VIP Interfacial Heterogeneity Very Important Paper

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Aqueous Heterogeneity at the Air/Water Interface Revealed by 2D-HD-SFG Spectroscopy**

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Abstract: *Water molecules interact strongly with each other through hydrogen bonds. This efficient intermolecular coupling causes strong delocalization of molecular vibrations in bulk water. We study intermolecular coupling at the air/water interface and find intermolecular coupling 1) to be significantly reduced and 2) to vary strongly for different water molecules at the interface—whereas in bulk water the coupling is homogeneous. For strongly hydrogen-bonded OH groups, coupling is roughly half of that of bulk water, due to the lower density in the near-surface region. For weakly hydrogen-bonded OH groups that absorb around 3500 cm^{-1}, which are assigned to the outermost, yet hydrogen-bonded OH groups pointing towards the liquid, coupling is further reduced by an additional factor of 2. Remarkably, despite the reduced structural constraints imposed by the interfacial hydrogen-bond environment, the structural relaxation is slow and the intermolecular coupling of these water molecules is weak.*

Water constitutes a unique environment for chemical reactions. With the strongly localized charge distributions on its atomic constituents, it can form strong hydrogen bonds (H-bonds) with reactants and reaction products, whilst maintaining its ability for ultrafast structural rearrangement to stabilize short-lived transition states and reaction intermediates. Moreover, it has the unique capability to rapidly dissipate the excess energy in exothermic reactions, thereby making reactions irreversible. A fundamental step in the energy dissipation is the redistribution of a vibrational quantum, for instance, of the O–H stretching vibration, which has been reported to occur on the 200 fs timescale in bulk water.[1] This ultrafast timescale results from the efficient delocalization of vibrational energy over several water molecules.[2] This strong delocalization and rapid energy dissipation of water molecules in bulk water have been elucidated using femtosecond two-dimensional infrared (2D-IR) spectroscopy.[3–5] In these experiments, a subset of H-bonded OH groups with a specific frequency is vibrationally excited. Subsequently, the change in the frequency of the excited group (“spectral diffusion”) is followed in time. Spectral diffusion in the O–H stretching region in pure H_2O takes place within 50–180 fs,[4,5] owing to fast energy transfer between water molecules, and was found to be homogeneous over the entire frequency range of the broad O–H stretching band. The spectral diffusion of isolated OH groups (of HOD in D_2O) occurs on timescales of 0.5–1 ps,[3,6] showing that the structural relaxation of the 3D water network is much slower. Therefore, the fast spectral diffusion in pure H_2O was attributed to the delocalized nature of a O–H stretching vibration in H_2O resulting in strongly coupled intermolecular vibrations of water molecules.[4] Thus, modulation of the OH frequency by low-frequency vibrations (e.g. librations)[5] and near-resonant energy transfer to neighboring OH groups[2] quickly scrambles the vibrational frequency.[7]

Given the large number of chemical reactions occurring on aqueous surfaces, for example, in atmospheric chemistry and on-water catalysis,[8] the energy transfer and dissipation pathways at aqueous interfaces are of paramount importance. At the air/H_2O interface, the H-bond network of water is interrupted and the delocalization of the O–H stretching mode is expected to be reduced. Spectral diffusion of interfacial water is therefore interesting, as it can provide direct insights into intermolecular coupling.

Here, we quantify the spectral diffusion of H-bonded water molecules at the air/H_2O water interface using surface-specific 2D heterodyne-detected sum-frequency generation (2D-HD-SFG) spectroscopy.[9] This approach relies on the generation of a field with the sum of the frequencies of an incoming broadband IR pulse and a narrowband visible pulse at the interface. The efficiency of this process is given by the second-order nonlinear optical susceptibility $\chi^{(2)}$. When the frequency of the incident IR pulse is in resonance with the O–H stretching vibration of interfacial water molecules, $\chi^{(2)}$ becomes large and the SFG signal increases in intensity. In this manner SFG provides the vibrational response of the topmost one or two monolayers of water molecules at the

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interface.[10] Here, we mix the SFG signal with a local oscillator generated in a SFG process at a gold mirror, so that we can determine the phase of the SFG signal, and thereby the real and imaginary parts of $\chi^{(2)}$ (for details see the Supporting Information).[11] The imaginary part, $\mathrm{Im}[\chi^{(2)}]$, is of particular interest, since it is the surface analogy of the bulk absorption spectrum.

Frequency-tunable (3100–3500 cm^{-1}) excitation pulses of roughly 100 cm^{-1} full-width at half-maximum were employed to excite a specific subensemble of water molecules. The dynamics of the excited vibrational quanta is traced using the SFG scheme. The changes in $\mathrm{Im}[\chi^{(2)}]$ as a function of the center frequency of the excitation pulse provide 2D-HD-SFG spectra. The experimental setup is shown in Figure 1. The IR-pump/SFG-probe spectra were recorded under p/ssp (IR pump/SFG, VIS probe, IR probe) polarization.

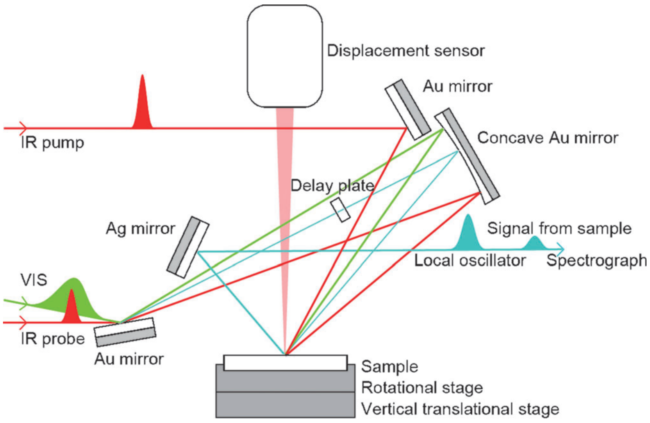

Figure 1. Schematic representation of the 2D-HD-SFG experiments.

The steady-state $\mathrm{Im}[\chi^{(2)}]$ spectrum at the air/H_2O interface (Figure 2a) shows a broad negative peak above 3200 cm^{-1} and a small positive peak below 3200 cm^{-1}, consistent with previous reports.[11,12] The negative peak indicates that OH groups at 3200–3500 cm^{-1} are on average pointing with their H atom towards the bulk.[11,13,14] The positive sign below 3100 cm^{-1} may arise from an anisotropic component of the polarizability[10] or multibody interactions.[13]

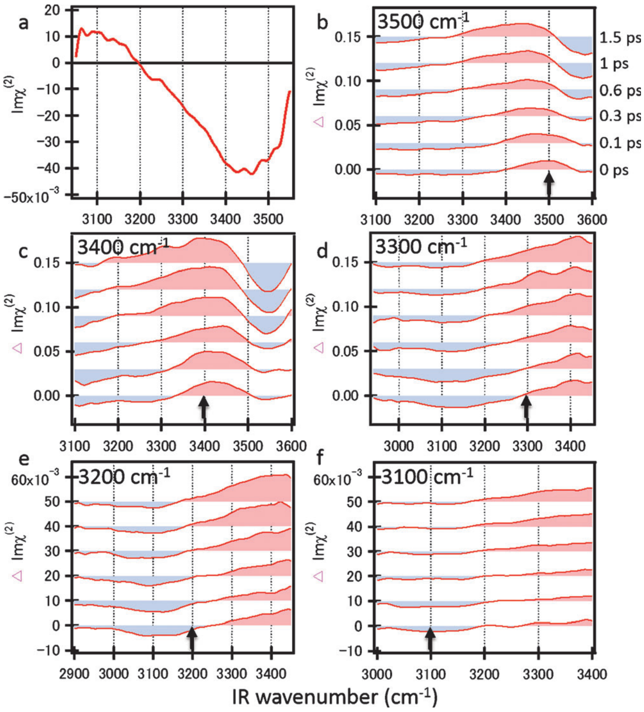

Figure 2. a) Steady-state $\mathrm{Im}[\chi^{(2)}]$ spectrum. b)–f) Time-resolved $\Delta\mathrm{Im}[\chi^{(2)}]$ spectra of the O–H stretching mode at the air/water interface. Waiting times after excitation are 0, 0.1, 0.3, 0.6, 1, and 1.5 ps (from bottom to top). The black arrows indicate the frequency of the pump pulses. Note the different *x*- and *y*-scales in panels (b)–(f).

Figure 2b–f shows the change in the second-order susceptibility $\Delta\mathrm{Im}[\chi^{(2)}(\omega_{\mathrm{pump}},t,\omega_{\mathrm{probe}})] = \mathrm{Im}[\chi^{(2)}{}_{\mathrm{pump\text{-}on}}(\omega_{\mathrm{pump}},t,\omega_{\mathrm{probe}})] - \mathrm{Im}[\chi^{(2)}{}_{\mathrm{pump\text{-}off}}(\omega_{\mathrm{probe}})]$ of the air/H_2O interface for different IR pump frequencies (ω_{pump}) at different waiting times *t* between the pump and probe pulses. Before discussing the observed spectral features, we will explain potential signal contributions. When the IR pump excites the O–H stretching mode from the ground state ($v_{\mathrm{OH}}=0$) to the first excited state ($v_{\mathrm{OH}}=1$), we observe at $t=0$ fs a bleach of the HD-SFG signal at the 0→1 transition frequency and an increase at the 1→2 transition frequency ($v_{\mathrm{OH}}=2$ is the second excited state) about 200–250 cm^{-1} lower than the 0→1 transition frequency due to its large anharmonicity.[15] When exciting a positive (negative) band in the $\mathrm{Im}[\chi^{(2)}]$ spectrum, one expects a negative (positive) signal in the $\Delta\mathrm{Im}[\chi^{(2)}]$ spectrum at the 0→1 excitation frequency, with a positive (negative) signal at the 1→2 transition, since the orientation of the O–H transition dipole moment for $v_{\mathrm{OH}}=1\rightarrow2$ is the same as for $v_{\mathrm{OH}}=0\rightarrow1$. Figure 2b shows the $\Delta\mathrm{Im}[\chi^{(2)}]$ spectra for $\omega_{\mathrm{pump}}=3500\ \mathrm{cm}^{-1}$. The $t=0$ ps spectrum shows the expected positive signal at 3500 cm^{-1} due to the bleach of the 0→1 transition, and a negative band below 3400 cm^{-1} due to the 1→2 transition. As time evolves from 0 to 1.5 ps, the positive band shifts from 3500 to 3400 cm^{-1} with a broadening of the bandwidth, that is, spectral diffusion occurs, arising from the frequency memory loss. Eventually, the absorbed energy is dissipated to low-energy states. The spectrum at 1.5 ps can be rationalized by a thermalized ground state, revealing a blueshift of the original steady-state $\mathrm{Im}[\chi^{(2)}]$ spectrum, resulting from an overall weakening of the H-bonds.[16] Among the studied five different pump frequencies (Figures 2b–f), the bleach in the $\Delta\mathrm{Im}[\chi^{(2)}]$ signals at 0 ps and the heated ground state at 1.5 ps is largest for $\omega_{\mathrm{pump}}=3400\ \mathrm{cm}^{-1}$ and smallest for $\omega_{\mathrm{pump}}=3100\ \mathrm{cm}^{-1}$ (note the different *y*-scale), which originates from the different absorbance of the IR pump pulse at each frequency. Similar to $\omega_{\mathrm{pump}}=3500\ \mathrm{cm}^{-1}$, the $\omega_{\mathrm{pump}}=3400\ \mathrm{cm}^{-1}$ and 3100 cm^{-1} data display bleach at the pump frequency at 0 ps, with signs according to the sign of the static $\mathrm{Im}[\chi^{(2)}]$ spectrum (Figure 2a). Note that the negative band below 3300 cm^{-1} in Figure 2c is due to the $v_{\mathrm{OH}}=1\rightarrow2$ transition, while for Figure 2f it originates from the bleach of the $v_{\mathrm{OH}}=0\rightarrow1$ transition. For $\omega_{\mathrm{pump}}=3200$ and 3300 cm^{-1} (Figures 2d and e), both the positive and negative features of the $\mathrm{Im}[\chi^{(2)}]$ spectrum are excited, and owing to their

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interference, the frequency where the observed bleach is maximum diverges from ω_{pump}. The maximum bleach is centered at 3100–3150 cm^{-1} at 0 ps.

One important observation from the data in Figure 2 is that the signals at 1.5 ps are very similar for all ω_{pump} except for 3500 cm^{-1}, where the zero crossing is at 3300 cm^{-1} instead of 3200 cm^{-1}. Apparently, the surface has not yet completely thermalized at 1.5 ps after the pumping at 3500 cm^{-1}.

The rate of spectral diffusion of interfacial water molecules at the air/H_2O interface can be quantified using 2D-HD-SFG plots displayed in Figure 3. The thick black lines in Figure 3 are the nodal lines (NL) separating the positive and negative peaks, and its temporal evolution provides the time constants of the spectral diffusion.[17] With increasing time, the NL slope decreases to zero, indicating that the system gradually loses memory of the initial excitation frequency. Figure 3 clearly illustrates that the NL slope decays differently below and above 3400 cm^{-1}. Apparently there are at least two subensembles of water molecules with different spectral dynamics. Note that in the 2D-HD-SFG spectra, the nodal curves arise not only from the cancellation between the $0 \rightarrow 1$ and $1 \rightarrow 2$ transitions as in 2D-IR spectra, but also from the interference of the positive and negative bands of the $\text{Im}[\chi^{(2)}]$ spectra. Given that the positive peak at 3400 cm^{-1} dominates the $\text{Im}[\chi^{(2)}]$ spectrum, the interference between the different contributions is negligible above 3200 cm^{-1} (the zero crossing in the static spectrum, see Figure 2a), and the interpretation of the NL slope in the 3200–3500 cm^{-1} region is directly comparable to 2D-IR experiments. The green lines in Figure 3 represent the linear fits to the NL for excitation frequencies ranging from 3200 to 3400 cm^{-1}. The temporal evolution of the inferred slope is plotted in Figure 4, showing the decay with a time constant of (240 ± 80) fs.[18] Thus, the spectral diffusion of the H-bonded O–H stretching mode at the air/H_2O interface is at least 1.4 times slower than that in pure bulk H_2O (50–180 fs).[4,5]

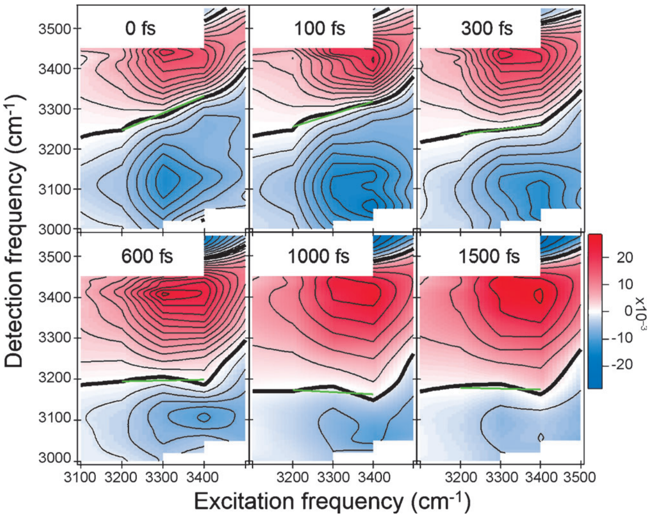

Figure 3. 2D-HD-SFG spectra of the air/water interface for various waiting times.

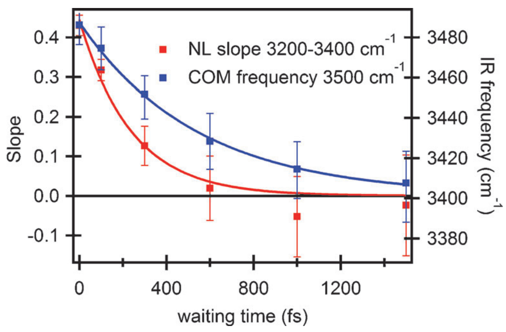

Figure 4. Plot of the NL slope and the COM frequency versus the waiting time. The solid curves show single exponential fits.

The 50–180 fs timescale observed for bulk water was rationalized not by structural relaxation, but by the delocalized nature of the O–H stretching mode resulting in strong anharmonic coupling to librational modes[4] and by near-resonant energy transfer to neighboring OH groups.[2,19] As the vibrational frequency (and thus hydrogen-bond strength) of the 3200–3400 cm^{-1} oscillators at the interface is comparable to that of bulk water, the lower frequency librations are expected to be located at frequencies similar to those in bulk H_2O. Thus, the timescale of the spectral diffusion due to anharmonic coupling should be little affected. However, the density of states is reduced at the interface resulting in less efficient intermolecular coupling. The reduced density of water molecules at the interface also reduces the number of acceptor dipoles for near-resonant energy transfer. Thus, the reduction of the density of water by a factor of about 2 (i.e. the air phase contains a negligible number of acceptors) leads to less efficient near-resonant and nonresonant coupling and also reduces the degree of delocalization of the O–H stretching vibration. Altogether this results in roughly twice as slow spectral dynamics, consistent with what has been observed for the air/D_2O interface.[20]

Our results thus indicate that OH groups with their SFG responses centered at 3200–3400 cm^{-1} show rather homogeneous dynamics with no appreciable frequency dependence of the spectral diffusion, similar to bulk water.[4,5] In contrast, the subensemble of 3500 cm^{-1} O–H chromophores exhibits significantly slower dynamics. Figure 3 shows that the bleaching frequency at 3500 cm^{-1} diffuses much more slowly than that at 3200–3400 cm^{-1}. As both populations overlap, and the thermal signal grows in over time, the temporal evolution of the NL slope at 3500 cm^{-1} does not allow for a quantification of spectral diffusion. To obtain quantitative information about the spectral dynamics of the weakly H-bonded subensemble, we consider the center of mass (COM) frequency of the positive feature of $\Delta\text{Im}[\chi^{(2)}]$ when the pump frequency is centered at 3500 cm^{-1} (Figure 2b).[21] As can be seen in Figure 4, the COM frequency, which is also a direct measure of spectral diffusion, decays on significantly longer timescales (540 ± 40 fs) than the NL slope. The presence of different timescales for the spectral diffusion of H-bonded water at the air/water interface indicates that the intermolecular coupling between the OH population at 3500 cm^{-1} and the remaining H-bonded water molecules is

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strongly reduced. In turn, this directly demonstrates that the spectral dynamics of water at the air/water interface is heterogeneous, unlike that of bulk water. Moreover, it confirms that the 3500 cm^{-1} O–H stretching mode originates from a different interfacial structure than the lower frequency O–H stretching modes. The interfacial 3500 cm^{-1} OH groups have previously been proposed to originate from those OH groups within water molecules in which the other end consists of a free OH group.[13,22,23] Apparently, these 3500 cm^{-1} OH groups at the interface are rather isolated. The timescale of spectral diffusion is much slower than a characteristic timescale of librational mode,[4] suggesting that the mechanism for its loss of frequency memory is very different from that of bulk H_2O. In fact, the timescale of spectral diffusion of $\approx$540 fs (Figure 4) is remarkably similar to the structural relaxation of the O–H stretching mode in bulk water of 0.5–1 ps,[3,6] suggesting that these OH vibrations are rather localized modes, similar to H–OD in D_2O. The slow dynamics of the 3500 cm^{-1} OH groups are all the more surprising, given that these H_2O molecules, which are sticking out of the interface, form fewer H-bonds than a water molecule in the bulk. Thus, one would expect that the H-bonded network imposes fewer structural constraints on them, leading to faster structural rearrangement. However, our results imply that for these water molecules the rearrangement of the H-bonded structure is rather slow, in agreement with recent theoretical predictions.[24]

In summary, we have investigated the intermolecular coupling strength of water vibrational modes at the air/H_2O interface using 2D-HD-SFG. The results reveal that the air/H_2O interface is rather inhomogeneous, in contrast to bulk water. Strongly H-bonded water molecules exhibit significantly slower spectral diffusion compared to bulk water. The 240 fs time constant for the spectral dynamics for strongly H-bonded O–H stretching modes with frequencies between 3200 and 3400 cm^{-1} shows good agreement with what would be expected if intermolecular coupling would dominate the loss of frequency memory. It is consistent with the intermolecular coupling being reduced by a factor of 2, relative to the coupling in bulk H_2O, indicating that slowing down of the spectral diffusion stems from the reduced water density at the interface. The mechanism of spectral diffusion for strongly H-bonded water molecules therefore appears to be similar to that of bulk water. However, for the 3500 cm^{-1} O–H stretching mode, spectral diffusion is even slower and occurs on a 540 fs timescale. Despite the substantial structural freedom of these O–H oscillators, they are weakly coupled to other water molecules and show remarkably slow spectral—and presumably structural—dynamics.

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