. At a H_2O mole fraction of 0.108 a small shoulder is observed at approximately 3460 cm^{-1} on the high frequency side of the blueshifted OH–SS–S peak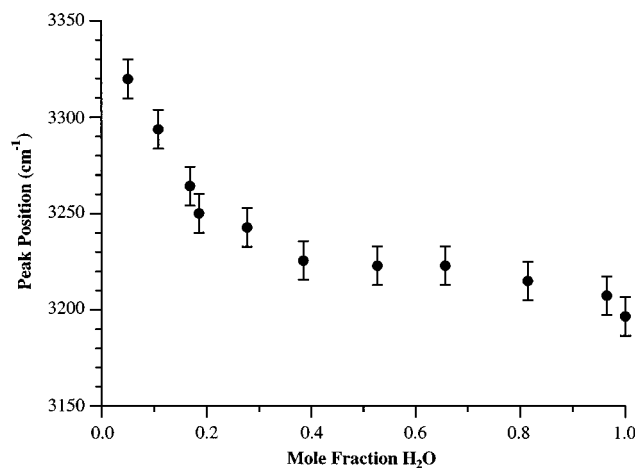. We attribute this peak to the uncoupled OH stretch (OH–S) from interfacial HOD molecules produced by isotopic exchange between H_2O and D_2O . The VSFG spectrum from the 0.05 mole fraction H_2O solution shows that this peak actually dominates the OH stretching spectral region due to the very small concentration of H_2O and the much larger (0.35 mole fraction) HOD concentration. The absolute intensity from the OH stretch of HOD is much weaker than the OH stretch of H_2O due to diminished hydrogen bonding and uncoupling of the OH stretching vibration of interfacial HOD molecules. HOD is both intermolecularly and intramolecularly uncoupled and thus has been extensively used in the determination of structural characteristics from vibrational spectra.[7,10,18] This work represents the first observation of the OH stretch from uncoupled HOD molecules at a liquid/liquid interface in the presence of a charged soluble surfactant.

Studies using polarized Raman spectroscopy have suggested a two species model for the hydrogen bonded HOD molecules in bulk water solutions.[8] While more complicated models are currently employed, the two species model is adequate for the analysis here. The first species is composed of HOD molecules with two equivalent strong hydrogen bonds while the second is composed of HOD molecules with one weak and one strong hydrogen bond. The OH stretch from the more strongly hydrogen bonded HOD in D_2O has been shown to occur between 3300 and 3500 cm^{-1} and is very temperature sensitive, shifting to higher frequencies with increased temperature. The peak position of the more strongly hydrogen bonded OH(OD) stretching mode in the liquid state varies from 3435 to 3489 cm^{-1} (2520 to 2568 cm^{-1}) as the temperature varies from 10 to 90 °C.[8] In contrast, the peak position of the more weakly hydrogen bonded OH(OD) from HOD in D_2O(H_2O) at approximately 3600 (2650 cm^{-1}) shows minimal temperature dependence.[8] That the OH stretch from interfacial HOD molecules at room temperature is located at approximately 3460 cm^{-1} agrees well with the position of the more strongly hydrogen bonded OH stretch. Further experiments are in progress to explore the temperature dependence of this mode.

Our VSFG studies of the hydrogen bonding and struc-

ture of water molecules at the CCl_4/water interface in the presence of a charged soluble surfactant provide new insight into differences between interfacial and bulk water molecules. We find that water molecules at the CCl_4/water interface both in the presence and absence of a charged soluble surfactant are predominantly in a tetrahedral arrangement much like the structure of ice whereas water molecules in the bulk are equally partitioned into waterlike and icelike modes at room temperature. Isotopic dilution studies have been used for the first time to understand the hydrogen bonding of water molecules at a liquid surface. A blueshift of approximately 120 cm^{-1} in the icelike peak is observed upon dilution which we attribute to intermolecular uncoupling of the OH oscillators. The similarity in the magnitude of this frequency shift with that of bulk amorphous and cubic ice as well as supercooled liquid water further confirms our conclusion that the interfacial water molecules are in an ice-like arrangement. At low H_2O mole fractions we find that we are sensitive to the OH stretching mode from uncoupled HOD at the CCl_4/water interface. This mode has been shown to be essential in the full characterization of the structure of bulk water in both liquid and solid phases from IR and Raman spectroscopic studies. Our future endeavors will include exploiting this mode to probe the interfacial hydrogen bonding environment as a function of temperature and the presence of structure making and breaking ions as well as to probe structural dependencies on the interfacial potential.

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