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Water Structure at Air/Acetonitrile Aqueous Solution Interfaces

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How is interfacial water organized beneath an acetonitrile monolayer at the air/acetonitrile aqueous solution interface? The method of vibrational sum frequency generation was used to address these issues. It was found that the different water structures expressed at different vibrational spectral regions, i.e. the "ice-like", the "liquid-like", and the non-hydrogen bonded "free" OD, responded differently as the acetonitrile bulk concentration was increased. At the bulk acetonitrile concentration that was sufficient to form an acetonitrile monolayer and at higher bulk concentrations, it was observed that there are no longer vibrational resonances that correspond to the oriented collective water vibrations, i.e. the "ice-like" and "liquid-like" structures of water as observed at the air/water interface. The story was different in the free OD vibrational region where a red-shifted resonance was found at acetonitrile concentrations sufficient to form an acetonitrile monolayer. Speculations on the origin of this resonance are presented.

Introduction

The structure of interfacial water is of importance in science, medicine, and technology.[1,2] The geometrical arrangements and packing of the molecules that comprise a water interface are a delicate balance of the intermolecular interactions of the water molecules with each other and with those of the other bulk phases. The unique chemical and physical properties associated with water surfaces, whether they are composed of one chemical species (neat water interface) or are multicomponent aqueous surfaces, are directly related to the orientational structure, molecular density, and the chemical composition of the interface. The vibrational spectrum of the water surface is of particular interest because the OH stretch modes are highly sensitive to the local molecular environment.[3−12] The water vibrational spectrum therefore provides a sensitive probe of the structure and energetics of the hydrogen-bond network at interfaces.

The interfacial structures as well as the bulk structures of binary nonelectrolyte aqueous solutions are of special interest.[2] Of these, the bulk properties of acetonitrile−water binary solutions have been studied extensively by many techniques because of its importance in many areas of chemistry ranging from synthesis to chromatography and electrochemistry.[13−16] Thermodynamics and diffusion studies indicate that the bulk behavior is far from that of an ideal solution.[15,16] At the air/CH_3CN−water solution interface, there is a preferential adsorption of acetonitrile because interfacial acetonitrile significantly lowers the interface energy relative to the air/water interface.[17,18]

Related to the studies discussed here is earlier work on the interfacial orientational structure and vibrational spectrum of CH_3CN at the air/CH_3CN−H_2O solution interface.[17,18] Evidence of an unexpected sharp change in the sum frequency generation (SFG) signals occurred when the bulk CH_3CN concentration increased from a mole fraction below 0.07 to 0.1.[17,19] This change was manifested by an abrupt shift in both the −CN vibrational frequency (14 cm^{-1}) and in the orientation of acetonitrile molecules (40°−70° tilt) at the interface. A sharp change in orientation at the same bulk acetonitrile concentration has been observed and reported to us in a private communication.[19] The vibrational frequency of the −CN chromophore at bulk concentrations below $X_{CH3CN} = 0.07$ was found to be characteristic of nitriles hydrogen bonded to proton donors such as water in bulk solution. At bulk concentrations greater than 0.1 mol fraction, the vibrational frequency of the interfacial −CN chromophore was observed to shift to a value that is near that in neat bulk acetonitrile, i.e. the non-hydrogen bonded form. This dependence of vibrational frequency on composition indicates that the acetonitrile molecules at the surface experience two different environments: one below 0.07 and one at and above 0.1 mol fraction. A model was proposed to account for the structural changes. It was suggested that at the higher bulk concentrations the acetonitrile molecules at the interface are no longer hydrogen bonded to water and have changed their orientation. The driving force for the structural change was attributed to the dipole−dipole interactions among the interfacial acetonitrile molecules. As the interfacial density of the CH_3CN molecules increase, their dipole−dipole interactions become more important. These interactions can be attractive or repulsive. The orientational rearrangement, which results from the CH_3CN dipole axis being at larger angles to the surface normal, reduces the repulsive dipole−dipole interactions and increases the attractive interactions, which thereby lowers the surface free energy (Figure 1).

In the present study, we address the question of the change in water structure as CH_3CN displaces the H_2O molecules at the interface. Are the water molecules beneath acetonitrile monolayer oriented or not? It has been well established that the presence of an insoluble monolayer significantly alters the structure of interfacial water. Unlike previous studies, which examined the water structure beneath an insoluble surfactant monolayer, the work reported here involves the presence of the molecules comprising the monolayer, in this case acetonitrile, that are in the bulk solution as well as at the interface. The acetonitrile molecules are free to enter and leave the interfacial region, whereas the surfactant cannot. Because the acetonitrile molecules are in the bulk solution, they compete with the water molecules for locations beneath the acetonitrile monolayers. A key issue is how the acetonitrile molecules below the monolayer affect the water hydrogen bonding network and the orientational

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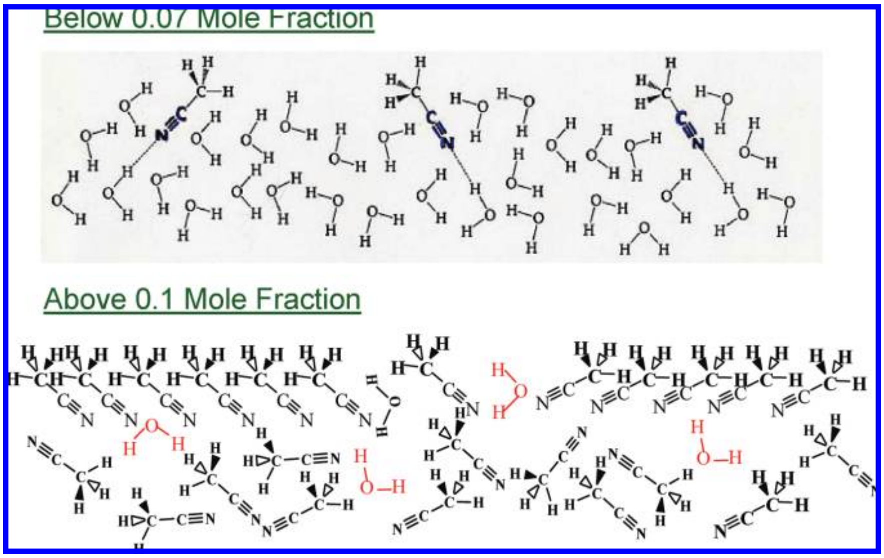

Figure 1. Speculations of the air/CH_3CN-H_2O interface below and above a CH_3CN monolayer.

alignment of the water molecules, to which SFG is sensitive. To examine these questions, we use SFG to probe the vibration of interfacial water at the air/acetonitrile−water solution interface, which complements earlier work that focused on the vibrations of interfacial acetonitrile. In this research we seek to obtain a broader description of the intermolecular interactions and structure at the air/CH_3CN solution interface.

Experimental Section

The detailed experimental setup has been discussed previously.[20,21] Briefly, an 800 nm regeneratively amplified Ti:sapphire system (Spitfire, Spectra Physics) seeded with a MaiTai 80 MHz, 80 fs oscillator, at a 1 kHz repetition frequency was employed in the present experiments. The signal generated by the input of the 800 nm fs pulse into an OPA is in the range of 1.1−1.6 μm, and the idler is in the range of 1.6−2.7 μm. By difference frequency generation in a 1 mm $AgGaS_2$ crystal, tunable infrared light between 3 and 8.5 μm with a bandwidth of about 150 cm^{-1} (fwhm) was generated. The reflected femtosecond beam from the regenerative amplifier was spectrally narrowed using a home-built pulse shaper to provide an 800 nm pump pulse with a bandwidth of 10 cm^{-1} and a time duration of 2.5 ps, determined from temporal cross-correlation measurements with the femtosecond 800 nm laser. The output power at 800 nm after pulse shaping was 21 μJ/pulse. The IR beam with a typical power of 6 μJ per pulse is focused onto the sample by a 100 mm focal length BaF_2 lens at an angle of 67° relative to the surface normal and a spot size of 120 μm. The visible light field is focused on a 210 μm spot size by a 250 mm focal length BK glass lens at an angle of 76° from the surface normal.

The SFG spectrum of air/neat H_2O extends from 3100 to 3750 cm^{-1}. Because the infrared light centered 3700 cm^{-1} is absorbed due to water vapor in the ambient environment, we use D_2O with the corresponding vibration at 2737 cm^{-1} ("free" OD stretching mode) as a substitute. Similarly we use D_2O to probe the stretch at 2500 cm^{-1}, which for H_2O is at 3450 cm^{-1}. The D_2O stretch at 2400 cm^{-1} corresponds to that at 3200 cm^{-1} for H_2O. Because of CO_2 absorption in the region of 2400 cm^{-1}, the intensity of our IR light at 2400 cm^{-1} was very weak, and we therefore used H_2O to investigate the corresponding vibration, which is at 3200 cm^{-1}. The SFG signals reported here were normalized by GaAs SFG intensities. To visualize the whole SFG spectra of interfacial water, we measured the SFG spectra at the 3200 cm^{-1} and shifted it to the corresponding region of interfacial D_2O, according to the reduced masses of H_2O and D_2O. The $-C{\equiv}N$ vibration at 2260 cm^{-1} does not appear in Figure 2 because the SFG spectra were measured at 3200 cm^{-1}.

A 0.3 m spectrograph was used which had one entry port and two exit ports (Acton Research), two gratings, 1200 grooves/mm blazed at 500 nm, and 150 grooves/mm blazed at 4 μm. The 500 nm blazed grating was chosen to measure SF signals from the H_2O and D_2O, and the 4 μm blazed grating was used for an IR intensity measurement. One exit was configured for detecting the dispersed signal with a liquid-nitrogen cooled, back-thinned charged coupled device (CCD) camera (Roper Scientific, 1340 by 400 pixels) operating at −120°.

CH_3CN was purchased from Sigma-Aldrich and used as received. Water of 18 MΩ/cm was used in the experiments, and the D_2O obtained from isotope company has a deuterate purity of 99.5%. The surface tension of each solution was measured using the Wilhelmy plate method.

Theoretical Considerations

To analyze the SFG signals from the air/acetonitrile−water solution interface, we shall briefly introduce some of the basic formulas used in this work. The sum frequency intensity is proportional to the square of the sum over all macroscopic sum frequency susceptibility terms separated into a nonresonant part $\chi_{NR}^{(2)}$ and a resonant part $\chi_R^{(2)}(\omega_{SF})$. SFG signals can be expressed as[20−24]

$$I^{SFG}(\omega) \propto |\chi_{NR}^{(2)} + \sum_q^n \chi_R^{(2)}(\omega_q)|^2$$

$$\chi_R^{(2)}(\omega_q) = \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q} \qquad (1)$$

Where, A_q contains the product of the Raman and infrared matrix elements of the qth normal mode, ω_q denotes the resonant frequency of the qth vibrational normal mode, ω_{IR} is the

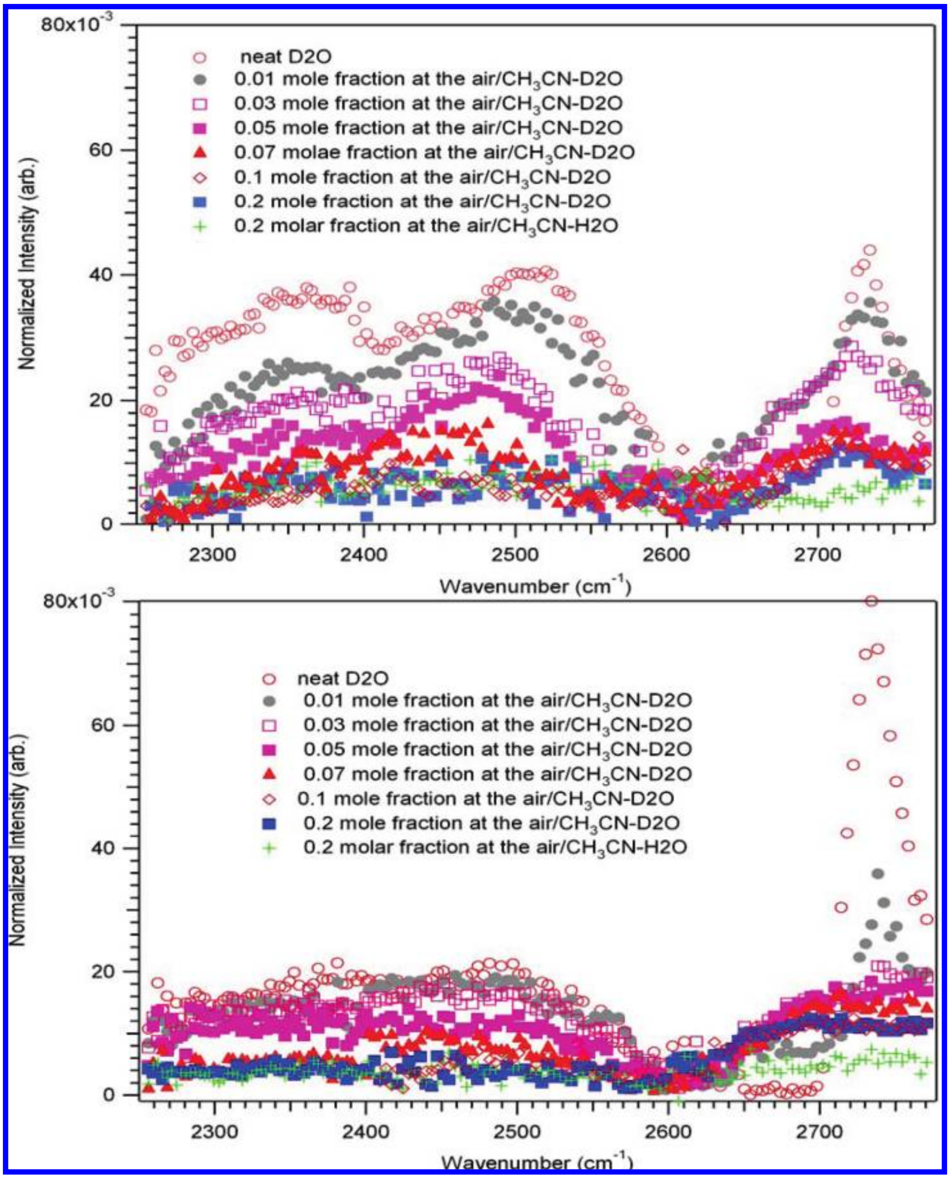

Figure 2. Sum frequency spectra of water at the air/CH_3CN−water interface at several bulk CH_3CN mole fractions. (A) SSP polarization combination. (B) PPP polarization combination.

frequency of the IR light, and Γ_q is the spectral width of the vibrational state.

Of the total 27 macroscopic susceptibility tensors $\chi^{(2)}_{IJK}$ (I, J, K being the three laboratory coordinates), 7 nonzero terms are nonvanishing for a rotationally isotropic interface ($C_{\infty v}$ symmetry), namely, $\chi^{(2)}_{XXZ} = \chi^{(2)}_{YYZ}$; $\chi^{(2)}_{XZX} = \chi^{(2)}_{YZY}$; $\chi^{(2)}_{ZXX} = \chi^{(2)}_{ZYY}$ and $\chi^{(2)}_{ZZZ}$.[18−24,27−30] In our experiments, the YZ plane was the plane of incidence for both the visible and IR beams. The two polarization combinations measured in each experiment were SSP and PPP, where the first letter denotes the polarization of the sum frequency, the second one denotes the polarization of the visible light, and the last one denotes the polarization of the IR light. These polarizations are connected with the laboratory coordinates by nonlinear Fresnel coefficients and appropriate projections. The seven nonzero macroscopic susceptibilities in the laboratory coordinates are obtained from the four polarization combinations.

Results and Discussion

To examine the effects of acetonitrile on the interfacial structure of water, we will start with the unperturbed water structure at a neat air/water interface. Although there are controversies, it is generally accepted that there are three types of OH stretching modes.[3−12] One has a fairly narrow spectrum at ~3700 cm^{-1}, which is attributed to a free OH extending into the vapor phase, i.e. the OH is not hydrogen bonded to other water molecules. In addition there are two broad and overlapping bands centered at ~3400 and 3200 cm^{-1} that are attributed to oriented hydrogen bonded collective water vibrations. The 3400 cm^{-1} vibration is often referred to as "liquid-like" because of its proximity to bonded OH stretching modes in bulk water. In a similar way, the 3200 cm^{-1} resonance is referred to as being "ice-like" because of its proximity to bonded OH in bulk ice. As noted earlier, D_2O is used rather than H_2O for experimental reasons. The peaks for the OD stretching modes at 2737 and 2500 cm^{-1} correspond respectively to the 3700 and 3400 cm^{-1} modes for the OH stretching modes. Measurements of the 3200 cm^{-1} OH stretching mode corresponds to the 2350 cm^{-1} resonance for the OD stretching mode (Figure 2). It is to be noted that the SFG spectra of D_2O is slightly dependent on the angle of incidence of the visible and IR beams. Thus in our experiments, which were performed at geometries that were

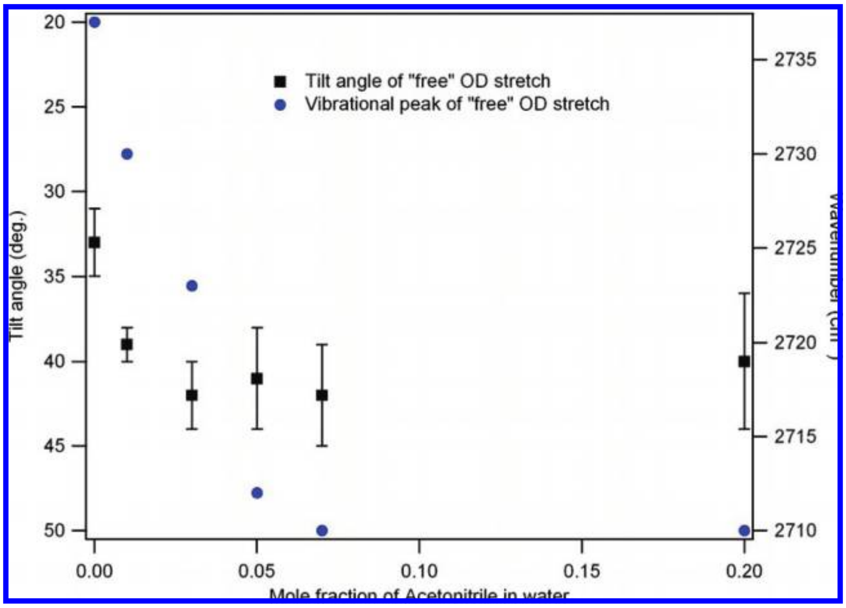

Figure 3. Tilt angles with respect to interfacial normal and spectral peaks as a function of mole fraction of acetonitrile in D_2O solution.

different from those in other laboratories,[25,26] we obtained slightly different SFG spectra.

In order to determine orientational structure, we used the intensity ratio method in our data analysis. Because the symmetry of the free OD is $C_{\infty v}$, there are three nonzero hyperpolarizability elements, which are $\beta^{(2)}_{zzz}$, $\beta^{(2)}_{xxz} = \beta^{(2)}_{yyz} = r\beta^{(2)}_{zzz}$, where z is parallel to the OD bond and x and y are perpendicular to the OD bond and $r = \beta^{(2)}_{xxz}/\beta^{(2)}_{zzz}$. The allowed susceptibility tensors for the OD chromophore are[20−24,27−34]

$$\begin{aligned}
\chi^{(2)}_{ZZZ} &= N_s[r\langle\cos\theta\rangle + (1-r)\langle\cos^3\theta\rangle]\beta_{zzz} \\
\chi^{(2)}_{XXZ} &= \frac{1}{2}N_s[(1+r)\langle\cos\theta\rangle + (1-r)\langle\cos^3\theta\rangle]\beta_{zzz} \\
\chi^{(2)}_{XZX} &= \frac{1}{2}N_s(1-r)[\langle\cos\theta\rangle - \langle\cos^3\theta\rangle]\beta_{zzz} \\
\chi^{(2)}_{ZXX} &= \frac{1}{2}N_s(1-r)[\langle\cos\theta\rangle - \langle\cos^3\theta\rangle]\beta_{zzz}
\end{aligned} \tag{2}$$

The orientation of the free OD axis is independent of the in-plane angle ϕ because the interface of a liquid is isotropic with respect to ϕ.

The calculation of the free OD orientation assumes a narrow orientational distribution. The orientation of the free OD stretch at the neat air/D_2O interface was found to be 33°± 2° with respect to the surface normal, which is in agreement with reported values for the free OH stretching at the air/H_2O interface (Figure 3).[7] As the acetonitrile mole fraction increases toward 0.07, the free OD tilts to larger θ values, i.e. toward the surface plane. The tilt angle was found to be 42°± 3°. At larger acetonitrile mole fractions the signal was very weak and yielded a large spread in orientations extending from 36° to 45° at a mole fraction of 0.2.

To gain information on the acetonitrile surface excess at the air/acetonitrile−water interface, the surface tension of the air/acetonitrile−water interface was measured as a function of the acetonitrile mole fraction in the bulk solution (Figure 4). Surface tension measurements in conjunction with the Gibbs adsorption equation were used to obtain the excess surface CH_3CN population. It is to be noted that the maximum in the CH_3CN excess occurs at a X_{ACN} of 0.07−0.1, which is where the abrupt changes in the orientation and the frequency of the −CN vibration were observed. The relationship of the abrupt change in frequency and orientation with the maximum in the acetonitrile excess is not known and is under investigation.

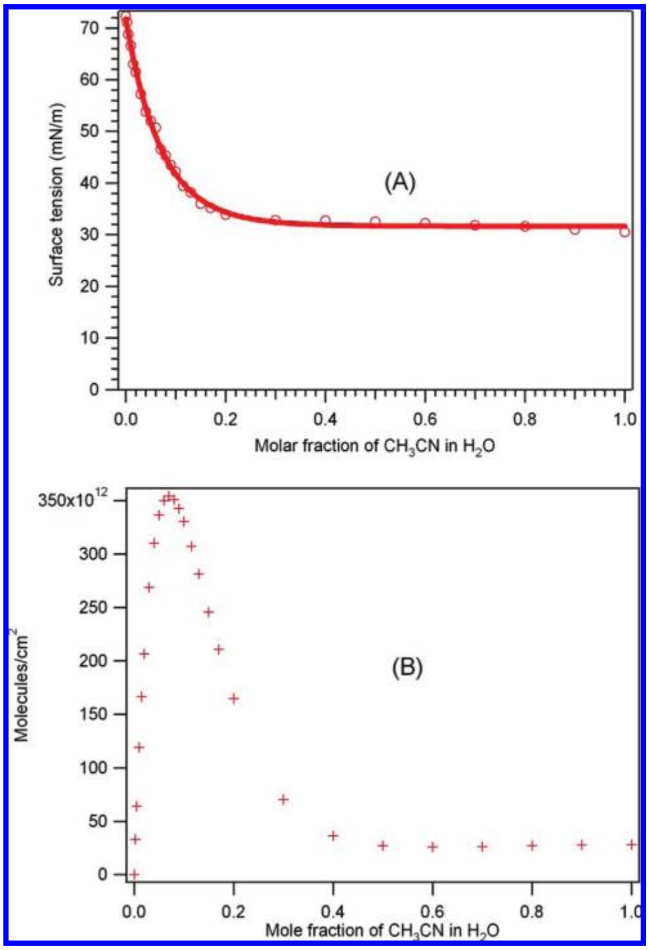

Figure 4. (A) Surface tension of air/acetonitrile−H_2O as a function of bulk acetonitrile mole fraction. (B) Surface excess of acetonitrile at the air/CH_3CN interface.

As with the observed decrease in surface tension we found on addition of acetonitrile that there was a decrease in the D_2O SFG intensities for the three spectral regions. It is seen in Figure 2 that the decrease in the intensity of the "ice-like" resonance at 2350^{-1} is more rapid than that for the "liquid-like" resonance at 2500 cm^{-1} and the free OD resonance at 2737 cm^{-1}. On further increase of CH_3CN to the higher mole fractions of 0.1 and 0.2, we observed no resonances at 2350 and 2500 cm^{-1}. This indicates that there are no oriented hydrogen bonded water−water structures, which are characteristic of this vibrational spectral region. However, there remains at the high CH_3CN mole fractions, a resonance in the free OD spectral region though it is somewhat red-shifted to 2710 cm^{-1} from the free OD (2737 cm^{-1}) at the neat air/D_2O interface. In addition to the experiments with D_2O, we measured the SFG spectra for CH_3CN in H_2O at 0.2 mol fraction. The motivation was to determine if the feature at 2710 cm^{-1} is due to CH_3CN or to D_2O. The absence of any resonance in the air/H_2O-CH_3CN interface at 2710 cm^{-1} for the $X_{CH3CN} = 0.2$ in Figure 2 indicates that the feature at 2710 cm^{-1} is not due to interfacial CH_3CN but originates from D_2O. One possible explanation of the 2710 cm^{-1} features is that there are oriented D_2O molecules located between the acetonitrile molecules of the top monolayer and the layer beneath, which are chiefly composed of acetonitriles. Another description is that D_2O molecules are positioned between the CH_3CN molecules in the top CH_3CN monolayer. The shift of the free OD vibrational frequency as the interfacial CH_3CN density increases reflects the difference in the environments, which in one case contains only water molecules at the neat air/D_2O interface versus chiefly CH_3CN molecules in the local environment of individual interfacial D_2O molecules at high CH_3CN mole fractions. In both cases, the van der Waals interactions of the free OD with the surrounding acetonitrile molecules shift the frequency of the free OD stretch to the red relative to its frequency when projected into the air side of the air/D_2O interface, as shown in Figure 2. A red shift in SFG experiments of the free OH stretch frequency at the H_2O/CCl_4 interface was observed[4] and attributed to attractive interactions between the free OH and the CCl_4 phase into which the free OH is projected. In an SFG study of the phospholipid surfactant/D_2O and the palmitic acid surfactant/D_2O interface,[35] a red-shifted broad resonance in the free OD stretch spectral region was observed. The observation of the red-shifted free OD at full monolayer coverage was attributed to interactions of D_2O with the hydrophobic alkane chains of the surfactants, resulting in a hydrophobic induced drying transition.[35] This would lead to D_2O at the hydrophobic interface with the alkane chains not being fully coordinated, and thereby yielding a free OD moiety. It is not clear at this time whether the free OD and free OH that are observed are due to their location in contact with organic molecules or for the H_2O/CCl_4 interface whether there is a drying transition induced separation of the water from the CCl_4 that is responsible for the free OH group. For the air/acetonitrile−water solution, it is not obvious where the dewetting would occur. However if the known microheterogeneity of the bulk acetonitrile water solution, i.e. water tends to aggregate in acetonitrile applies to the interface clusters, perhaps there could be a drying transition at the water cluster/CH_3CN interface. The size of large water clusters in the bulk consisting of 200 or so water molecules is estimated to occur above an acetonitrile fraction of 0.2−0.7.[12−15] In our experiments although the bulk mole fraction is 0.2 or less, the effective mole fraction at the interface would be larger. At a water cluster/CH_3CN inteface, there could be a drying transition separating the water cluster and the surrounding acetonitrile molecules, which could yield free OD. However for the free OD stretch to generate an SFG signal would require that the free OD groups have a net orientation. Isotropic orientations would not produce a coherent SFG signal. As indicated earlier, oriented D_2O molecules between CH_3CN molecules in the top layer of CH_3CN or between CH_3CN molecules of the top monolayer and the layer beneath could generate a van der Waals red-shifted free OD in the SFG spectra. It is speculative as to which of the models, drying transition or van der Waals interactions, or some other model is applicable.

Conclusions

Changes in the interfacial water structure induced by the addition of acetonitrile to an aqueous solution have been investigated using vibrational sum frequency generation. It was found that the displacement of interfacial water molecules by acetonitrile molecules diminished the SFG amplitude more rapidly in the more organized, "ice-like" water spectral region than in the higher energy more "liquid-like" vibrational spectral region. At acetonitrile mole fractions that were sufficient to form an acetonitrile monolayer, it was found that there were no longer vibrational resonances detected in both the "ice-like" and "liquid-like" spectral regions. This finding indicates that there are no oriented collective vibrations that characterize this spectral region in the absence of acetonitrile. In contrast, the effects of acetonitrile on the free OD spectral region were markedly different at coverages at and above an acetonitrile monolayer. A resonance was observed at 2710 cm^{-1}, which is red-shifted from the free OD stretch of 2737 cm^{-1} at the air/neat D_2O interface. Some speculations as to the origin of the observed resonance are that the 2710 cm^{-1} resonance is due to a free OD stretch, a D_2O molecule in the acetonitrile interface monolayer located between acetonitrile molecules, or possibly free OD between the top and lower acetonitrile regions.

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References and Notes

(1) Adamson, A. *Physical Chemistry of Surfaces*, 5th ed.; John Wiley and Sons, Inc.: New York, 1990.

(2) Chattoraj, D. *Adsorption and the Gibbs Surface Excess*; Plenum Press: New York, 1984.

(3) Du, Q.; Freysz, E.; Shen, Y. R. *Science* **1994**, *264*, 826–828.

(4) Scatena, L. F.; Brown, M. G.; Richmond, G. L. *Science* **2001**, *292*, 908.

(5) Gopalakrishnam, S.; Liu, D. F.; Allen, H. C.; Kuo, M.; Shultz, M. J. *Chem. Rev.* **2006**, *106*, 1155.

(6) Du, Q.; Superne, R.; Freysz, E.; Shen, Y. R. *Phys. Rev. Lett.* **1993**, *70*, 2313–2316.

(7) Gan, W.; Wu, D.; Zhang, Z.; Feng, R. R.; Wang, H. F. *J. Chem. Phys.* **2006**, *124*, 114705.

(8) Liu, W. T.; Zhang, L. N.; Shen, Y. R. *J.Chem. Phy.* **2006**, *125*, 144711.

(9) Liu, D.; Ma, G.; Levering, L. M.; Allen, H. C. *J. Phys. Chem. B* **2004**, *108*, 2252–2260.

(10) Miranda, P. B.; Xu, L.; Shen, Y. R.; Salmeron, M. *Phys. Rev. Lett.* **1998**, *81*, 5876.

(11) Gurau, M. C.; Kim, G.; Lim, S. M.; Albertorio, F.; Fleisher, H. C.; Cremer, P. S. *ChemPhysChem* **2003**, *4*, 1231.

(12) Sovago, M.; Campen, R. K.; Wurpel, G. W. H.; Müller, M.; Hakker, H. J.; Bonn, M. *Phys. Rev. Lett.* **2008**, *100*, 173901.

(13) Harris, K. R.; Newitt, P. J. *J. Phys. Chem. B* **1999**, *103*, 7015–7018.

(14) Venables, D. S.; Schmuttenmaer, C. A. *J. Chem. Phys.* **1998**, *108*, 4935.

(15) Takamuku, T.; Tabata, M.; Yamaguchi, A.; Nishimoto, J.; Kumamoto, M.; Wakita, H.; Yamaguchi, T. *J. Phys. Chem. B* **1998**, *102*, 8880–8888.

(16) Paul, S.; Chandra, A. *J. Chem. Phys.* **2005**, *123*, 184706.

(17) Zhang, D.; Gutow, J. H.; Eisenthal, K. B.; Heinz, T. F. *J. Chem. Phys.* **1993**, *98*, 5099.

(18) Kim, J.; Chou, K. C.; Somorjai, G. A. *J. Phys. Chem. B* **2003**, *107*, 1592.

(19) Zhang, Z.; Wang, H. F., private communication.

(20) Rao, Y.; Comstock, M.; Eisenthal, K. B. *J. Phys. Chem. B* **2006**, *110*, 1727.

(21) Rao, Y.; Song, D. H.; Turro, N. J.; Eisenthal, K. B. *J. Phys. Chem. B* **2008**, *112*, 13572.

(22) Rao, Y.; Tao, Y. S.; Wang, H. F. *J. Chem. Phys.* **2003**, *119*, 5226.

(23) Zhuang, X.; Miranda, P. B.; Kim, D.; Shen, Y. R. *Phys. Rev. B* **1999**, *59*, 12632.

(24) Wang, H. F.; Gan, W.; Lu, R.; Rao, Y.; Wu, B. *Int. Rev. Phys. Chem.* **2005**, *24*, 191–256.

(25) Tian, C. S.; Shen, Y. R. *Chem. Phys. Lett.* **2003**, *470*, 1–6.

(26) Sovago, M.; Campen, R. K.; Bakker, H. J.; Bonn, M. *Chem. Phys. Lett.* **2009**, *470*, 7–12.

(27) Wang, J.; Paszti, Z.; Even, M. A.; Chen, Z. *J. Am. Chem. Soc.* **2002**, *124*, 7016–7023.

(28) Voges, A. B.; Al-abadleh, H. A.; Musorrariti, M. J.; Bertin, P. A.; Nguyen, S. T.; Geiger, F. M. *J. Phys. Chem. B* **2004**, *108*, 18675.

(29) Esenturk, O.; Walker, R. *J. Chem. Phys.* **2006**, *125*, 174701.

(30) Fourkas, J. T.; Walker, R. A.; Can, S. Z.; Gershgoren, E. *J. Phys. Chem. C* **2007**, *111*, 8902.

(31) Bordenyuk, A.; Benderskii, A. *J. Chem. Phys.* **2005**, *122*, 134713.

(32) Liu, J.; Conboy, J. *J. Phys. Chem. C* **2007**, *111*, 8988.

(33) Kataoka, S.; Cremer, P. *J. Am. Chem. Soc.* **2006**, *128*, 5516.

(34) Shultz, M. J.; Schnitzer, C.; Baldelli, S. *Int. Rev. Phys. Chem.* **2000**, *19*, 123.

(35) Ma, G.; Chen, X. K.; Allen, H. C. *J. Am. Chem. Soc.* **2007**, *129*, 14053.

JP902933E