Vibrational Response of Hydrogen-Bonded Interfacial Water is Dominated by Intramolecular Coupling

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Using the surface-specific vibrational technique of vibrational sum-frequency generation, we reveal that the double-peaked structure in the vibrational spectrum of hydrogen-bonded interfacial water molecules originates from vibrational coupling between the stretch and bending overtone, rather than from structural effects. This is demonstrated by isotopic dilution experiments, which reveal a smooth transition from two peaks to one peak, as D_2O is converted into HDO. Our results show that the water interface is structurally more homogeneous than previously thought.

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Interfacial water is of importance for a variety of disciplines including electrochemistry, (photo-) catalysis, and biology [1]. Water interfaces are characterized by the interruption of the bulk hydrogen-bonded network, which gives interfacial water its unique properties (e.g., high surface tension). When a water OH group forms a hydrogen bond, the OH stretch frequency of this group decreases by an amount determined by the H-bond strength. As such, the frequency and line shape of the O-H stretch vibration of water provides a sensitive marker of the local environment of water molecules.

Different types of vibrational spectroscopies have therefore been applied to study water at interfaces. Among these, Vibrational Sum-Frequency Generation (VSFG) Spectroscopy [2–10] has been shown to be a particularly versatile tool due to its inherent suppression of the isotropic bulk signal. Typically in VSFG spectroscopy, an infrared (IR) and a visible (VIS) beam are combined at the interface to generate a signal with a frequency that is the sum of the infrared and visible frequencies. When the IR frequency is resonant with the O-H stretch vibration of interfacial water, the sum-frequency signal is strongly enhanced, providing the vibrational spectrum of essentially one monolayer of water molecules.

For example, the VSFG spectrum of the heavy water-air interface [Fig. 1(a)] contains spectral features originating from specific interfacial water molecules: the "free-OD" from water molecule with an O-D bond protruding from the surface ($\nu_{\mathrm{free}} \approx 2740\ \mathrm{cm}^{-1}$) [2–7] and two peaks in the H-bonded frequency region ($\nu_1 \approx 2400$ and $\nu_2 \approx 2500\ \mathrm{cm}^{-1}$). Although it is clear that such VSFG spectra reflect details of the interfacial water structure, the assignment of the two prominent peaks has been much debated. In one explanation, the two peaks have been attributed to two distinct substructures of interfacial O-D groups with weak and strong hydrogen bonds, and have been referred to as "icelike" and "waterlike," respectively [2–7,11,12]. Alternatively, the double-peak structure has been attributed to vibrational coupling between the two O-H (O-D) oscillators within one water molecule giving rise to symmetric and the asymmetric water modes [13,14]. Yet other approaches have also included the structural inhomogeneities in the hydrogen-bond interaction strength on the VSFG spectral response of the water-air interface [13,14].

Here, we provide a completely new assignment of the double-peak structure of the vibrational spectrum of the interfacial water. Our results reveal that the vibrational response does not originate from intermolecular coupling (e.g., strong and weak H-bonded water species), nor from symmetric and asymmetric water modes, but from symmetric stretch vibrations split by a Fermi resonance (FR) with the overtone of the water bending mode. This assignment is demonstrated here for different interfaces, and shows that generally the interfacial water structure is simpler than previously thought.

The SFG setup has been described in detail elsewhere [15,16]. VSFG spectra were recorded under *ssp* and *pss* (SFG, VIS, IR) polarization conditions, in the 2000–2900 cm^{-1} region, while scanning the wavelength of the IR laser. The incident angles for the VIS and IR beams are 50° and 55°, respectively, with respect to the surface normal for water-air interface and 35° and 40° for water-lipid interface. The spectra were normalized using a reference signal from z-cut quartz. Lipid monolayers of 1,2-dipalmitoyl-3-trimethylammonium-propane (DPTAP, Avanti Polar Lipids) were prepared at a surface pressure of 25 ± 3 mN/m at room temperature ($23 \pm 1\ ^\circ\mathrm{C}$) in a homemade Teflon trough. The water subphase consists of isotopic mixtures of D_2O (Cambridge Isotope Laboratories, Inc., 99.93% purity, used without further purification) and H_2O (Millipore, 18 MΩ-cm). In the experiments presented here, the O-D, rather than the O-H, stretch vibrations are probed, as our tunable infrared source works more effectively in this frequency range. Spectra in the O-H region differ only by a scaling of the frequency axis. This suggests that there are no significant differences

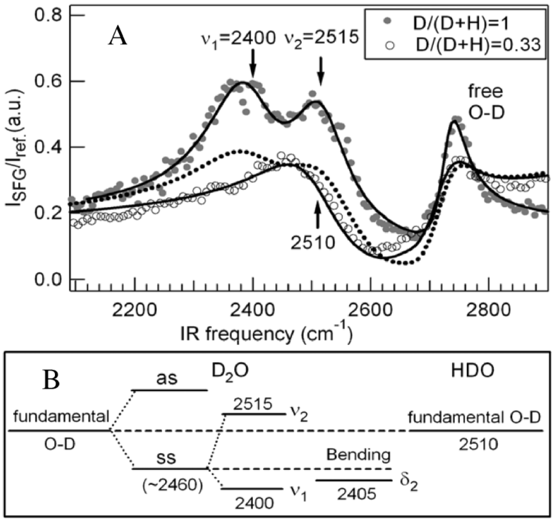

FIG. 1. (a) VSFG spectra of the heavy water-air interface for *ssp* polarization. Fits to the data are shown by the solid lines. Simulated data for the "icelike" and "waterlike" hypothesis are shown by the dotted line. Peak positions are indicated in the graph. For pure D_2O [ratio $D/(D + H) = 1$, closed circles], two resonances are clearly identified in the O-D stretch region. For a sample with $D/(D + H) = 0.33$ (open circles), the contribution from D_2O modes is less than 10%, and HDO modes dominate the spectrum. (b) Energy level diagram for D_2O and HDO water molecules. The fundamental O-D stretch vibration is coupled intramolecularly, giving rise to symmetric (*ss*) and asymmetric (*as*) modes. Because of Fermi resonance with the overtone of the bending mode (δ_2), the *ss* mode is further split into a low and a high frequency band (labeled here ν_1 and ν_2). For an HDO water molecule, the intramolecular modes are decoupled, allowing the determination of the fundamental O-D stretch vibration. The corresponding frequency of each energy level is specified, except for the *as* mode, in cm^{-1}.

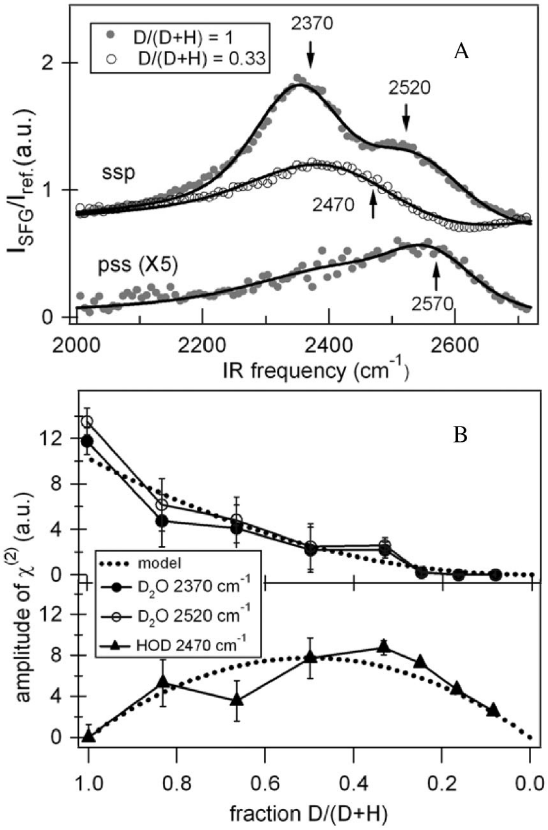

FIG. 2. (a) VSFG spectra of the lipid-water interface for *ssp* and *pss* polarization combination. The *ssp* spectra have been offset for clarity. Fits to the data are shown by the thin solid lines. The positions of the peaks are indicated, in cm^{-1}. (b) Variation of the amplitudes of the nonlinear susceptibility components of the three modes as a function of the mole fraction of deuterium in the water subphase. Upper panel: the amplitudes of 2370 and 2520 cm^{-1} peaks and the concentration of D_2O (dashed line). Lower panel: the amplitude of 2470 cm^{-1} peak and the concentration of HDO (dashed lines). The isolated O-D stretch peaks around $D/(D + H) = 0.5$, since the HDO concentration peaks at this mole fraction.

in water structure at interfaces for either pure H_2O or D_2O, and therefore for HDO. Isotopic dilution experiments are well suited for simplifying water's complex vibrational response, as going from D_2O to HDO, the two O-D stretch modes are decoupled, and the fundamental O-D vibration of HDO can be detected [see Fig. 1(b)].

Figure 1 displays VSFG spectra of the water-air interface for pure D_2O and a D_2O:H_2O mixture (1:2 molar ratio, corresponding to a deuterium mole fraction of $D/(D + H) = 0.33$). Spectra obtained from the water-lipid interface, for which the SFG signal is strongly enhanced due to increased water ordering and the surface electric field at the charged surface [4,17,18], are presented in Fig. 2. The spectra in the H-bonded region are remarkably similar for the two very different interfaces. Upon isotopic dilution of the water, the double-peaked feature vanishes for both water-air and water-lipid interfaces. In comparison to previous reports [6,7], the spectrum in the OD-stretch region clearly appears as a *single* resonance. We note that for $D/(D + H) = 0.33$, HDO molecules are 4 times more abundant than D_2O molecules. Given that the VSFG signal depends on the square of the interfacial molecular density, the signal in the O-D stretch region will be dominated by HDO molecules.

The spectra were fitted following the procedure described in Ref. [6]. The fit reveals peak positions (ω_n) and widths (fwhm Γ_n) for the two prominent peaks for the water-air interface at 2400 (140) and 2515 (120) cm^{-1}, respectively. The isolated O-D stretch frequency of HDO water molecule is 2510 (140) cm^{-1} (for $D/D + H = 0.33$). For the water-lipid interface, the peaks are redshifted and broadened due to the interaction of the interfacial water with the lipids. The peak positions (and widths) are found to be 2370 (140) and 2520 (180) cm^{-1} for pure D_2O and 2470 (240) cm^{-1} for HDO. Because of interference between nonresonant and resonant contributions in the SFG spectrum, the SFG line shape is distorted: the peak positions observed in the SFG spectrum are shifted from the resonance frequency.

Experiments with varying isotope ratio for DPTAP monolayers reveal a smooth transition from the D_2O to the HDO spectrum upon the isotopic dilution of D_2O. Figure 2(b) shows the amplitudes A_n of the nonlinear susceptibilities of the three different modes obtained from a global fit to the data. For these fits, the width and the center frequency of the 2370 and 2520 cm^{-1} peaks are obtained from experiments on pure D_2O and the parameters for the isolated O-D stretch of HDO are obtained from spectra at low deuterium content. In the fitting procedure, the peak positions ω_n and widths Γ_n are kept fixed for all spectra, and only the amplitudes A_n are free to vary. The amplitude values follow closely the concentrations of D_2O and HDO in the samples [dashed lines in Fig. 2(b)].

The observation that the two O-D stretch peaks merge into one upon isotopic dilution of D_2O directly demonstrates that the double-peaked structure observed for the isotopically pure water does not originate from weakly and strongly H-bonded water molecules. If the ''icelike or waterlike'' hypothesis had been correct, the structure of the VSFG spectrum should have remained identical and only the amplitudes of the overall spectrum should have decreased upon isotopic dilution [see the simulated, dotted spectrum in Fig. 1(a)]. The appearance of a new spectral feature in the SFG spectrum, as the molecular symmetry is broken in going from D_2O to HDO, suggests that the two O-D stretch peaks of interfacial D_2O originate from intramolecular coupling, which is ''switched off'' upon going from D_2O to HDO. The two peaks may originate, for instance, from coupling between the two O-D stretches in D_2O, leading to symmetric (*ss*, low frequency) and asymmetric (*as*, high frequency) modes, as has been suggested previously [13,14]. However, an interpretation of the spectrum in terms of *ss* and *as* modes can be ruled out on the following grounds: If the $\nu_1 = 2400$ and $\nu_2 = 2515\ \text{cm}^{-1}$ correspond to the *ss* and the *as* modes, respectively, then the frequency of the fundamental O-D vibration of the HDO water molecule would be expected at $\nu(\text{O-D}) \approx [\nu_1 + \nu_2]/2 = 2460\ \text{cm}^{-1}$ [see Fig. 1(b)], in the approximation $m_D \ll m_O$. However, the observed OD stretch frequency in HDO for the water-air interface is found at $2510 \pm 20\ \text{cm}^{-1}$. Second, if the $\nu_2 = 2515\ \text{cm}^{-1}$ peak originates from the *as* mode, then it should appear more markedly in the *ppp* and *pss* spectra, as stated by SFG polarization selection rules [10]. This is not observed experimentally (Fig. 2): both peaks have vanishingly small intensities for *pss* polarization combination, and a new spectral feature appears at 2570 cm^{-1}. This peak was previously assigned to the other O-D bond of the interfacial water molecule which has a free O-D bond [10], but may also have a contribution from the *as* mode. Hence, the two prominent peaks cannot be assigned to *ss* and *as* modes, and, in fact, both have symmetric character, as both peaks are most prominent in *ssp* SFG mode [10].

The fact that the symmetric mode appears as a double-peaked structure for D_2O, but not for HDO, indicates the symmetric mode is split by an anharmonic intramolecular interaction. Indeed for bulk water, the symmetric stretch vibration is known to be affected by a Fermi resonance (FR) with the overtone of the water bending mode [19–21]. Such a Fermi resonance (FR) can occur when two states have similar energy. For bulk D_2O, the bending mode frequency is centered around 1210 cm^{-1} [22] which places the overtone of the bending mode in the vicinity of the symmetric stretch mode [Fig. 1(b)]. The anharmonic interaction with the bend overtone splits the continuum of states associated with the symmetric mode into a low and a high frequency band, giving rise to the double-peaked structure in SFG spectrum. The dip in SFG intensity between the peaks is therefore a so-called Evans window in the O-D stretching band reflecting the loss of spectral intensity in the middle of the stretch band [19–21]. This FR-induced splitting has previously been used to explain the vibrational water response in Raman spectroscopy [20] (although this has been debated [23]) and ultrafast energy flow between OH stretch and bend modes, as observed in pump-probe IR experiments in bulk water [19]. The FR between the *ss* and bend overtone explains why, upon isotopic dilution, the double-peaked structure collapses into one resonance: for HDO, the bend fundamental is located at ~1450 cm^{-1} [24], so that the overtone is at ~2900 cm^{-1}, at much higher frequency than the *ss* mode. As a result, the Evans window does not appear for HDO. It also explains why the HDO frequency does not lie in between the two peaks, but rather at 2510 cm^{-1}: this is precisely the frequency of the decoupled O-D stretch in HDO in bulk water [24].

The new assignment of the spectral features presented here explains many previously observed spectroscopic features of interfacial water, and has significant implications for interpreting water VSFG spectra. Most importantly, the intramolecular coupling with the bend overtone makes the frequency of the symmetric stretch doublet relatively insensitive to the local H-bonding strength. This can be understood as follows: owing to the multitude of H-bonding states, there is a (dynamic) distribution of vibrational frequencies for the stretch vibration. The overtone of the pure bending mode (which is a forbidden transition and has a very low vibrational cross section compared to the stretch mode) interacts most strongly with those frequencies within the stretch manifold that are resonant with the bend overtone. The Evans window therefore appears at approximately the frequency of the overtone. The bend overtone is much less affected by the H-bonding interactions than the stretch [22]. Variations in the stretch mode central frequency therefore only give rise to changes in the spectral weight on both sides of the window. As a result, the D_2O interfacial water spectrum is relatively insensitive to the details of local environment, as the intramolecular coupling dominates the vibrational response.

To characterize the hydrogen bonding, one should therefore rely on changes in the HDO frequency. The systems studied here serve as an excellent example. Interfacial water molecules at water/lipid interface have stronger hydrogen bonds and greater structural inhomogeneity than at the water-air interface, due to association with the lipids. This is apparent from the fundamental O-D vibration peak in HDO, which is redshifted and broadened for DPTAP monolayers (2470 cm^{-1}, width 200 cm^{-1}) compared to the air-water interface (2510 cm^{-1}, width 140 cm^{-1}). In contrast to the D_2O (or H_2O) interfacial water spectrum, the uncoupled HDO peaks are unbiased reporters of the local H-bonding environment.

Another example where our assignment of the SFG water spectrum has implications is in understanding the interfacial water response as a function of temperature and water ion content. When the temperature is increased, a decrease in the 3200 cm^{-1} peak and an increase in the 3400 cm^{-1} peak have been reported [2]. These changes in the spectrum have been interpreted as an increase in the disorder of the surface structure. However, no significant shift in the central frequency of either of the two peaks was observed, as one would expect when the hydrogen bonds become weaker with increasing temperature. With the new assignment of the spectral features presented here, we can explain the temperature dependence of water SFG spectra: the continuum of the symmetric stretch vibrations shifts to the blue upon an increase in temperature due to the weakened H-bonding structure. The positions of the maxima that appear due to coupling to the bend overtone are determined by the Evans window, which remains nearly at the same frequency due to the insensitivity of the bending mode to temperature ($\sim 0.05\ \mathrm{cm}^{-1}/\mathrm{K}$ vs $\sim 1\ \mathrm{cm}^{-1}/\mathrm{K}$ for the stretch mode) [22,25]. The changes in relative intensities of the two peaks therefore reflect the overall weakening of H-bonds, but do not point to a conversion of water species. The same argumentation explains the effect on interfacial water spectra of different hydrogen-bond making (F^- and SO_4^{2-}) and breaking (Cl^-, Br^-, I^-) ions [7,13,26,27]. With our new assignment, the observed changes in relative peak amplitudes result from a constant frequency Evans window, with a redistribution of the symmetric stretching states toward lower or higher frequency for H-bond strengthening and H-bond weakening ions, respectively.

In conclusion, our results show that the interfacial water response in the H-bonded region originates from intramolecular coupling of vibrational modes, rather than from the existence of distinct water substructures. The two prominent peaks observed at aqueous interfaces are assigned to the symmetric stretch mode split by the Fermi resonance with the overtone of the bending mode.

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