Ultrafast Energy Transfer between Interfacial and Bulk Water at the Air-Water Interface

Abstract

In the previous chapter we developed a femtosecond time-resolved SFG spectroscopy scheme to study the vibrational dynamics of interfaces. In this chapter we shall be using this scheme to study the O-H stretch vibrational lifetime of hydrogen-bonded water molecules at the neat water/air interface. The vibrational lifetime in the frequency range of 3200 to 3500 cm$^{-1}$ is found to closely resemble that of bulk water, indicating ultrafast exchange of vibrational energy between surface water molecules and those in the bulk.
3.1 Introduction

Interfacial water plays an important role in many biological, chemical and physical processes (see e.g. [95–97] and references therein). The air-water interface, owing to the asymmetric nature of its terminated hydrogen bond network, has been shown to play an eminent role in the heterogeneous chemistry of a variety of atmospheric and geochemical processes. For instance, through a number of simulations and experiments on simple aqueous salt solutions (eg, NaCl), the anions (particularly halides) have been found to be present at the air-water interface at enhanced concentrations than in the bulk water itself; the cations on the other hand, prefer to remain solvated in the bulk phase [98]. This is consistent with observations of hydrogen bonding in aqueous ionic clusters. Cations form hydrated clusters in which the ion binds to water oxygen atoms. The water molecules are distributed fairly symmetrically around the ion. In contrast, anions bind to water hydrogen atoms. The water molecules are arranged asymmetrically around the ion, enabling hydrogen bonding between them. This behavior is seen for the larger anions Cl\(^{-}\), Br\(^{-}\), and I\(^{-}\) [99]. Hence, sodium cations should prefer the homogeneous environment in the bulk liquid, whereas large anions should form asymmetric structures near the interface. This observation indicates the potential of the terminated H-bond network at the air-water interface to cause preferential adsorption of a number of reactive species at the interface and subsequently enhance the surface reactivity. Halide ions at the surfaces of atmospheric aerosol particles play an important role in controlling oxidant levels in the marine boundary layer of the atmosphere. Even a number of gases, like Cl\(_2\) and Br\(_2\) have been shown to have higher adsorbed concentrations at the air-water interface than in the bulk of solvent [100].

The air-water interface has also shown to be a preferential adsorption site for biologically important species like single-stranded DNA [101]. Therefore one can only imagine, the immense potential the air-water interface has, in a variety of natural or artificial heterogeneous chemical reactions. However, because of the experimental difficulties in investigating liquid interfaces in general, and the most prevalent water-air interface in particular, knowledge of the structural and dynamical interface properties has not yet reached the same degree of sophistication that has been attained for bulk water. [102]

Non-linear optical techniques, such as Second Harmonic Generation (SHG) and Sum Frequency Generation (SFG) [26,103] spectroscopy are generally surface specific and have been shown to be selectively sensitive to the outermost few monolayers of water molecules [104–106]. Vibrational SFG (VSFG) is a particularly powerful tool, as it allows the molecular vibrations of surface water to be probed, which are known to be sensitive reporters of the hydrogen-bonding water environment. Briefly, VSFG relies on the coherent interaction of infrared (IR) and visible (VIS) fields at the surface, to produce a field with a frequency that is the sum of the two incident fields. This surface-specific process is resonantly enhanced by surface vibrations. Indeed, the application of SFG to investigate water at the water/air interface has revealed important new insights in the interfacial water structure [61,62] and orientation. [107]. It has been shown, for instance, that a significant fraction of surface water molecules (\(\sim 20\%\)) have a free O-H group sticking into the vapor. These free, non hydrogen-bonded O-H groups are characterized by a relatively high vibrational frequency of the
O-H stretch. For the H-bonded interfacial water molecules, the spectrum is broad and featureless, a situation reminiscent of the vibrational spectrum of bulk water. A typical SFG spectrum of water at the neat water-air interface is shown in figure 3.1.

In studies of bulk water, a wealth of information about the properties of water has been obtained by the study of the vibrational dynamics of the O-H stretch vibration through the use of non-linear infrared (pump-probe) spectroscopy (see e.g. [108–112]). The motivation for much of this work lies in the realization that the ultrafast femtosecond behaviour of water molecules contains additional information on the structural and dynamic behaviour in its hydrogen-bonded environment. In pump-probe spectroscopy, by exciting certain vibrational modes with a pump IR pulse, a non-equilibrium perturbation is introduced in the molecule and with the delayed probe pulse, one can essentially take snapshots of the excited vibrational mode in time, as it relaxes back to its original equilibrium state. Such non-linear spectroscopies have been shown to be extremely useful in unraveling different aspects of water dynamics, including intermolecular energy transfer, reorientational motion, and the effects of ions thereon. In addition to investigations of bulk water, there has been much interest in how the water vibrational dynamics are affected by confinement and/or the binding to molecules that mimic a biological environment [113–115].

In this chapter, we shall present our pump-probe studies on water molecules at the air/water interface by using the novel femtosecond IR pump-VSFG probe spectroscopic technique. In these studies, the frequencies of the IR pump and probe pulses are resonant with a symmetric stretch vibrational mode\(^1\) of the hydrogen-bonded interfacial water molecule. The pump pulse excites this vibrational mode and the modulation of the interfacial SFG spectrum originating from the IR probe and up-conversion visible pulses, is monitored as a function of the pump-probe delay [83, 84, 87, 103, 116]. The time evolution of recovery of the SFG signal then reflects the vibrational relaxation of the interfacial water molecules. The femtosecond time-resolved SFG study that is presented here, is thus a one-colour pump-probe experiment that allows us to selectively probe the lifetime dynamics (\(T_1\)) of the O-H stretch vibration and provide new insights in the structure and dynamics of water at the neat water-air interface.

### 3.2 Static and Time-resolved VSFG experiments

Two independent setups have been used in this study: one for static SFG spectroscopic studies and one for the time-resolved studies. We used the easily tunable static SFG setup to record the broadband (2000-2900 cm\(^{-1}\)) SFG spectrum of heavy water D\(_2\)O at the neat water-air interface as shown in figure 3.1. In this setup, the IR frequency can be easily scanned from 2000 cm\(^{-1}\) to 2900 cm\(^{-1}\), which is why D\(_2\)O was used for the static measurements, instead of H\(_2\)O. The D\(_2\)O spectrum ranges from ~2250 cm\(^{-1}\) to ~2850 cm\(^{-1}\) and resembles the frequency-shifted H\(_2\)O spectrum.\(^2\)

\(^1\)The fundamental O-H symmetric stretch mode being isoenergetic with the overtone of the water bending mode, leads to Fermi resonance coupling of the two modes

\(^2\)The features of the D\(_2\)O spectrum are essentially the same as the H\(_2\)O spectrum, only red-shifted in frequency due to a larger reduced mass of the O-D oscillator. Assuming the O-H and O-D force constants to be the same, \(\nu_{OH}/\nu_{OD}=\sqrt{\mu_{OD}/\mu_{OH}} \approx 1.374\)
Figure 3.1. The SFG spectrum of O-D at the neat D$_2$O-air interface is shown in light grey. The top axis represents the IR frequency scaling for the equivalent H$_2$O spectrum. The solid line is a fit to the observed SFG spectrum, assuming two inhomogeneously broadened resonances and a single Lorentzian for the dangling O-D vibration. The linear infrared absorption spectrum of H$_2$O is also shown here (solid blue line), to show the contrast between the O-H in bulk and at the surface.

In the static SFG experiment, the SFG signal is spectrally dispersed by a monochromator and detected by a CCD camera. The spectral resolution is limited by the bandwidth of the visible beam and is $\sim 20$ cm$^{-1}$. The reduced spectral resolution explains, as discussed in chapter 2, why the intensity of the spectrally narrow free O-D peak is relatively low compared to the H-bonded peaks, when comparing the results of figure 3.1 to other reports in literature.

The TR-SFG setup is much more involving owing to the requirement of generating high energy mid-IR pump pulses, which limits the tunability to the O-H stretch region (2900-4000 cm$^{-1}$), with a bandwidth$^3$ of $\sim 150$ cm$^{-1}$. In the experiments, the central frequency of pump and probe pulses are set at fixed positions within the $\sim 400$ cm$^{-1}$ SFG resonance as indicated by the arrows across the SFG spectrum in figure 3.2.

In the TR-SFG experiments on neat water-air interface, distilled Millipore-filtered water (H$_2$O, 18 MΩ-cm resistivity) at pH 7 was used in a home-built Teflon trough. The trough was rotated at 5 rpm to suppress the effect of sample heating. The one-colour TR-SFG experiments were performed at fixed IR pump and probe frequencies across the hydrogen-bonded spectrum (3200-3500 cm$^{-1}$) as indicated by the dotted arrows in figure 3.2. The foci of the pump IR, the probe IR and the visible pulses were overlapped spatially and temporally at the surface of the water. The temporal overlap

$^3$For transform-limited Gaussian pulses, one can simply compute the bandwidth that can be covered with a pulse of duration, $\Delta \tau$ (in s) by using the equation, $\Delta \nu = 0.441/c \Delta \tau$ where $c = 3 \times 10^{10}$ cm/s and $\Delta \nu$ is the bandwidth in cm$^{-1}$. 

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of all three beams was optimized by monitoring the IIV-SFG signal (see *Getting started* in Chapter 2). Subsequently, the TR-SFG experiment was performed by monitoring the SFG signal while delaying pump pulse with respect to the probe (IR + visible) using a mechanical delay line. These experiments were performed from -0.5 ps to 3 ps pump-probe delays in steps of 100 fs. The SFG signal was filtered using bandpass filters and a monochromator and was detected in a spectrally-integrated manner with a Photo Multiplier Tube (R9910, Hamamatsu). Because the SFG signal is less than 0.1 detected photon per laser shot, and the pump-induced modulation typically 10% thereof, 25 scans were averaged, each consisting of 20 points (10,000 laser shots per point). The 1 kHz pump beam was chopped to 500 Hz and the normalized, differential SFG signal was computed as the ratio between the signals with and without the pump.

At the neat water-air interface, the largest resonant VSFG signal is generated by the $\chi^{(2)}_{xxz}$ ($= \chi^{(2)}_{yyz}$) components of the stretch dipoles of the H$_2$O molecule. If the xz-plane (see figure 3.3) is defined as the plane of incidence for the IR probe and visible beams (and plane of reflection for the SFG beam), then the polarization vector in the xz-plane (and perpendicular to direction of beam propagation) is defined as $P$ and the polarization vector perpendicular to the xz-plane is defined as $S$. In this beam geometry, the polarization combination required to probe the $\chi^{(2)}_{xxz}$ ($= \chi^{(2)}_{yyz}$) component is $S,S$ and $P$ for SFG, visible and IR probe beams, respectively. TR-SFG experiments were also performed with two different pump polarizations ($P$ and $S$, parallel and perpendicular to the surface normal) in order to investigate anisotropy effect on the pump-probe SFG signal. The polarizations of all beams could be rotated independently using $\lambda/2$-plates mounted on a motorized
3.3 Results and Discussion

3.3.1 Static SFG Results

Except for the shift in frequency due to the mass difference, the D$_2$O spectrum is equivalent to previous reports of SFG spectra of H$_2$O \[62, 63\]. The narrow resonance in the SFG spectra at $\nu = 3690$ (2730) cm$^{-1}$ has been shown to be due to the dangling O-H (O-D) bond. The hydrogen-bonded O-H however, is represented by a broad, double peaked spectral feature spanning from $\sim 3100$ to 3550 cm$^{-1}$ (see figure 3.1). The solid line shown in the spectra, is a fit to the data assuming two inhomogeneously broadened resonances and a single Lorentzian for the dangling O-D vibration. Figure 3.1 also shows the linear infrared absorption spectrum of H$_2$O (dotted lines), which reveals that the infrared response of the H-bonded part of the surface spectrum is markedly different from that of the bulk.

The assignment of the broad double-peaked feature, however has been a subject of intense debate in recent literature: on the one hand, in analogy with the IR spectrum of liquid water and ice, it has been argued that the two apparent peaks at $\sim 3200$ and at $\sim 3450$ cm$^{-1}$ are the result of strongly hydrogen bonded ('ice-like') water, and weakly hydrogen bonded ('liquid-like') water, respectively. This argument has been bolstered by a series of MD simulations that have been interpreted to suggest that each spectral feature is actually a combination of multiple, distinct, water structures \[117–124\].
However, on the other hand, it has also been argued based on analogy to gas phase water molecules, other simulations and interpretations of the spontaneous Raman spectra of bulk water, that the two peaks can largely be explained as the symmetric and asymmetric vibrational modes of the water molecule \cite{104,125}. Recently published work, however, by showing that each peak has a similar dependence on IR and VIS polarization, has demonstrated that both peaks result from vibrational modes with the same symmetry thus ruling out the latter interpretation \cite{126}. Recent isotopic dilution experiments show that a third mechanism best explains the double peaked nature of the interfacial water spectrum. At both the air/water and lipid/water interfaces the two peaks collapse to one upon isotopic dilution, showing that the two-peak structure is not the result of a distribution of H-bonded structures \cite{127}. Owing to the frequencies and polarization dependencies of the SFG response \cite{126}, the interpretation in terms of symmetric and asymmetric vibrational modes can also be discarded. The variety of experimentally observable characteristics of the double peaked spectral feature can be thus best explained if the visible dip in the spectrum is the result of a Fermi resonance between the bend overtone and the stretch fundamental \cite{127}. Such coupling has been demonstrated to exist, using two-colour IR pump-probe experiments in bulk water \cite{111,128,129}.

### 3.3.2 Time-resolved SFG Results

The typically broad and featureless time-averaged SFG spectra of the hydrogen-bonded O-H species almost immediately prompts us to ask whether the underlying dynamic structure of water is indeed different. The results of the pump-probe measurements of the relaxation of O-H stretching modes of hydrogen-bonded water after pumping at frequencies $\nu_{\text{pump}} = 3200, 3300, 3400$ and $3500$ cm$^{-1}$, are depicted in figure 3.4. Also shown in figure 3.4 is the third-order IR+IR+VIS (IIV) SFG signal, which is used to determine time zero ($\Delta t = 0$) and quantify the time resolution in each experiment.

The normalized pump-probe SFG signal of the water-air interface reveals a pump-induced decrease in the signal that is observed after $\Delta t = 0$. At 3400 and 3500 cm$^{-1}$, this is followed by a recovery of the signal that deviates from the level before $\Delta t = 0$; at lower frequencies, it is followed by an additional, slower decrease. The initial decrease in SFG is due to excitation of the O-H stretch mode to its first excited state by the pump pulse. Owing to the large vibrational anharmonicity of $\sim 300$ cm$^{-1}$ \cite{130}, SFG generated from the excited state ($v = 1 \rightarrow 2$) is shifted out of the spectral window. The recovery at 3400 and 3500 cm$^{-1}$ reflects vibrational relaxation, and the long-time offset is caused by an increase in the local temperature due to the energy deposited by the pump pulse, which is eventually converted to heat. The pump-induced temperature increase in the focus has been calculated to be approximately 15 K. As observed in the transients, this offset goes from $\sim 0$ at $\nu_{\text{pump}} = 3500$ cm$^{-1}$ to much smaller than 0 at $\nu_{\text{pump}} = 3200$ cm$^{-1}$, in accordance with an expected blue shift of the spectrum due to the pump-induced heating that results in a weaker hydrogen-bonded network.

From the data in figure 3.4, two timescales seem apparent: a fast ($\sim 100$ fs) relaxation time corresponding to the recovery of the pump-induced bleach signal (most clearly evident at $\nu = 3500$ cm$^{-1}$, and the slower ($\sim 500$ fs) timescale by which the final SFG level is reached (most apparent at
Figure 3.4. TR-SFG one-colour pump-probe transients across the hydrogen-bonded H$_2$O spectrum. Time-resolved SFG data for interfacial water for $\nu_{\text{pump}}$ = 3200, 3300, 3400 and 3500 cm$^{-1}$ (traces are offset for clarity). Polarizations of the SFG, VIS probe, IR probe and IR pump were S, S, P and S. The solid lines are the fits based on a four level system explained in the text. The lower trace is the third-order IR+IR+VIS SFG signal (shown for $\nu = 3300$ cm$^{-1}$). Indeed, a four-level energy scheme characterizing such a system shown in figure 3.5 provides a very good description of the experimental data.

In bulk studies it was shown that vibrational relaxation from $\nu=1$ occurs through an intermediate state $\nu^*$, which is a mixed state of the ground state of the stretch vibration and other modes that accept energy from the $\nu=1$ state $|131\rangle$. From $\nu^*$ relaxation then occurs to the system at elevated temperature, which is a long-lived state with optical properties different from the original ground state. This explains the observed long-time signal offset in the data. The following physical picture thus emerges: the ground state ($\nu=0$) is depleted by the pump, and relaxation from the excited state ($\nu=1$) occurs to an intermediate state ($\nu^*$), before reaching the new ground state ($\nu'=0$) at elevated temperature. We calculate the population in each level by solving the coupled differential equations,

$$\frac{dN_0(t)}{dt} = -I(t, \tau_{\text{fwhm}})\sigma_0(N_0 - N_1)$$  \hspace{1cm} (3.1)

$$\frac{dN_1(t)}{dt} = I(t, \tau_{\text{fwhm}})\sigma_0(N_0 - N_1) - \frac{N_1}{T_1}$$  \hspace{1cm} (3.2)

$$\frac{dN_{\nu^*}(t)}{dt} = \frac{N_1}{T_1} - \frac{N_{\nu^*}}{\tau_{\text{eq}}}$$  \hspace{1cm} (3.3)
Figure 3.5. A four-level energy description for intermolecular vibrational relaxation.

\[
\frac{dN_{v'}(t)}{dt} = \frac{N_{v'}}{\tau_{eq}}
\]  

(3.4)

where,

\[
\frac{dN_x(t)}{dt} = \text{the rate of population change in level } x \text{ at time, } t
\]

\[
I(t, \tau_{\text{fwhm}}) = \text{the Gaussian pump pulse with a certain pulse duration, } \tau_{\text{fwhm}}
\]

\[
\sigma_0 = \text{is the absorption cross-section for the } 0 \rightarrow 1 \text{ transition,}
\]

We know that the SFG intensity is proportional to the square of the population difference between the ground \((N_0)\) and the excited vibrational state \((N_1)\). Therefore,

\[
I_{\text{SFG}} \propto (N_0 - N_1)^2
\]  

(3.5)

At room temperature the thermal excitation of the vibrational excited state is very low, so that, \(N_1 \sim 0\). If we define \(\Delta N\) as the population that is transferred from the ground to the excited state by the pump pulse, then \(N_0 \rightarrow (N_0 - \Delta N)\) and \(N_1 \rightarrow \Delta N\), so that:

\[
I_{\text{SFG}} \propto (N_0 - 2\Delta N)^2 = N_0^2 - 4N_0\Delta N + 4(\Delta N)^2
\]  

(3.6)

This demonstrates that the technique is relatively sensitive to population changes, as the differential signal is dominated by the second term, which is proportional to 4 times the population transfer. The third term is quadratic in the population difference and can generally be neglected, since the degree of pump-induced population transfer is generally small. The pump-probe differential TR-SFG signal can then be approximated as:
where Δn is the normalized excited state population and ΔI_{SFG} the differential TR-SFG signal. Considering the populations in all four levels of the 4-level system, the effective, time-dependent susceptibility $\chi^{(2)}_{\text{eff}}$ reads:

$$\chi^{(2)}_{\text{eff}} = [N_0(t) - N_1(t)]\chi_0 + N_{v^*}(t)\chi_{v^*} + N_{v'}(t)\chi_{v'}$$

(3.9)

where the time dependence is contained in the time-dependence of the occupation of the different levels, each with their own SFG activity $\chi_x$.

Note that the differential TR-SFG signal ($\Delta I_{SFG}$) is then proportional to the population difference $\Delta N$, between the ground and excited state. The time constant reflecting population decay in the experiments is $T_1$. The two time constants obtained from the four level model describe the vibrational relaxation to the intermediate state ($T_1$) and the thermalization process ($\tau_{eq}$). Such dynamics are reminiscent of observations for bulk water [130,132] and observations for water at the water-silica interface [87]. The TR-SFG data can be described very well using $T_1=190$ fs obtained from bulk water measurements [130] and a $\tau_{eq}=400 \pm 100$ fs (solid lines in figure 3.4). We found no evidence for a frequency dependence of $T_1$, in analogy with the recent hole burning experiments of water at the water/silica interface [87].

Moreover, we also performed polarization-resolved pump-probe experiments whereby the pump polarization was altered between P and S polarizations, and the pump-probe signal was acquired at all delay times as in the TR-SFG transients. From the data presented in figure 3.6, it is apparent that within the time resolution of the experiment, pumping with either horizontal (S-) or vertical (P-) polarized light results in the same efficiency of excitation of the surface molecules. This randomization of the excitation polarization is the first clear and direct indication of a very fast energy transfer between the isotropic bulk molecules and the surface molecules: although we selectively probe the outermost few molecular layers of water molecules, the excitation depth is determined by the absorption length of IR light in water (a few $\mu$m). A large reservoir of isotropic excitations is therefore present right below the surface, which exchanges rapidly with excitations at the surface. Further evidence for ultrafast energy exchange with the bulk comes from the observed timescales as noted earlier, which correspond very well to the timescales observed in bulk water. Hence, it is clear that the vibrational dynamics of the hydrogen-bonded water at the surface are dominated by ultrafast vibrational energy transfer processes. For bulk water, the fast spectral diffusion has been attributed to extremely fast Förster energy transfer [132]; the same mechanism is apparently operational at the water-air interface. The cartoon shown in figure 3.7 depicts the Förster energy transfer-type relaxation mechanism.

This also explains the similarity between the dynamics at the water-air interface and those at
the hydrophilic and hydrophobic silica/water interface recently reported using SFG in total internal reflection (TIR) geometry [87]. For the latter interface, McGuire *et al.* reported somewhat similar dynamics, with $T_1=300$ fs and $\tau_{eq}=700$ fs. Although the rigid silica surface (required for TIR-SFG) has been shown to induce order in the interfacial water compared to water at the water/air interface [107], the effect of the increased order on the vibrational dynamics is limited due to the ultrafast energy transfer processes that dominate the observed relaxation behaviour. Future experiments with isotopically diluted water to suppress the energy transfer will enable answering the question to what extent the vibrational dynamics at the surface are intrinsically different from those in bulk.

**A Note about Coherent Artifacts:** It has been demonstrated that coherent artifacts may contribute to a pump-probe signal [133]. This can result in a change in the SFG signal unrelated to the vibrational dynamics. These artifacts should be more pronounced when the pump and probe IR polarizations are parallel. When comparing results for orthogonal and parallel pump and probe polarizations (as shown for $\nu_{pump} = 3300$ cm$^{-1}$ in figure 3.6), the results are very similar. Since coherent artifacts are expected to be much larger in the situation of parallel polarization, the resemblance of the two data sets indicate that the data represent the true dynamics and is not influenced

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**Figure 3.6.** P- and S-pump dependence on TR-SFG at 3300 cm$^{-1}$
Figure 3.7. Cartoon depicting Förster-type intermolecular energy transfer. After excitation of the O-H oscillator, a very fast Förster-type energy transfer randomizes the excitation energy and polarization; subsequently relaxing to an intermediate state ($v^*$) and finally to a thermally equilibrated state ($v'$).

by coherent artifacts. This check was performed for all frequencies. A second argument against coherent artifacts is the observation that the first minimum in the signal (corresponding to the maximum population of the excited vibrational state) is always found at positive delay times. This is most clearly visible in the data for 3500 and 3400 cm$^{-1}$. This clearly indicates that the decrease of the signal is due to population being transferred to the excited state.

3.4 Conclusions

In conclusion, we have demonstrated ultrafast energy transfer between surface and bulk water at the air-water interface using a novel pump-probe TR-SFG experiment. Although the spectral response differs appreciably for bulk and surface water, the O-H stretch vibrational dynamics at the surface are indistinguishable from that in the bulk, in the 3200-3500 cm$^{-1}$ hydrogen-bonded region.