Water interacting with interfaces, ions and itself
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10 ULTRAFAST VIBRATIONAL
ENERGY TRANSFER AT THE
WATER-AIR INTERFACE

One of the unique properties of water is the very efficient transfer of vibrational energy between molecules, which arises as a result of strong dipole-dipole interactions between the O-H oscillators. Although we have a sound understanding of this energy transfer process in bulk water, we know less about how, and how quickly, energy transfer occurs at the water surface. Here, we use ultrafast two-dimensional surface-specific vibrational spectroscopy to probe the interfacial energy dynamics of heavy water (D$_2$O) at the water/air interface. The measurements reveal the presence of surprisingly rapid energy transfer, both between hydrogen-bonded interfacial water molecules (intermolecular), and between O-D groups sticking out from the water surface and those located on the same molecule and pointing towards the water bulk (intramolecular).

10.1 INTRODUCTION

The hydrogen bond structure of water surfaces strongly differs from that of bulk water. For instance, at planar hydrophobic surfaces, including the water/air interface, approximately one in every four interfacial water molecules has a free, non-hydrogen-bonded O-H group that protrudes into the hydrophobic phase [40, 41].

For a complete, molecular-scale understanding of the chemical processes that occur at the water interface one requires insights not only into its structure, but also into the rates and mechanisms of energy transfer and dissipation. In bulk water, energy flow mechanisms and dynamics have been quantified using femtosecond infrared laser techniques [32, 97, 171]. The O-H stretch vibrations of the water molecules were found to show rapid resonant (Förster) energy transfer on a timescale of $<100$ fs, largely as a result of the strong dipole-dipole interactions between the O-H oscillators.

As the rates and pathways of interfacial energy transfer processes are relevant for chemical transformations at aqueous interfaces, the question that presents itself is, how do the local structural changes affect the mechanism and timescale of energy flow at an aqueous interface? The challenge of characterizing the
structure of the outermost surface molecules has been met by sum frequency generation (SFG) spectroscopy of their O-H stretch vibrations [40, 41, 53, 117, 138, 143, 148, 153, 149]. 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 only in the surface region [142]. If the infrared light is resonant with the O-H stretch vibration of surface water, this process is resonantly enhanced. Initial SFG studies made use of the distinct correlation that exists between the local hydrogen bonding strength and the O-H stretch vibrational frequency of an OH group in a water molecule. These studies indicated that, in addition to the free O-H groups pointing away from the surface [40, 41], different types of hydrogen-bonded interfacial water also exist [40, 41, 138], and that the interfacial layer is limited to approximately one monolayer [149].

In bulk water, very rapid resonant (Förster) energy transfer between O-H vibrations of different water molecules was demonstrated by measuring the anisotropy dynamics [171] and the ultrafast spectral diffusion of the OH stretch vibrations [32]. The spectral diffusion was measured using two-dimensional infrared (2D-IR) spectroscopy [31, 76]. In this technique a vibration is excited with a femtosecond infrared laser pulse and the effect of this excitation on other, nearby vibrations is monitored with a second femtosecond infrared laser pulse. In this way, rapid hopping of the excitation over different vibrations was observed. For water at interfaces, a similar efficient vibrational energy transfer has been suggested to take place [104, 145]. This suggestion was based on time-resolved SFG experiments of the water-fused silica [104] and the water/air [145] interfaces, and specifically from the absence of any spectral dynamics of the excited O-H stretch vibrations.

We studied the interfacial energy flow dynamics using surface specific 2D-IR sum-frequency generation (2D-SFG) spectroscopy [23]. This technique combines the unique capabilities of 2D-IR spectroscopy with the surface specificity and (sub)monolayer sensitivity of SFG spectroscopy (see sections 2.6.1 and 2.6.2).

10.2 EXPERIMENT

In our SFG-2D-IR experiment, we used an IR-pump–SFG-probe scheme. The pump with a limited spectral width (typically set at 100 cm$^{-1}$) is continuously tuned across the absorption band of water (2100 - 3000 cm$^{-1}$). For the detection process, broadband mid-IR and narrowband visible upconversion pulses were mixed at the interface to generate a conventional SFG signal. The experimental details are the same as for the experiments presented in previous chapter (see section 9.2). In order to obtain sufficient time resolution for determining vibrational dynamics, the 2D-SFG spectra were composed from the transient spectra recorded at delay times of -1200, -600, -300, 0, 300, 600, 900, 1200, 2100, 3000 and 6000 fs following procedure described in section 9.2.

We studied heavy water (D$_2$O) rather than normal water, because the intermolecular energy transfer is expected to be slower due to the smaller transition dipole moments of the O-D stretch vibrations and the narrower homogeneous
10.3 Results and discussion

Figure 10.1 shows an example of a 2D-SFG spectrum in the O-D stretch region of the D\textsubscript{2}O/air interface at 0 fs delay between the excitation and detection pulses. The 2D-SFG spectra were constructed following the procedure described in previous chapter (see section 9.2). Along the horizontal (excitation) axis, the linear absorption spectrum of bulk D\textsubscript{2}O is shown. The steady-state SFG spectrum along the vertical axis reveals the free O-D group, sticking out of the surface, with a vibrational frequency of 2750 cm\textsuperscript{-1}. Between 2100 and 2600 cm\textsuperscript{-1}, a broadband response of hydrogen-bonded water molecules is apparent. The solid line is a linear fit to the signal maxima at different excitation frequencies, resulting in a line with a slope of 0.23 ± 0.06. The finite slope of the diagonal response at small delay is direct evidence for the heterogeneity of hydrogen-bonded water molecules at the water/air interface. The spectral heterogeneity reflecting the distribution of hydrogen bond strengths can be quantified by assuming that the vibrational response can be described by a Gaussian distribution of Lorentzian lines, the latter being characterized by a width $\Gamma_{\text{hom}}$. 
In the previous chapter we have introduced an inhomogeneity parameter $\Upsilon$ and determined that $\Upsilon = 0.31$. Our results revealed that the homogeneous linewidth $\Gamma_{\text{hom}} \approx 240 \text{ cm}^{-1}$, with the overall linewidth of the absorption band amounting to $310 \text{ cm}^{-1}$. The large homogeneous linewidth explains the spectrally broad response directly after excitation with a relatively narrow-band excitation pulse.

In addition to the response along the diagonal, distinct (off-diagonal) cross-peaks are apparent in the two-dimensional spectrum, highlighted by the dotted lines in the two-dimensional spectrum of figure 10.1. The origin and implications of these cross-peaks for the interfacial heterogeneity will be discussed later in more detail. The spectral heterogeneity within the hydrogen-bonded region, reflecting structural inhomogeneity, is very short-lived. Figure 10.2 shows transient spectra at different delay times, following excitation using a pump pulse centered at a relatively high frequency of $2625 \text{ cm}^{-1}$. The maximum in the signal shifts from high to low frequencies; that is, the signal displays spectral diffusion on a $\sim 600 \text{ fs}$ timescale. Exciting and detecting the differential SFG signal near the peak of the SFG spectrum, provides us with a relatively good way of determining the lifetime of the O-D stretch vibration, as the effect of spectral diffusion and slow ingrowth of the thermal signal are minimized (the derivative of the spectral response $\frac{d\Delta \text{SFG}(\nu)}{d\nu}$ is essentially zero). We find that the vibrational relaxation of the O-D stretch mode occurs with a time constant of $1 \pm 0.1 \text{ ps}$. Figure 10.3 (A-E) shows that the two-dimensional spectra evolve on a similar timescale. For long delay times, the signal is dominated by thermal effects, which give rise to both positive and negative signals in the differential SFG response, due to a blueshift of the SFG response. The time constant for the thermal relaxation step was not directly quantified, but, as is evident from figure 10.3 E, the thermal signal around $\sim 2630 \text{ cm}^{-1}$ exhibits a delayed ingrowth [96], and at $2100 \text{ fs}$ the thermal signal is still weak in comparison to the signal of the excited OD vibrations. In our analysis, we can therefore neglect contributions from the thermal signal to spectral diffusion for timescales up to $\sim 3 \text{ ps}$.

The spectral diffusion can be quantified from the time-dependent slope of the diagonal response of the two-dimensional spectra, as summarized in figure 10.3F. Such spectral diffusion may be due to structural relaxation at the water interface, so that by hydrogen bond rearrangement, strongly hydrogen-bonded water molecules can become weakly bonded and vice versa. However, spectral diffusion is also indicative of intermolecular energy transfer. For bulk H$_2$O, very efficient transfer of vibrational energy between different water molecules has been demonstrated [32, 79, 128, 171]. This energy transfer is expected to contribute significantly to the spectral diffusion within the O-D stretch vibrational band, as vibrational energy transfer can occur between differently hydrogen-bonded O-D groups, with different frequencies. Although we cannot exclude a contribution from structural relaxation to the dynamics, we first explore whether vibrational energy transfer, expected also to be very efficient at the interface, provides a sufficient explanation of the observed spectral dynamics.
10.4 Interfacial Intermolecular Energy Transfer

We modeled the decay of the time-dependent slope $S(t)$, which is a measure of heterogeneity, using the model for resonant energy transfer in D$_2$O [128]. The decay of the slope is directly proportional to the decay of the frequency-frequency correlation function, as demonstrated previously for conventional 2D-IR [84]. The decay of this correlation function originates from energy transfer between O-D groups of different frequency. Assuming that energy transfer is the only mechanism scrambling the frequency, and that each transfer step leads to a complete randomization of the vibrational frequency, we can express the slope at time $t$ for a concentration of O-D groups of $C_{OD}$ (in MÅ$^{-3}$) = 2C$_{D2O}$ as (see section 2.5.1):

$$S(t) = S_0 \exp \left( -\frac{4\pi^3/2}{3} C_{OD} N_A \frac{\sqrt{r_0^6} t}{T_1} \right) \quad (10.1)$$

where $N_A$ is Avogadro’s number, $r_0$ is the distance over which the energy transfer occurs with 50% efficiency, and $S_0$ is the initial slope value. The dipole-dipole coupling strength is represented by the term $\sqrt{r_0^6}/T_1$. This term is proportional to the transition dipole moments of donor and acceptor. The Förster radius $r_0$ is the distance between donor and acceptor for which energy transfer plays a role within the lifetime $T_1$. If $T_1$ increases, then $r_0$ also increases, not because there is a change in the dipole coupling, but because there is more time for the energy transfer to take place within the lifetime of the excitation. Following references [128, 171], the radius $r_0$ is referenced here to $T_1 = 1700$ fs, the intrinsic
Figure 10.3. 2D-SFG spectra of the D$_2$O water-air interface at various delay times after the excitation. Panels A-E: Solid lines represent the IR frequencies corresponding to the maximum SFG response as a function of the excitation frequency. Red (blue) indicates a decrease (increase) in the SFG signal, as shown by the scale bar in panel E. The slopes of the solid lines are plotted as a function of delay in panel F. The solid line in panel F is the result of a model calculation that accounts for the spectral diffusion by resonant Förster energy transfer (see main text) with $r_0 = 2.4 \pm 0.3$ Å (error indicated by gray shaded area).
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vibrational lifetime of the O-D stretch vibration of HDO in bulk H$_2$O. We note that $T_1$ is much shorter than the radiative lifetime of the transition.

Using this equation we find a very good description of the dynamics with $r_0 = 1.9 \pm 0.2$ Å. This value is appreciably smaller than the value of $r_0 = 2.3 \pm 0.2$ Å found for bulk D$_2$O [128]. This indicates that energy transfer between the O-D vibrations is slower at the D$_2$O surface than in the bulk. This slower energy transfer can probably be attributed to the lower density of acceptors for D$_2$O molecules near the interface. For the topmost layer of D$_2$O molecules, the number density of available acceptors is expected to be only half the number density of D$_2$O molecules in the bulk. In appendix 10.7 we derive a modified equation for the energy exchange between an O-D group at the surface and a bulk-like hemisphere below it:

$$S(t) = S_0 \exp \left( -\frac{2\beta^3}{\sqrt{3}} C_{OD} N_A \sqrt{\frac{r_0^6 t}{T_1}} \right) \quad (10.2)$$

This equation differs from the previous equation in the two times smaller exponential factor. The result of fitting this model to the data is shown as the line in figure 10.3 F. Fitting this model we find $r_0 = 2.4 \pm 0.3$ Å, indistinguishable within the error from the 2.3 Å found for bulk D$_2$O [128]. The success of equation 10.2 in describing the data implies that the 2D-IR SFG technique probes the D$_2$O/air interface over a penetration depth less than $r_0$. As $r_0$ is similar to the intermolecular separation in liquid D$_2$O, this finding demonstrates that the 2D-SFG technique only probes the outermost molecules of the D$_2$O surface.

Although this energy transfer model provides a quantitative description of the observed spectral dynamics, this does not prove the model is correct. A rigorous test of the validity of the model is the measurement of the spectral diffusion rate in dependence on the isotope dilution [128, 171]. The result of a spectral diffusion measurements on a 1:1 mixture of D$_2$O and H$_2$O is shown in figure 10.4. The figure shows frequency-resolved transient SFG spectra at different delay times after excitation at 2625 cm$^{-1}$ for pure D$_2$O (left), and at 2560 cm$^{-1}$ for a 1:1 D$_2$O/H$_2$O mixture (right). The conventional SFG spectrum changes slightly upon isotopic dilution [147], and therefore somewhat different excitation frequencies were chosen to achieve the same excitation density. It is evident from these results that the spectral diffusion dynamics slows down upon isotopic dilution. The results are summarized in figure 10.5, which shows the frequency of the bleach maximum at different delay times. The solid lines in figure 10.5 are calculations following the intermolecular energy transfer model presented above, and are the same as the dashed lines in figure 10.4. These results are in quantitative agreement with the Förster energy transfer model, showing the expected slow-down of the spectral diffusion dynamics for the 2-fold diluted sample. Given that the structural, molecular dynamics remain unchanged upon isotopic dilution, this result proves that the spectral diffusion, and the time-dependent slopes of the 2D spectra, are the result of efficient intermolecular energy transfer, which justifies the use of the proposed model.

The observation that the energy transfer model provides a quantitative description of the observed spectral dynamics suggests that structural dynamics
Figure 10.4. Isotopic dilution measurements show that spectral diffusion slows down with increasing isotopic dilution. Frequency-resolved transient SFG spectra at different delay times after excitation at 2625 cm$^{-1}$ for pure D$_2$O (left) and 2560 cm$^{-1}$ for 1:1 H$_2$O/D$_2$O mixture (right). Both experiments reveal a red shift of the maximum of the SFG signal. The dashed lines are calculations following the intermolecular energy transfer model described in the text. The experiments for 1:1 H$_2$O/D$_2$O isotopically diluted sample reveal a slowdown of the spectral diffusion dynamics, precisely as expected for the energy transfer, due to the 2-fold lowering of the concentration of O-D groups C$_{OD}$.

...do not contribute significantly to the spectral diffusion process. This observation is not very surprising, considering the very short timescale over which spectral diffusion due to Förster energy transfer occurs. 2D-IR studies of the structural dynamics of isotopically diluted water samples, for which there is no resonant energy transfer, have shown the presence of only a minor structural relaxation component on a 100 fs timescale [3, 98]. The dominant structural rearrangement of the hydrogen bond network of bulk water was observed to take place on longer timescales [3, 98]. The 2D-SFG spectra thus allow us to follow the dynamics of intermolecular energy transfer between interfacial water molecules in real time, revealing the predominance of dipole-dipole interactions in conjunction with the truncation of the water structure at the interface. The 2D-SFG spectroscopy results presented here allow for the quantification of the energy flow rate. The fact that simple geometric arguments (energy transfer into a half-sphere) completely account for the timescale on which resonant energy transfer occurs at the water/air interface, is consistent with the molecularly sharp density profile at the interface [113, 152].
10.5 Efficient interfacial intramolecular energy transfer

We now turn to the off-diagonal cross-peaks observed in the two-dimensional spectra at (excitation, detection) frequencies of both $(2580, 2750 \text{ cm}^{-1})$ and $(2750, 2580 \text{ cm}^{-1})$, highlighted as dotted circles in figure 10.1. The presence of these cross-peaks implies the occurrence of energy transfer between the free O-D stretch and a vibration on the blue side of the hydrogen-bonded peak. Considering the large energy mismatch between these two frequencies, this coupling cannot be due to resonant dipole-dipole interactions between the two O-D groups. The interaction must therefore rely on an interaction between the donor and acceptor vibration in which the energy mismatch is taken away or supplied by a third, low-frequency degree of freedom. The coupling is therefore at least of third order in the vibrational coordinates (that is, the donor, acceptor and a low-frequency mode), which means that this coupling is anharmonic. The anharmonic coupling is most likely through-bond and therefore rather of intra- than of inter-molecular nature. This means that the resonance at $2580 \text{ cm}^{-1}$ on the blue side of the hydrogen-bonded peak belongs to the O-D group which is part of the same water molecule that has a free O-D group at $2750 \text{ cm}^{-1}$ sticking out of the surface. This assignment agrees with previous polarization-resolved [51] and isotope-dependent [149] static SFG experiments, which have indicated that the hydrogen-bonded O-D group attached to the free O-D has a vibrational frequency on the blue side of the broad hydrogen-bonded absorption band. The two-dimensional spectra presented here unambiguously reveal the strong coupling between these two O-D groups.

We investigate the dynamics of the $(2750, 2750 \text{ cm}^{-1})$ and $(2750, 2580 \text{ cm}^{-1})$ spectral features, as shown in figure 10.6. The dynamics of the cross-peak re-
Figure 10.6. A: Dynamics of the free O-D vibration excited and detected at 2750 cm$^{-1}$ (red), and the cross-peak excited at 2750 cm$^{-1}$ and detected at 2580 cm$^{-1}$. The signal of the free O-D stretch at 2750 cm$^{-1}$ shows a rapid initial decay, and the cross-peak shows a delayed rise. These dynamics are due to an ultrafast energy transfer from the excited free O-D vibration sticking out of the surface to the O-D group that is located on the same water molecule and pointing into the bulk. After equilibration, the two modes relax together with the same effective rate. B: Schematic representation of the interfacial energy redistribution process with the time constants obtained from fit of the data to the model described in the main text.

reveals that the mechanism of vibrational relaxation is rather intricate; the somewhat delayed in-growth of the cross-peak indicates rapid vibrational energy transfer from the free O-D to the hydrogen-bonded O-D within the same D$_2$O molecule. The rapid equilibration of vibrational energy between the two modes is followed by a decay due to vibrational relaxation, presumably through the hydrogen-bonded O-D group. A model that includes in parallel both the energy equilibration and the vibrational relaxation provides a very good description of the data, as shown by the solid lines in figure 10.6. The model is described in the appendix 10.8. From the fit we obtain a time constant of $k_1 = (300 \pm 60 \text{ fs})^{-1}$ for the energy transfer from the free O-D to the hydrogen-bonded OD. The time constant for the reverse process fulfills detailed balance: $k_1/k_{-1} = \exp[(2750 - 2580)/k_B T]$ which implies that $k_{-1} = (780 \pm 150 \text{ fs})^{-1}$. Vibrational relaxation of the hydrogen-bonded O-D group occurs with a time constant of $900 \pm 50 \text{ fs}$, in good agreement with the $\sim$1 ps lifetime inferred from the diagonal response, when exciting and detecting the hydrogen-bonded O-D groups. The results are summarized in figure 10.6. The lifetime is similar to the previously reported $\sim$1 ps lifetime of the free O-H of H$_2$O [104]. For this free O-H the relaxation is expected to take a similar path as the free O-D at the D$_2$O surface, namely a rapid equilibration of the vibrational energy over the two O-H groups of the H$_2$O molecule, followed by the cooperative relaxation of the two groups. In the present 2D-SFG experiment we can resolve the first equilibration process thanks to the dynamics of the cross-peaks. In this way, we find that the free O-D groups serve as efficient antennas for vibrational energy, and rapidly transfer this energy to the hydrogen-bonded O-D group within the same molecule. The
10.6 Conclusions

In summary, we demonstrate that 2D-IR SFG data reveal the occurrence of surprisingly fast intra- and intermolecular energy transfer processes at aqueous interfaces. The results show that energy transfer among O-D stretching modes of water on the surface is rapid and efficient and that O-D excitations rapidly exchange between surface and bulk. This information on interfacial energy flow patterns is essential for understanding chemistry at aqueous interfaces: the occurrence of endothermic and exothermic reactions at aqueous surfaces, be it on catalytic water interfaces, in atmospheric chemistry or at cell membrane surfaces, requires the efficient transport of vibrational energy to and from the surface.

10.7 Appendix: Vibrational energy transfer over a half-sphere

We use the same procedure as we used before in section 8.5 to derive the vibrational energy transfer between water molecules located at the surface. Briefly, combining the two probabilities: the probability that the molecule is excited at time $t=\tau$ (equation 2.37) and the probability of finding an accepting molecule for each of the $N$ oscillators in the system (equation 2.38) we arrive at:

$$\rho(t) = \left\{ \frac{2\pi}{V} \int_0^R \exp\left(-\frac{tr_0^6}{T_1r^6}\right) r^2 dr \right\}^N,$$

where $V$ is now the volume of hemisphere $V = 2\pi R^3/3$, $R$ is a radius of the hemisphere and $N$ is the number of the O-D oscillators in the system. Performing the integration, we obtain:

$$\rho(t) = \left\{ \exp\left(-\frac{tr_0^6}{T_1r^6}\right) + \sqrt{\frac{\pi tr_0^6}{T_1R}} \text{Erf}\left(\sqrt{\frac{\pi tr_0^6}{T_1R}}\right) \right\}^N,$$

Using the expression for the concentration of the O-D oscillators (expressed in MÅ$^{-3}$):

$$C_{OD} = \frac{3N_{OD}}{2\pi R^3 N_A},$$

we can eliminate the hemisphere radius $R$ from expression 10.4. Performing the power expansion in terms of $1/N$ and eliminating higher order terms (since for $N\to\infty$ they become negligible) we obtain the expression:

$$\rho(t) = \exp\left(\frac{2\pi^{3/2} C_{OD} N_A \sqrt{tr_0^6}}{3\sqrt{T_1}}\right).$$

vibrational energy then delocalizes further as a result of resonant dipole-dipole coupling of the hydrogen-bonded O-D group with other water molecules.
The above expression describes resonant vibrational energy transfer for a molecule located at the surface, and assumes that the energy transfer step leads to a complete randomization of the vibrational frequency, i.e.
that the energy step leads to a complete decay of the frequency-frequency correlation function. Note that the rate of energy transfer is smaller than the rate of energy transfer of a molecule located in the bulk (see section 2.41). This difference arises from the lower number of acceptors in a hemisphere, compared to that in a sphere.

Figure 10.7 shows a schematic representation of the resonant vibrational energy transfer for an interfacial water molecule (left) and a molecule located in the bulk (right).

10.8 Appendix: Interfacial intramolecular energy transfer

In the following we present the model and the corresponding differential equations describing the intramolecular coupling process between the free O-D groups (denoted 'F') and the hydrogen-bonded O-D groups (denoted 'HB'). The subsequent relaxation involves the transition from the excited hydrogen-bonded O-D group to a state at a somewhat elevated temperature (denoted 'T'). Energy transfer from F to HB occurs with rate $k_1$; the reverse rate is given by $k_{-1}$. We assume that vibrational relaxation - with rate $k_2$ occurs only from the HB state into the T state.

If we denote the occupation of each of the states as $N_X$, where $X = F$, HB or T. Initially the excitation pulse, characterized by the time-independent intensity $I(t)$, gives rise to population of $N_F$. The time-dependent occupation of each state is given by:
\[ \frac{\partial N_F}{\partial t} = \sigma_{01} I(t) [N_0 - N_F] - k_1 N_F + k_{-1} N_{HB} \]

\[ \frac{\partial N_{HB}}{\partial t} = k_1 N_F - k_{-1} N_{HB} - k_2 N_{HB} \]

\[ \frac{\partial N_T}{\partial t} = k_2 N_{HB} \] (10.6)

The forward and backward rates \( k_1 \) and \( k_{-1} \) are linked by the Boltzmann factor that accounts for the energy difference between the two levels:

\[ \frac{k_1}{k_{-1}} = \exp \left( \frac{(2750 - 2580)}{k_B T} \right) \] (10.7)

Owing to the fact that the differential signals are detected on the background of the steady state SFG signal, the differential SFG signals for the free and hydrogen-bonded O-D groups are simply proportional to \( N_F \) and \( N_{HB} \), both with a contribution (accounting for the long-time signal offset) from \( N_T \).