Interfacial Water Structure Revealed by Ultrafast Two-Dimensional Surface Vibrational Spectroscopy

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Knowledge of the interfacial water structure is essential for a basic understanding of the many environmental, technological and biophysical systems in which aqueous interfaces appear. Using ultrafast two-dimensional surface-specific vibrational spectroscopy we show that the structure of heavy water (D_2O) at the water-air interface displays short-lived heterogeneity and is very different from that at the water-lipid interface.

Water differs markedly from liquids of similar molecular weight in properties like specific heat, phase behavior and dielectric constant. Many of these special properties can be traced back to the unique intermolecular interactions that occur through hydrogen bonds between the hydrogen atoms and oxygen atoms of different water molecules[1]. At the surface or interface of water, the water hydrogen-bonded network is abruptly interrupted, conferring yet different properties on interfacial water[2]. Despite its importance for disciplines such as electrochemistry, atmospheric chemistry and membrane biophysics, the structure of interfacial water has remained highly debated[2-16].

The challenge of specifically probing molecules at the outermost surface layers of water has been overcome with sum-frequency generation (SFG) spectroscopy of the O-H stretch vibrations of the water molecules. In an SFG experiment, infrared and visible laser pulses are overlapped in space and time on the surface, and the sum-frequency of the two laser fields can be generated, but in the top molecular layers only[17]. If the infrared light is resonant with the O-H stretch vibration of surface water, this process is resonantly enhanced. The shape and intensity of the SFG spectrum are determined by the frequency dependence of the second-order non-linear susceptibility $\chi^{(2)}$. Information about the interfacial water structure is then inferred through the correlation between the O-H stretch vibrational frequency of an O-H group in a water molecule and its local hydrogen-bonded environment.

Initial SFG studies revealed distinct peaks in SFG spectra of interfacial water, as exemplified in the SFG spectra of the water-air and water-lipid interfaces shown in Figure 1. The lipid is a standard cationic lipid, 1,2-dipalmitoyl-3-trimethylammonium-propane (DPTAP). The two peaks appearing at ~2350 and ~2500 cm^{-1} have been assigned in different ways, to 'ice-like' and 'liquid-like' structures[3-5] and to the result of intra- and intermolecular coupling[14, 18]. There is surprising similarity between the two spectra,

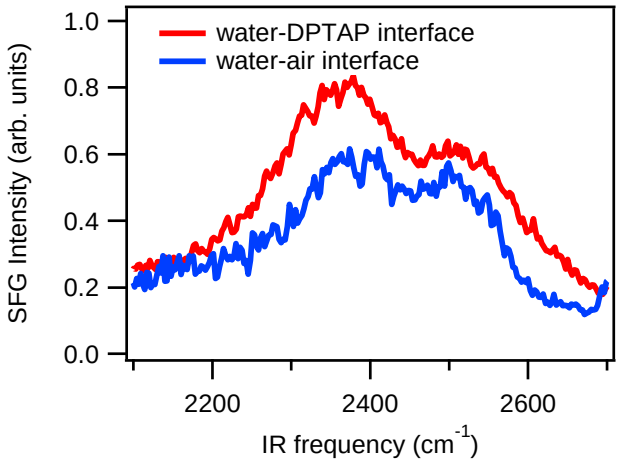

Figure 1. Normalized SFG spectra at the D_2O water-air (blue) and water-lipid (DPTAP, red) interfaces. Note the remarkable similarity. The spectrum for the water-lipid interface has been offset by 0.2 for clarity.

raising the question whether the interfacial water structure is also very similar. The spectra reported in Fig. 1 are SFG intensity spectra, with $I_{SFG} \sim |\chi^{(2)}|^2$. Heterodyne detected SFG measurements, which allow one to disentangle the real and imaginary parts of the vibrational response ($Re[\chi^{(2)}]$ and $Im[\chi^{(2)}]$), have shed additional light on the origin of the SFG spectra[19, 20]. $Im[\chi^{(2)}]$ reflects the dissipative part of the response function, and constitutes the surface equivalent of a bulk absorption spectrum. These experiments have shown that, while the water-DPTAP I_{SFG} spectrum directly reflects $Im[\chi^{(2)}]$, the situation is more subtle for the water-air interface, where up to three resonances have been identified in the hydrogen-bonded region of the O-H stretch band[19, 20].

In bulk water, the complex absorption spectrum has been unraveled and interpreted in terms of water structure and structural dynamics by measuring the ultrafast frequency fluctuations and correlations of the O-H stretch vibration, with the help of 2-dimensional infrared (2D-IR) spectroscopy[21-24].

Here, we analyze the origin of the interfacial water SFG spectrum in terms of structure and dynamics of interfacial water using surface-specific two-dimensional infrared sum-frequency generation (2D-IR-SFG)spectroscopy[25]. In this fourth-order ($\chi^{(4)}$) nonlinear optical technique, a tuneable infrared (IR) pulse excites a subset of water molecules from the ground (v=0) to the first vibrationally excited (v=1) state. Vibrationally excited OD groups no longer contribute to the SFG signal, due to the self-anharmonicity of the vibrational potential. Hence, a subset of (weakly or strongly) hydrogen-bonded interfacial water molecules is excited, and the interfacial response is detected over a wide frequency range, i.e. for all interfacial water molecules. If there are distinct sub-ensembles of water molecules, this would be apparent in this experiment. The response is measured as a function delay time τ_{delay} between excitation and a pair of IR and visible (VIS) detection pulses that generate SFG at the interface. This technique combines the unique capabilities of 2D-IR with the surface specificity and (sub-) monolayer sensitivity of SFG spectroscopy.

The left column of Fig. 2 shows 2D-SFG spectra in the O-D stretch region of the D_2O-air interface. It shows the interfacial water response as a function of excitation (horizontal axis) and detection (vertical axis) frequencies at different delay times between excitation and detection pulses. We studied heavy water (D_2O) to reduce the effect of intermolecular energy transfer between water molecules. In the experiment, we use an intense infrared pulse of ~100 cm^{-1} bandwidth, tuned in steps of 75 cm^{-1} across the entire water band to resonantly excite the vibrations of specific subsets of D_2O molecules. The effect of the excitation is monitored across a wide (500 cm^{-1}) frequency range using SFG.

For the water-air interface, clearly only one feature is observed in the 2D-SFG spectrum, although the SFG spectrum contains two peaks. This can be traced to the fact that the excitation axis of the 2D-SFG spectrum is determined by the IR absorption of the surface water molecules, rather than by their SFG intensity spectrum. This absorption spectrum contains only one broad peak in the hydrogen-bonded region, as is evident from both the IR absorption spectrum of bulk water and the frequency dependence of the $Im[\chi^{(2)}]$ spectrum[19, 20].

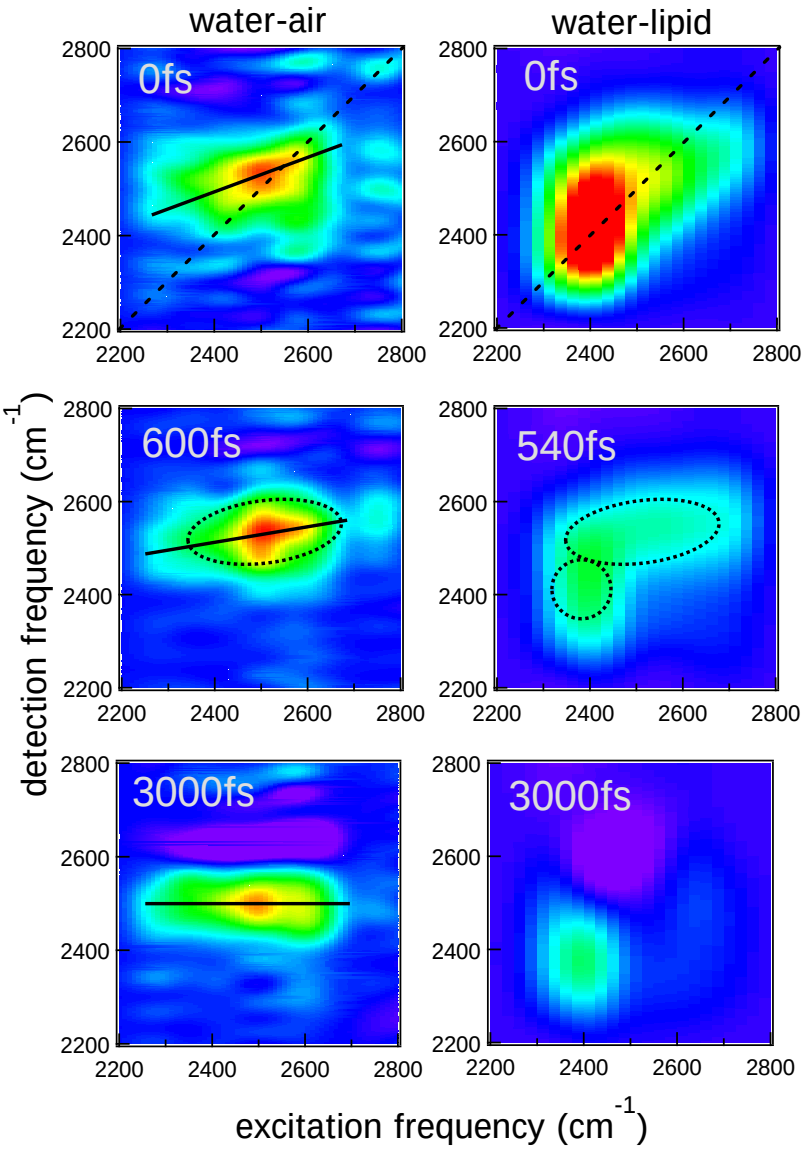

Figure 2. 2-dimensional SFG spectra of the D2O water-air (left column) and water lipid (right column) interfaces at various pump-probe delay times indicated in the graphs. The dashed lines in the upper panels denote the diagonal; the solid lines in the left column indicate the average slope of the diagonal peaks. Dotted circles/ovals indicate different water types.

Figure 2 shows that the water-air interface is fairly homogeneous in its response and hence its structure. Nonetheless, some heterogeneity can be concluded from the 2D spectra. For a completely inhomogeneous surface, the response in a 2D spectrum would lie along the diagonal (dashed line in Fig. 2; slope=1), as only those water molecules are affected that have been resonantly excited. For a completely homogeneous surface, the response would give rise to spherical line-shape: irrespective of

the excitation frequency, the response would always be the same. The observed 2D spectral response in the H-bonded region clearly lies in between these two extremes. The solid lines in the spectra are linear fits to the signal maxima at different excitation frequencies, resulting in a line whose initial slope of 0.23±0.06 decreases with waiting time. This is direct evidence for heterogeneity of interfacial water, although the heterogeneity is clearly limited (the slope is only 0.23). Hence, the 2D spectra show that a continuum of different hydrogen-bonded interfacial water structures exists within the broad H-bonded spectral feature, with no evidence for distinct ('ice-like' and 'liquid-like') substructures.

The apparent decay of the slope of the diagonal feature in the 2D spectra is due to rapid spectral diffusion. Such spectral diffusion can be due to structural relaxation processes[23, 24, 26], but may also be indicative of intermolecular energy transfer: vibrational energy transfer can occur between differently hydrogen-bonded O-D groups with different frequencies[23, 24, 27, 28] due to dipole-dipole coupling between different O-D groups. Irrespective of the cause of the spectral diffusion, the initial slope of 0.23 sets a lower limit on the intrinsic heterogeneity of water at the water-air interface.

We can translate the slope of 0.23 into the homogeneous and inhomogeneous linewidths of the interfacial water vibration. Assuming that the vibrational response can be described by a Gaussian distribution of Lorentzian lines characterized each by a width of respectively Δ and Γ_{hom}, we can define an inhomogeneity parameter $\Delta/(\Delta+\Gamma_{hom})$. In the inhomogeneous limit, $\Delta/(\Delta+\Gamma_{hom})=1$; it equals zero in the homogeneous limit. The initial slope in the 2D spectrum of 0.23 corresponds to a value of the inhomogeneity parameter of 0.31. Tentatively, this means that approximately 30% of the water molecules at the interface are sufficiently differently hydrogen-bonded that they have limited spectral overlap with other molecules.

Remarkably, the results obtained for water-lipid interface shown in the right column of Fig. 2, reveal a completely different picture of water at lipid interfaces. Distinct (weakly and strongly H-bonded) water molecules can be identified at the water-lipid interface (Fig. 2, right column), with strongly different vibrational dynamics. Strongly H-bonded water molecules on the red side of the peak show very fast vibrational dynamics (indicated by the circle in the center image): after 600 fs most of the bleach has vanished), while the peak at higher frequency (oval in center plots) has the same shape and displays the same dynamics as that observed for the water-air interface. Note that the two ovals drawn in the center panels are identical. The results obtained here are consistent with, and further refine our earlier time-resolved one-color study of water dynamics at lipid interfaces[29]. In this previous study, single-color lifetime measurements indicated the presence of two distinct water species, which is unambiguously proven here. The strongly H-bonded water molecules apparently do not exchange vibrational energy with the near-surface water molecules, and are therefore concluded to interact with the lipid head group, explaining their absence at the water-air interface. The presence of distinct peaks in the 2D-SFG spectrum has been predicted theoretically[30], although interpreted somewhat differently. The strongly H-bonded water molecules observed here are expected to play an important role in protein function and proton transport along the membrane. The presence of strongly hydrogen-bonded water molecules at the lipid interface that do not exhibit exchange with bulk water on picosecond timescales is important for understanding lipid hydration.

In summary, the similarity between the static SFG spectra of water at the water-air and water-lipid interfaces (Fig. 1) is shown to break down in the 2D-SFG measurements (Fig. 2), which reveal that the water structure is very different for these interfaces. The technique of 2D-SFG is thus shown to provide a new way of investigating the structure and previously inaccessible structural dynamics of aqueous interfaces.

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