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Water Interacting with interfaces, ions and itself

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9 Interfacial Water Structure

We study the structure of water at interfaces with ultrafast two-dimensional surface-specific vibrational spectroscopy. We find that the structure of heavy water at the water-air interface is highly heterogeneous and strongly differs from that at the water-lipid interface.

9.1 Introduction

Water differs markedly from liquids of similar molecular weight in properties such as 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 [11]. At the surface or interface of water, the water hydrogen-bonded network is abruptly interrupted, conferring yet different properties on interfacial water [143]. Despite its importance for disciplines such as electrochemistry, atmospheric chemistry, and membrane biophysics, the structure of interfacial water has remained highly debated [6, 26, 40, 41, 44, 51, 53, 111, 138, 143, 144, 147, 148, 150, 153].

The challenge of specifically probing molecules at the outermost surface layers of water has been met 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 a surface, and the sum-frequency of the two laser fields is generated, but in the top molecular layers only [142]. 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 the SFG spectra of interfacial water, as exemplified in the SFG spectra of the water-air and water-lipid interfaces shown in figure 9.1. The lipid is a standard cationic lipid, 1,2-dipalmitoyl-3-trimethylammonium-propane (DPTAP). The two peaks appearing at $\sim$2350 and $\sim$2500 cm$^{-1}$ have been assigned in different ways, to “ice-like” and “liquid-like” structures [40, 41, 138] and to the result of intra- and intermolecular
There is surprising similarity between the two spectra, suggesting that the interfacial water structure is also very similar. The spectra reported in figure 9.1 are SFG intensity spectra, with $I_{\text{SFG}} \sim |\chi^{(2)}|^2$. Heterodyne detected SFG measurements, which allow one to disentangle the real and imaginary parts of the vibrational response ($\text{Re} [\chi^{(2)}]$ and $\text{Im} [\chi^{(2)}]$), have shed additional light on the origin of the SFG spectra [74, 116]. $\text{Im} [\chi^{(2)}]$ 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 $I_{\text{SFG}}$ spectrum directly reflects $\text{Im} [\chi^{(2)}]$, the situation is more subtle for the water-air interface, where $\text{Im} [\chi^{(2)}]$ can differ significantly from the $I_{\text{SFG}}$ spectrum [74, 116].

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 spectral whole burning [7, 50] and two-dimensional infrared (2D-IR) spectroscopy [46, 136].

### 9.2 Experiment

Here, we analyze the origin of the interfacial water SFG spectrum in terms of the structure and dynamics of interfacial water using surface-specific two-dimensional infrared sum-frequency generation spectroscopy [23].

In the experiment, we used an IR-pump – SFG-probe scheme (see section 3.4), in which the pump spectrum was spectrally narrow and continuously tuned across the absorption band of water. The laser pulses used in the experiment were generated with the laser system and the frequency conversion processes described in sections 3.1 and 3.2. As a pump we used an intense infrared...
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pulse (∼12 μJ) of ∼80-150 cm⁻¹ bandwidth (pulses duration of ∼150–180 fs), tuned in steps of 75 cm⁻¹ across the entire water band to resonantly excite the vibrations of specific subsets of D₂O molecules. For the detection process, broadband mid-IR (∼500 cm⁻¹ bandwidth and energy of ∼6.5 μJ and pulse duration of ∼60 fs) and narrowband visible (15 cm⁻¹ bandwidth and energy of ∼10 μJ) upconversion pulses were mixed at the interface to generate a conventional SFG signal. The experimental time resolution, determined by the cross-correlation between the pump and the IR detection pulses is approximately 200 fs. Both the pump and the IR detection pulses were continuously monitored with a frequency-resolved IR detection set-up (see section 3.3) consisting of an ORIEL monochromator and a 2x32-pixel, mercury-cadmium-telluride (MCT) array detector. Different pump frequencies (2275, 2350, 2425, 2500, 2575, 2625, 2750 and 2825 cm⁻¹) were used to excite the hydrogen-bonded and the free O-D part of the interfacial O-D stretch absorption band. The spectra of these pulses are shown in figure 9.2. All experiments were performed at least twice to ensure their reproducibility.

2D-SFG spectra were composed from the transient spectra recorded at delay times of 0, 600/540 and 3000 fs following standard procedures [28]: vertical cuts at specific excitation frequencies were calculated using a weighted average of transient spectra at different pump frequencies, with the weights determined by the relative intensities of the pump spectra at that frequency, as inferred from the spectra in figure 9.2. The resulting 2D-SFG spectrum was Fourier-filtered to remove high-frequency noise resulting from the detection. Care was taken while removing the high-frequency noise not to affect the 15 cm⁻¹ experimental resolution (determined by the bandwidth of the VIS pulses), that is, to avoid smearing out experimental features in the recorded two-dimensional spectrum. Within the frequency window 2400-2800 cm⁻¹, the two-dimensional spectra could be determined with an accuracy better than 1% of the original SFG spectra; outside this window the low IR probe energy caused some noise. In the experiment, the pump frequency that determined the horizontal axis of the two-dimensional vibrational spectrum was scanned. The vertical axis is defined by the infrared frequency of the SFG probing process. The experiments were preformed in the S/S/P (SFG/VIS/IRprobe) polarization configuration with respective incident angles of 56°, 40° and 70° with respect to the surface normal. The polarization of the pump pulses was P. The third-order cross-correlation between the IR pump, IR probe and visible pulses generated from the heavy water surface was used to optimize the spatial overlap and to define the position of τ = 0.

Heavy water - D₂O (Cambridge Isotope Laboratories, Inc., 99.96 atom %D; pH=∼5.5) was used without further purification. 1,2-dipalmitoyl-3-trimethylammonium-propane - DPTAP was purchased from Avanti Lipids and used without further purification. The teflon sample trough was cleaned with piranha solution (3:1 volume ratio of sulfuric acid and 30% hydrogen peroxide solution). During the experiment the trough was rotated to avoid accumulated heating by the laser pulses. The vertical sample position was controlled by a feedback loop to compensate for water evaporation. The entire set-up was enclosed and flushed with N₂ gas to remove spectral distortions originating
Figure 9.2. Pump spectra used in the experiment. Dotted line indicates infrared probe spectrum.

from CO\textsubscript{2} absorption in the air.

9.3 Results and discussion

The left column of figure 9.3 shows 2D-SFG spectra in the O-D stretch region of the heavy water (D\textsubscript{2}O)-air interface. It shows the interfacial water response as a function of the excitation (horizontal axis) and detection (vertical axis) frequencies at different delay times between the excitation and detection pulses.

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 back 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 \cite{74, 116}. Along the detection axis we also observe only one broad peak, which most likely results from the specific incidence angles of IR probe and VIS pulses. It has been shown previously that the shape of the SFG spectrum depends on the incidence angle of the two beams \cite{146}.

For a completely inhomogeneous surface, the response in a 2D spectrum would lie along the diagonal (dashed line in figure 9.3; 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 a spherical lineshape: irrespective of the excitation frequency, the response would always be the same (see section 2.6.2). The observed 2D spectral response in the H-bonded region of the water-air interface clearly lies in between these two extremes (see figure 9.3). 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 the 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 [3, 32, 79], but may also be indicative of intermolecular energy transfer: vibrational energy transfer can occur between differently hydrogen-bonded O-D groups with different frequencies [32, 79, 128, 171] 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 (full width at half-maximum) of $\Delta_{\text{inh.}}$ and $\Gamma_{\text{hom.}}$, respectively, we can define an inhomogeneity parameter $\Upsilon = \Delta_{\text{inh.}}/(\Delta_{\text{inh.}} + \Gamma_{\text{hom.}})$. In the inhomogeneous limit, $\Upsilon = 1$; 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 $\Upsilon = 0.31$. The obtained inhomogeneous and homogeneous linewidths are $\Delta_{\text{inh.}} = 115$ cm$^{-1}$ and $\Gamma_{\text{hom.}} = 240$ cm$^{-1}$, which yield the overall linewidths of the O-D stretch absorption band of $\sim 310$ cm$^{-1}$. A detailed description of the procedure of obtaining the inhomogeneity parameter $\Upsilon$ can be found in appendix 9.5.

Remarkably, the results obtained for water-lipid interface shown in the right column of figure 9.3, 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 (figure 9.3, 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 [20]. 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 [115], and interpreted in terms of water species exhibiting different spectral diffusion dynamics. Nagata et al. concluded that the near-bulk water nonadjacent to lipids (residing at higher frequency) has faster spectral diffusion than the top-layer water directly hydrating the lipids (residing at lower frequency). The strongly H-bonded water molecules observed here are expected to play an important role in protein function and
Figure 9.3. Two-dimensional SFG spectra of the D$_2$O water-air (left column) and water-lipid (right column) interfaces at various pump-probe delay times indicated in the graphs. The dashed line in the upper panels denotes the diagonal. The solid lines in the left column represents the average slope of the diagonal peaks. The dotted ovals indicate the bulk-like water, whereas the solid circle denotes the lipid-associated water.
proton transport along the membrane.

9.4 Conclusions

In summary, the similarity between the static SFG spectra of water at the water-air and water-lipid interfaces (figure 9.1) is shown to break down in the 2D-SFG measurements (figure 9.3), which reveal that the water structure is very different for these interfaces. 2D-SFG spectrum of water-air interface is characterized by a single spectral feature possessing a short-lived heterogeneity. For the water-lipid interface we find two distinct spectral features in the 2D-SFG spectrum, which indicates presence of two distinct water species. 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.

9.5 Appendix: Inhomogeneity Parameter

In order to quantify how homogeneous/inhomogeneous our interfacial water is, we define an inhomogeneity parameter:

\[ \Upsilon = \frac{\Delta_{\text{inh.}}}{\Delta_{\text{inh.}} + \Gamma_{\text{hom.}}} \]  

which relates the inhomogeneous broadening linewidth \( \Delta_{\text{inh.}} \) to the homogeneous linewidth \( \Gamma_{\text{hom.}} \). In the homogeneous limit \( \Delta_{\text{inh.}} \to 0 \) so \( \Upsilon = 0 \). For an extremely inhomogeneous system \( \Delta_{\text{inh.}} \gg \Gamma_{\text{hom.}} \) and \( \Upsilon = 1 \).

The vibrational absorption band can be described by an inhomogeneous (Gaussian) distribution \( G(\nu_{\text{inh.}}, \nu_0) \) of homogeneously broadened lineshapes...
Figure 9.5. The effect of inhomogeneous broadening on the slope of the SFG response. The larger is the $\Delta_{\text{inh.}}/\Gamma_{\text{hom.}}$ ratio, the more inhomogeneous the systems is and $T \rightarrow 1$.

(Lorentzians - $L(\nu, \nu_{\text{inh.}})$) characterized with widths (FWHM) $\Delta_{\text{inh.}}$ and $\Gamma_{\text{hom.}}$ respectively (see figure 9.4):

$$F(\nu, \nu_0, \nu_{\text{inh.}}) = G(\nu, \nu_0)L(\nu, \nu_{\text{inh.}}), \quad (9.2)$$

where

$$G(\nu_{\text{inh.}}, \nu_0) = \exp \left( - \frac{2.7726(\nu_{\text{inh.}} - \nu_0)^2}{\Delta^2_{\text{inh.}}} \right), \quad (9.3)$$

and

$$L(\nu, \nu_{\text{inh.}}) = \frac{\Gamma_{\text{hom.}}}{(\nu - \nu_{\text{inh.}})^2 + \Gamma^2_{\text{hom.}}}. \quad (9.4)$$

$\nu_{\text{inh.}}$ is the central frequency of a homogenous lineshape and $\nu_0$ is a central frequency of the broadening gaussian function. It should be noted that this approach is a simplification, because we assume that the inhomogeneous broadening has a Gaussian shape, and because we do not distinguish the symmetric and asymmetric stretch vibration contributions to the overall absorption band. The overall lineshape of the absorption band is given by $\int F(\nu, \nu_0, \nu_{\text{inh.}}) d\nu_{\text{inh.}}$. We further calculate the probability of exciting each subset of water molecules $E_{\text{exc.}}$ with a pump spectrum described with a Gaussian shape with a width $\Delta_{\text{pump}}$ (figure 9.4, red line). The excitation probability for a given subset is given by the overlap of the homogenous lineshape with the pump spectrum (outlined with the dashed red line in figure 9.4):

$$E_{\text{exc.}}(\nu_{\text{inh.}}, \nu_0, \nu_{\text{pump}}) = \int L(\nu, \nu_{\text{inh.}})G(\nu_{\text{inh.}}, \nu_0)P(\nu, \nu_{\text{pump}}) \, d\nu, \quad (9.5)$$

where $P(\nu, \nu_{\text{pump}})$ is the pump spectrum defined as:

$$P(\nu, \nu_{\text{pump}}) = \exp \left( - \frac{2.7726(\nu - \nu_{\text{pump}})^2}{\Delta^2_{\text{pump}}} \right). \quad (9.6)$$
For a given pump spectrum and inhomogeneity, the pump-probe signal profile $S(\nu, \nu_0, \nu_{\text{pump}})$ is given by the sum of the excitation probabilities of all of the subsets multiplied by their homogeneous lineshapes:

$$S(\nu, \nu_0, \nu_{\text{pump}}) = \int E_{\text{exc.}}(\nu_{\text{inh.}}, \nu_0, \nu_{\text{pump}}) L(\nu, \nu_{\text{inh.}}) d\nu_{\text{inh.}} \quad (9.7)$$

In figure 9.5 we show the relation between the pump frequency ($\nu_{\text{pump}}$) and the maximum of the pump-probe signal ($\max(S(\nu, \nu_0, \nu_{\text{pump}}))$) for various ratios between the homogeneous ($\Delta_{\text{inh.}}$) and inhomogeneous ($\Gamma_{\text{hom.}}$) linewidths. From figure 9.5 we can thus find a combination of inhomogeneous and homogeneous linewidths $\Delta_{\text{inh.}}$ and $\Gamma_{\text{hom.}}$ such that the slope of the pump-probe (IR-pump SFG-probe) response corresponds to that in the experimental data. We obtain the absolute values for $\Gamma_{\text{hom.}}$ and $\Delta_{\text{inh.}}$ by fitting the $\int F(\nu, \nu_0, \nu_{\text{inh.}}) d\nu_{\text{inh.}}$ with a given $\Gamma_{\text{hom.}}/\Delta_{\text{inh.}}$ ratio to the $\text{D}_2\text{O}$ linear absorption band.