

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

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We report a femtosecond time-resolved study of water at the neat water-air interface. The O-H stretch vibrational lifetime of hydrogen-bonded interfacial water is measured using surface-specific 4th-order nonlinear optical spectroscopy with femtosecond infrared pulses. 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.

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Interfacial water plays an important role in many biological, chemical, and physical processes (see, e.g., [1–3] and references therein). 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 [4].

Nonlinear optical techniques, such as second harmonic generation and sum frequency generation (SFG) [5,6] spectroscopy are generally surface specific and have been shown to be selectively sensitive to the outermost few monolayers of water molecules [7–9]. SFG is a particularly powerful tool, as it allows the vibrations of surface water to be probed, which are known to be sensitive reporters of the hydrogen-bonding water environment. Indeed, the application of SFG to investigate water at the water-air interface has revealed important new insights in the water interfacial structure [10,11] and orientation [12]. 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,” nonhydrogen-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.

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 nonlinear infrared spectroscopy (see, e.g., [13–17]). The motivation for much of this work lies in the realization that the ultrafast femtosecond behavior of water molecules contains additional information on the structural and dynamic behavior of this important liquid. Nonlinear spectroscopy has been shown to be extremely useful in unraveling different aspects of water dynamics,

including 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 [18–20].

Here, we present an extension of these ultrafast techniques applied to water at the air/water interface. Our approach is based on femtosecond vibrational SFG, which 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. The addition of a third femtosecond laser pulse to this scheme allows the vibrational excitation of the water molecules, which changes the original SFG intensity [6,21–24]. 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 allows one to selectively probe the lifetime dynamics (T_1) of the O-H stretch vibration and provides new insights in the structure and dynamics of water at the neat water-air interface.

Two independent setups are used in our study: one for static spectroscopic studies and one for time-resolved studies. In the static experiments, D_2O is studied, rather than H_2O , for reasons of limited tunability of the setup. For the time-resolved experiments, pure H_2O was employed.

In the static SFG experiment, the SFG signal is spectrally dispersed and detected using an intensified CCD (Roper Scientific). The resolution is limited by the bandwidth of the VIS beam and is typically 10 cm^{-1} . The static SFG spectrum of the deuterated water-air interface in the O-D stretch region is depicted in the inset of Fig. 1. Except for the shift in frequency due to the mass difference, the D_2O spectrum is equivalent to previous reports of SFG spectra of H_2O [10,11]. The frequency axis is therefore

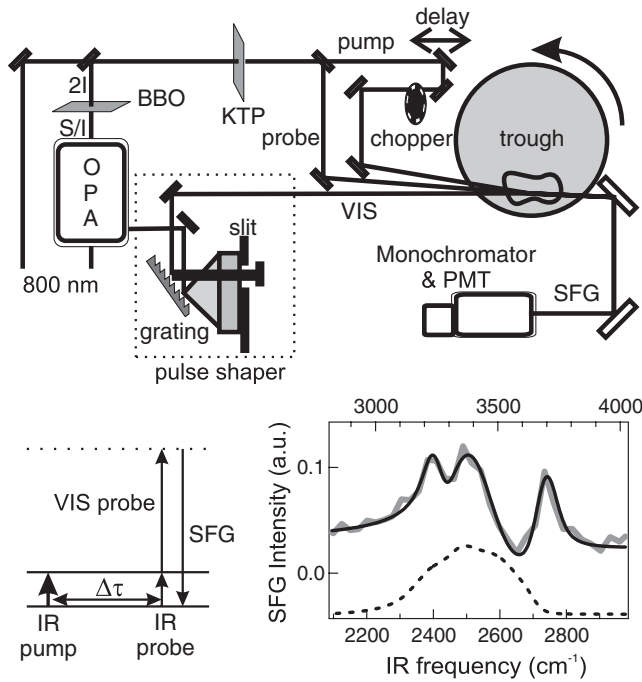


FIG. 1. Upper panel: A schematic overview of the setup explained in the text. Lower panel: the TRSFG energy diagram (left) and the static SFG spectrum (gray line) of deuterated water, D_2O , with fit (black line) along with the linear infrared absorption spectrum of D_2O (dashed line, offset for clarity).

readily converted from the O-D to the O-H range (upper abscissa in the figure). The spectrum is interpreted in terms of the well-known D_2O (H_2O) resonances centered at ~ 2400 and ~ 2500 cm^{-1} (~ 3200 and ~ 3400 cm^{-1}), which have been proposed to be due to the O-D (O-H) stretch vibration of strongly hydrogen-bonded (“icelike”) water, and weakly hydrogen-bonded water, respectively. The resonance at $\nu = 2730$ (3690) cm^{-1} is due to the dangling O-D (O-H) bond. The solid line is a fit to the data assuming two inhomogeneously broadened resonances and a single Lorentzian for the dangling O-D vibration, and agrees well with previous reports [25]. Figure 1 also shows the linear infrared absorption spectrum of D_2O , which reveals that the response of the H-bonded part of the surface spectrum is markedly different from that of the bulk. The question that immediately rises is whether the dynamics are also different.

The experimental scheme for the time-resolved measurements on nondeuterated H_2O is schematically depicted in Fig. 1. Distilled Millipore filtered water (18 M Ω cm resistivity) of pH 7 is used in a homemade Teflon trough. The trough is rotated at 4 rpm to suppress the effect of sample heating. Tunable, intense IR pulses are generated using a two-step method [19]: First, 1 out of 3 mJ of 800 nm Ti:sapphire light (100 fs pulse duration, 1 kHz repetition rate) is used to pump a commercial OPG/OPA (TOPAS, light conversion). In the second step, the idler beam at ~ 2.2 μm is doubled in a β barium borate crystal and subsequently mixed with the remaining 2 mJ of the

Ti:sapphire fundamental to generate the difference frequency in a 3 mm thick $KTiOP_4$ crystal resulting in 120 fs IR pulses with an energy of ~ 50 μJ tunable around ~ 3000 nm, with a duration of ~ 100 fs. Next, the infrared beam was split into the pump and IR probe (intensity ratio 2.5:1). The visible pulse originates from the residual 800 nm light of the OPA, after passing through a homemade pulse shaper.

The infrared pump, the infrared probe, and the visible probe were focused and intersected at the air-water interface and the SFG signal was detected in reflection. The IR probe and VIS probe beams lie in a vertical plane and have incident angles of 46° and 50° , respectively, with respect to the surface normal. The IR pump is incident at an angle of 10° with respect to the plane of the probe beams and 56° with respect to the surface normal. The focal sizes of the IR pump, IR probe, and VIS probe were 150 μm , 100 μm , and 100 μm , respectively. The polarizations of all beams could be rotated independently using $\lambda/2$ plates. The pump pulse was variably delayed using a mechanical delay line. The SFG signal was filtered using pass filters and a monochromator and was detected with a photo multiplier tube (R9910, Hamamatsu). Because the SFG signal is less than 0.1 detected photon per laser shot, typically 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.

The results of the pump-probe measurements of the relaxation of O-H stretching modes of water after pumping at frequencies $\nu_{pump} = 3200, 3300, 3400,$ and 3500 cm^{-1} , are depicted in Fig. 2. The dynamics of the dangling O-H are currently not within the capabilities of the setup. Also shown in Fig. 2 is the third-order IR + IR + VIS (IIV) SFG signal, which is used to determine time zero ($\Delta t = 0$) and the experimental 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 anharmonicity of the vibration of ~ 300 cm^{-1} [26], SFG generated from the excited state ($\nu = 1 \rightarrow 2$) 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 calculated pump-induced temperature increase in the focus is approximately 15 K.

It has been demonstrated that coherent artifacts may contribute to the signal [27]. This can result in a change in the SFG signal unrelated to the vibrational dynamics.

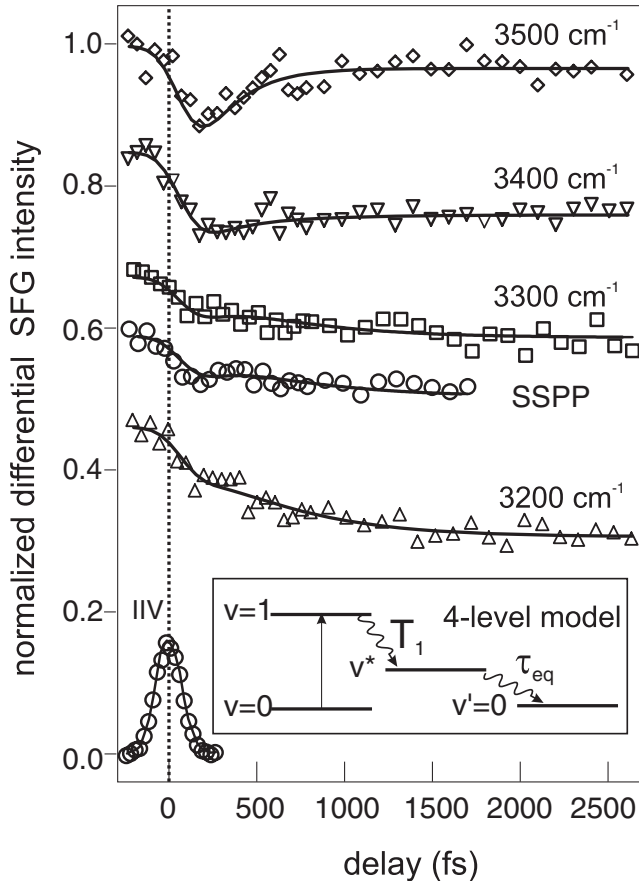


FIG. 2. Time-resolved SFG data for interfacial water for $\nu_{\text{pump}} = 3200, 3300, 3400,$ and 3500 cm^{-1} (traces are offset for clarity). Polarizations of the SFG, VIS probe, IR probe and IR pump were $S, S, P,$ and $S,$ except for the additional trace at $\nu_{\text{pump}} = 3300 \text{ cm}^{-1}$ for which pump and probe polarization are parallel. The solid line is a calculation based on a four-level system depicted in the inset, explained in the text. The lower trace is the third-order IR + IR + VIS SFG signal (shown for $\nu = 3300 \text{ cm}^{-1}$). The inset shows the four-level system used to model the data.

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 $\nu_{\text{pump}} = 3300 \text{ cm}^{-1}$ in Fig. 2), 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 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.

In the data in Fig. 2, two time scales seem apparent: a fast (~ 100 fs) relaxation time corresponding to the recovery of the pump-induced bleach signal (most clearly evident at $\nu = 3500 \text{ cm}^{-1}$), and the slower (~ 500 fs) time scale by which the final SFG level is reached (most apparent at $\nu = 3200 \text{ cm}^{-1}$).

Such dynamics are reminiscent of observations for bulk water [26,28] and observations for water at the water-silica interface [24]. In bulk studies it was shown that vibrational relaxation from $\nu = 1$ to $\nu = 0$ occurs through an intermediate state ν^* , which is a mixed state of the ground state and other modes that accept energy from the $\nu = 1$ state [28]. From ν^* relaxation then occurs to the “hot” ground state, which is long-lived and has optical properties different from the original ground state, caused by an increase in sample temperature. This explains the observed long-time signal offset in the data presented here. 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 (ν^*), before reaching the new hot ground state ($\nu' = 0$).

Indeed, the four-level system characterizing such a system (see inset in Fig. 2) provides a very good description of the experimental data. We calculate the population in each level by solving the coupled differential equations and compute the signal from the ground and hot ground state. Note that the signal is proportional to the square of the population difference between the ground and excited state. Accordingly, the time constant reflecting population decay in the experiments is 2^*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 (τ_{eq}).

The data can be described very well using $T_1 = 190$ fs obtained from bulk water measurements [26] and a $\tau_{\text{eq}} = 400 \pm 100$ fs (solid lines in Fig. 2). We find no evidence for a frequency dependence of T_1 , in analogy to recent hole burning experiments of water at the water-silica interface [24]. For bulk water, the fast spectral diffusion was attributed to extremely fast Förster energy transfer [28]; the same mechanism is apparently operational at the water-air interface. The long-time offset of the normalized SFG signal goes from ~ 1 at $\nu_{\text{pump}} = 3500 \text{ cm}^{-1}$ to much smaller than 1 at $\nu_{\text{pump}} = 3200 \text{ cm}^{-1}$, in accordance with a blueshift of the spectrum due the pump-induced heating that results in a weaker hydrogen-bonded network.

For the water-air interface, there is previous evidence from static SFG data that the hydrogen-bonding network at the surface is similar to that in bulk [29]. At the same time, it is known that the orientation of the water molecules at the surface is not isotropic [10,11,29], and the surface and bulk spectra clearly differ (Fig. 1). From the data presented here it is apparent that within the time resolution of the experiment, pumping with either horizontal or vertical polarized light results in the same efficiency of excitation of the surface molecules. This is the first clear indication of

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 μm). 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 time scales, which correspond very well to the time scales observed in bulk water. Hence, it is clear that the hydrogen-bonded network vibrational dynamics at the surface are dominated by ultrafast vibrational energy transfer processes.

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 [24]. For the latter interface, McGuire *et al.* reported somewhat faster dynamics, with $2^*T_1 = 300$ fs and $2^*\tau_{\text{eq}} = 700$ 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 [12], the effect of the increased order on the vibrational dynamics is limited due to the ultrafast energy transfer processes that dominate the observed relaxation behavior. 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.

In conclusion, we have demonstrated ultrafast energy transfer between surface and bulk water at the air-water interface. 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.

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