



*Ultrafast Dynamics of Interfacial Water*

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## Summary

In this thesis, we focus on the structure, structural dynamics, and the energy relaxation of interfacial water molecules at the air/water interface using time-resolved sum-frequency generation (TR-SFG) spectroscopy. Aqueous interfaces exist everywhere and play important roles in our daily life: The gas/water interface covers 70% of our planet; oil on top of water is a common example of liquid/water interface; and solid/water interface like electrodes in electrolytes can be seen in batteries. Insights into the mechanism of the chemical reactions and physical processes at aqueous interfaces can be obtained through studies of the molecular structures and dynamics of these interfaces. Among these interfaces, the air/water interface is one of the simplest aqueous interfaces as well as a model hydrophobic interface.

A noninvasive way of investigating the molecular properties of the air/water interface is to use surface-sensitive vibrational spectroscopy, which selectively probes the net non-zero transition dipole moment along the surface normal, due to symmetry breaking at the interface. Thanks to the high sensitivity of the vibrational frequency to the interactions with the surrounding molecules, the vibrational spectra reflect the local molecular structures in condensed phases. For instance, the water OH stretching mode frequency is lowered with increasing hydrogen bond strength, so that the frequency and lineshape of this mode can be used as a reporter for the microscopic structures around the water molecules. The remaining challenge is then to obtain the vibrational spectrum of specifically those water molecules located at the interface.

The surface-sensitive vibrational spectroscopy we propose here is sum-frequency generation (SFG) spectroscopy. As described in chapter 1, the SFG spectroscopy is an even-

order nonlinear spectroscopy, whose selection rules result in the suppression of the signal from isotropic media such as the bulk water. In SFG spectroscopy, an infrared (IR) and a visible (VIS) beam are overlap temporarily and spatially at the interface to generate a signal whose frequency is the sum of the IR and VIS pulse frequencies. If the IR frequency is resonant with the molecular vibrations, the SFG signal will be strongly enhanced, thereby providing the vibrational spectrum of specifically the surface molecules. Thus, the SFG spectra provide us the information on the interfacial water structures, through the central frequencies and linewidths of the vibrational transitions.

The linewidth of the O-H stretch spectra in principle has two contributions: Firstly, quasi-static differences in the local environment of the OH groups can cause inhomogeneous broadening. Secondly, homogeneous broadening effects arise from dynamic, time-dependent changes in the instantaneous vibrational frequency due to several possible processes: structural rearrangements leads to variations in hydrogen bonding strength; anharmonic coupling to thermally excited low frequency modes (such as the hydrogen bond mode); intermolecular dipole-dipole coupling, leading to near-resonant energy transfer, and finally the finite energy lifetime of the vibration contributes to the linewidth. It is not possible to determine the magnitude of these separate contributions to the linewidth using conventional one-dimensional SFG spectroscopy. In contrast, higher-order, time-resolved techniques are capable of distinguishing homogeneous broadening from inhomogeneous broadening. By exciting the interfacial molecules with a resonant IR pump pulse and probe the population decay with the SFG probe signal, we can reveal the lifetimes of these molecular vibrations. The polarization-resolved technique enables us to extract the reorientational motion (i.e. structural dynamics) and vibrational relaxation of water molecules, while the two-dimensional (2D) technique shows the

spectral diffusion and the energy coupling between different modes. The experimental setups of these techniques are presented in chapter 2.

In chapter 3 we investigate the reorientational motion of non-hydrogen-bonded ‘free’ (also called ‘dangling’) OH groups that point towards the vapor phase. Vibrational excitation of the dangling OH bonds along a specific polarization axis induces a transient anisotropy of excited OH groups on the surface. The decay of this anisotropy arises from both the reorientation and vibrational relaxation of vibrationally excited free OH groups. By using time- and polarization-resolved SFG spectroscopy with the help of the MD simulation, we found that the in-plane diffusivity is  $D_\phi = 0.32 \text{ rad}^2/\text{ps}$ , while the out-of-plane diffusivity  $D_\theta = 0.36 \text{ rad}^2/\text{ps}$ , which is  $\sim 3$  times faster than the H-bonded OH groups in the bulk water. Moreover, in contrast to the bulk, where a jump-like mechanism dictates reorientation, the reorientation dynamics of the interfacial water occurs in a largely diffusive manner. It is also shown that the vibrational relaxation of the free OH groups occurs with a time constant of  $\sim 800 \text{ fs}$ , which is slower than the H-bonded OH groups in the bulk water.

The mechanism of this vibrational relaxation has been studied in chapter 4. The dissipation of the excess energy of a free OH can be through the reorientation of the free OH into the bulk phase, thereby forming a hydrogen bond (REOR), or through intramolecular energy coupling from the free OH to the hydrogen OH within the same water molecules (IET). In both cases, the resulting hydrogen-bonded OH groups can release its excess vibrational energy quickly. IR-pump/SFG-probe measurements of both the free OH of  $\text{H}_2\text{O}$  at the air/ $\text{H}_2\text{O}$  interface and of HOD at the air/ $\text{H}_2\text{O}:\text{D}_2\text{O}$  mixture interface allow us to clarify that REOR contributes to one third of this energy relaxation while two thirds is the result of IET. Two-color time-resolved experiments allow us to determine the timescales of the forward (from free OH to H-bonded OH)

and backward (from H-bonded OH to free OH) processes of IET and REOR. These properties typically occur on a  $\sim 1$  ps timescale. In this chapter we also unravel the factors that control the spectral line shape of the free OH groups at the air/water interface.

Interfacial water consists of the dangling OH groups as well as the H-bonded OH groups. The H-bonded OH groups show an infrared spectral response similar to that of bulk water. Although these OH groups exhibit a similar spectral response as in the bulk water, their structure and dynamics are distinctly different. This is demonstrated in chapter 5, where we study the spectral diffusion and vibration relaxation of the H-bonded OH groups of hydrogen-bonded interfacial water molecules using 2D phase-sensitive SFG spectroscopy. The measured 2D spectra reveal that the spectral diffusion of the strongly H-bonded OH groups ( $< 3400$   $\text{cm}^{-1}$ ) occurs on a  $\sim 280$  fs time scale, approximately 1.5 times slower than in bulk water. Weakly H-bonded OH groups contributing the spectra at  $3500$   $\text{cm}^{-1}$  (part of which are the hydrogen-bonded parts of the water molecules that have an OH group sticking out) show slower dynamics due to the decoupling of the intra-/intermolecular energy transfer. These results clearly demonstrate that the interruption of the hydrogen bond at the water-vapor interface slows down the water dynamics in contrast with bulk water.

In chapter 6 we employ TR-SFG experiments to survey the propagation of the shock wave generated at the air/water interface into the bulk phase. We study different air/aqueous sodium halide solutions interfaces that exhibit different surface activities of the halide ions. The SFG field radiated away from the air/liquid interface, interferes with the field transmitted into the bulk, which is partially reflected from the IR pump-induced shock wave front. Because the effective path length of the reflected beam increases with time, the interference of the optical responses leads to time-dependent sinusoidal oscillations of the SFG signals, whose periods

provide information on the velocity of the propagation of the shock waves in the liquid. Our results show that the acoustic velocities of different sodium halide solutions are similar, although the phase shift of the oscillations are different. The different phase shift of the oscillation is attributed to originate from the electric-quadrupole and magnetic-dipole contributions of the bulk phase of different sodium halide solutions.

In summary, we survey the dynamics of the interfacial water at the air/water interface. We reveal that the ultrafast vibrational energy transfer dynamics and spectral diffusion of the OH stretch mode at the interface differs from those in the bulk significantly; the rotational motion is 3 times faster than in the bulk and energy relaxation is dominated by the rotational dynamics as well as the vibrational energy transfer from the free OH group to the H-bonded OH groups of a water molecule with the free OH group. These insights can only be obtained by conducting the time-resolved surface-specific spectroscopic studies presented in this thesis.