Ultrafast dynamics of interfacial water
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Chapter 6
Probing the Generation and Propagation of Shock Waves at the Air/Liquid Interface Using Sum Frequency Generation Spectroscopy

In the previous chapters, we employed time-resolved SFG experiments to survey the microscopic structure and ultrafast dynamics of water. The IR pump pulses were used to excite the molecular vibrations and the probe pulse was used to detect the response of the system to this perturbation. On the other hand, pump pulses can also be used to excite a quasi-instantaneous decrease in water density through a temperature jump, resulting in a shockwave that can propagate into the bulk. Here, we investigate the generation and propagation of shock waves at the air-aqueous solution interface using time-resolved SFG spectroscopy. 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 leads to time-dependent sinusoidal oscillations of the SFG signals. The oscillation periods of the SFG signals provide information on the sound velocity in the liquid. Interestingly, depending on the details of the aqueous solution under study, we observe large variations in the phase difference between the directly reflected SFG light and that reflected from the wave front. These different phase shifts are tentatively attributed to the different interfacial water structures which originate from different surface activities of halide ions at the interface.

6.1 Introduction
Shock waves are fast mechanical transients generated by sudden compression of the material, causing a weak leading edge followed by a stronger, faster trailing edge, which constitutes the shock front [117]. The investigation of shock waves provides information on the hydrodynamic properties of the bulk medium such as the flow of pressure, temperature, and density. Pulsed lasers provide not only a simple means to initiate the shock wave at a well-defined moment, they also allow one to control its momentum and to synchronize the shock wave with a wide variety of optical and electronic diagnostics, enabling, e.g. the detailed
study of the mechanism of shock wave generation. There are several mechanisms by which shock waves can be generated using laser pulses [118], but in all cases the surface plays a pivotal role. Hence the chemical and physical properties of the surface in steady state and during the generation and evolution of the shock wave are particularly important. Owing to its surface specificity, femtosecond time resolution, and molecular sensitivity, SFG spectroscopy [13] has proven to be a very useful and valuable tool for detecting the molecular structures at interfaces during shock wave generation. For example, it has been used to demonstrate that hydrocarbon chains at a metal surface tilt as a result of shock waves being launched from that surface [119].

In addition to the purpose of investigating the effects of the shock wave on the orientation of molecules, time-resolved SFG has been used to track the vibrational energy relaxation at interfaces, where intense pulses are employed to excite a significant fraction (typically ~ 10%) of specific molecular vibrations at the interface, to follow interfacial vibrational relaxation in real time, as shown in chapters 3, 4, and 5. The vibrational relaxation is then monitored by (weaker) probe pulses, which are generally sensitive to the ground state population of the molecular vibrations. Since the SFG signal typically originates specifically from surface molecules, SFG spectroscopy is frequently used to probe the vibrational dynamics in the outermost molecular layer of the bulk material [23,24,26,84]. Clearly, if the lifetimes of the relevant vibrational states are short-lived (which is typically the case for condensed phase materials), the excess vibrational energy will be converted to low-frequency vibrations and ultimately heat will be released at the interface on very short timescales, which is precisely the requirement for launching a shock wave. Although the shock wave can create an asymmetric dielectric environment, and SFG is sensitive to broken symmetry, it has not yet been determined how the generation of the shock wave may affect the time-dependent SFG signals. Here, we investigate the generation and propagation of shock waves using IR-pump/SFG-probe spectroscopy at different air-aqueous sodium halide solutions interfaces. The surface activities of the different halide ions and their effect on the orientation of interfacial water molecules are known to depend on the size and polarizability of the halide ion. The modulation of the microscopic structure of the water interface by ions has been addressed previously: Theoretically, MD simulations have shown that larger anions with larger polarizabilities are enriched at the air-water interface [120]. Experimentally, SFG spectra show that large anions cause significant distortion of the surface hydrogen-bonding network [121]. However it is unclear whether, and to what extent, these different surface
activities of ions will affect the generation and detection of shock waves from the different aqueous interfaces.

In this chapter, we discuss the experimental observation of shock waves launched at aqueous surfaces, detected by large time-dependent, oscillatory variations in the SFG signals generated from these interfaces following vibrational excitation. These oscillations are characterized by their amplitude, phase and oscillation time. The phase is found to be a function of the solute, and is presumably related to the different interfacial water structures for different solutes; the period of the oscillation of the IR-pump/SFG-probe signals is determined by the speed with which the shock wave propagates from the surface into the bulk, which in turn is determined by the bulk density [122,123].

6.2 Experimental section
The one-color TR-SFG experimental setup is described in detail in chapter 2, section 2.2.2 and 2.2.3. The samples were NaI, NaBr, NaCl, and NaF dissolved in distilled Millipore filtered water (18MΩ-cm resistivity) or D2O (Cambridge Isotope Laboratories, Inc., 99.93% purity, used without further purification) with a mole fraction of 0.036x (corresponding to a molarity of 2.07M) for NaI, NaBr, and NaCl and 0.015x (0.84M) for NaF. The samples were placed in a homemade Teflon trough which was rotated at 8 rpm to reduce cumulative heating. The IR-pump/SFG-probe spectra were recorded under p/ssp (IR pump/SFG, VIS probe, IR probe) polarization conditions. The IR pump pulse was variably delayed with respect to the SFG probe signal using a mechanical delay line. The normalized IR-pump/SFG-probe is defined as the ratio between the integrated intensities with and without the pump.

6.3 Results and discussion
To investigate the generation and propagation of the shock wave from the surface into the bulk phase, IR-pump/SFG-probe experiments with different sodium halide solutions have been performed. The results are shown in Fig. 6.1, from pure H2O, NaF, NaCl, NaBr, to NaI solution, in the order of increasing size of halide anions. In the experiments, the O-H stretch vibrations of water are excited at 3350 cm⁻¹ with an intense excitation pulse, and the effect of the excitation is probed with the time-delayed SFG probe pair, probing the O-H stretch vibrations, also at 3350 cm⁻¹. On very short time scales (within 2 ps), the normalized SFG
FIG. 6.1 IR-pump/SFG-probe data for hydrogen-bonded OH at air/water interface for various sodium halide solutions, from pure H$_2$O, NaF, NaCl, NaBr, to NaI solution, in the order of the size of halide anions. The IR pump and IR probe are both at 3350 cm$^{-1}$. The solid lines are the fitting curves with a damped sinusoidal oscillation model. Data are offset by multiples of 0.5 for clarity.

TABLE 6.1 The period of oscillation ($\tau$) and the phase shift ($\Delta \phi$) of IR-pump/SFG-probe data for different sodium halide solutes in H$_2$O solvents. The phase shift is defined relative to the negative sine wave.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Period of oscillation $\tau$ (ps)</th>
<th>Phase shift $\Delta \phi$ (rad)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.036x-NaI</td>
<td>179±1</td>
<td>0.18±0.02</td>
</tr>
<tr>
<td>0.036x-NaBr</td>
<td>174±1</td>
<td>-0.45±0.03</td>
</tr>
<tr>
<td>0.036x-NaCl</td>
<td>164±2</td>
<td>1.96±0.05</td>
</tr>
<tr>
<td>0.015x-NaF</td>
<td>174±4</td>
<td>2.05±0.09</td>
</tr>
<tr>
<td>Pure H$_2$O</td>
<td>182±3</td>
<td>-0.36±0.06</td>
</tr>
</tbody>
</table>

signals show transient bleaches, due to the excitation of the population from the ground to the first excited state. After 10 ps, these data show oscillatory features which are damped on a timescale of several nanoseconds. The solid traces are fitting curves with a damped sinusoidal oscillation model, i.e. $I(t) = Ae^{-t/T}\sin(t\tau+\Delta \phi)$, where $T$ is a time constant of the exponential decay function, $\tau$ is the oscillation period, $\Delta \phi$ is the phase shift related to the negative sine wave, and $A$ is the offset of the signal. The fit parameters are listed in Table 6.1. The oscillation periods $\tau$ of these traces are nearly the same (~ 175 ps), which are not sensitive to
the halide ion species, while the phase shift differs from solution to solution. The amplitude of the oscillation increases as the size of the anions increases. This is attributed to the fact that NaBr and NaI aqueous solutions have strong enrichment of halide anions at the interfaces compared to the bulk, causing significant amount of charge to be present at the surface with a corresponding distortion of the H-bonding network and an enhancement of the SFG signals, while the interfacial water structures for NaF and NaCl aqueous solutions are roughly the same as the air-water interface [121]. To elucidate the origin of the observed oscillations, we investigated several properties of these oscillatory SFG signals.

Figure 6.2(a) shows the result of a power-dependent experiment, where Fig. 6.2(b) displays the amplitude of the oscillation verses IR pump power. As the IR pump energy is reduced from 21 through 14 to 7 μJ per pulse, the amplitudes of the oscillations decrease proportionally, while the periods remain unchanged. This indicates that the density change of the shock wave front, which is roughly proportional to the refractive index change [124], is proportional to the incident IR pump power. However, as we changed the concentration of NaI solutions from 0.012x, 0.025x, to 0.036x, the properties of the oscillations remain unchanged, both for the amplitudes and the periods, which implies that at these ion concentrations, the surface is saturated with halide ions (Fig. 6.3).

![Graphs showing pump-probe data and amplitude of oscillation vs IR pump power.](image)

**FIG. 6.2** (a) Pump-probe data with pump power of 21, 14, and 7 μJ, respectively. (b) The amplitudes of the oscillations versus the IR pump power. The amplitude of the oscillation is proportional to the pump power.

The oscillation period is also influenced by the incident angle of the IR probe and VIS probe beams. Figure 6.4 shows the IR-pump/SFG-probe traces of 0.036x NaI solution with two different incident angles for the probe pulse pair. The red data are obtained with incident angles of IR probe = 37.0° and VIS probe = 42.9°, which leads to a reflective angle of 41.7° and a refractive angle of 30.1° of the SFG signal. The blue data are obtained with the incident
angles of IR probe = 44.6° and VIS probe = 50.4°, which leads to a reflective angle of 49.2° and a refractive angle of 34.8° of the SFG signal. The oscillation period for the red trace is 175±1 ps, and for the blue one is 183±1 ps. The ratio of the periods of the two traces (0.956) is close to the ratio of sec θ (0.949), where θ is the refractive angle of the SFG signal.

FIG. 6.3 Pump-probe data with different concentrations of NaI solution. The amplitude and the oscillation period are roughly the same for 0.036x, 0.024x, and 0.012x NaI solutions.

FIG. 6.4 Pump-probe data with different incident angles of IR/VIS probe. The period of the oscillation is proportional to sec θ, where θ is the refractive angle of the SFG signal.

The oscillation is also affected by the properties of the solvent. Figure 6.5 shows the IR-pump/SFG-probe traces of 0.036x NaI solution in H_2O (red curve) and D_2O (blue curve). For NaI in H_2O solution, the IR pump and probe are both at 3350 cm\(^{-1}\), which leads to a 634.6
nm SFG signal. For NaI in D$_2$O solution, the IR pump and probe are both at 2500 cm$^{-1}$, which generates the SFG signal at 670.5 nm. The acoustic velocities are 1498 m/s for H$_2$O and 1400 m/s for D$_2$O, while the oscillation periods are 177±1 ps for H$_2$O (denoted by red curve) and 193±2 ps for D$_2$O (denoted by blue curves). This indicates that the oscillation period is roughly proportional to the probe SFG wavelength over the acoustic velocity of the liquid.

![Normalized SFG signal graph](image)

**FIG. 6.5** Pump-probe data for NaI in H$_2$O and D$_2$O solvents. The period of the oscillation is proportional to the acoustic velocity of the solution.

As shown above, the amplitude of the oscillation is influenced by the intensity of the pump pulse, while the period is affected by the incident angle of the incoming beam, the wavelength of the SFG signal, and the sound velocity of the aqueous solutions. We conclude from these properties that the oscillation of the IR-pump/SFG-probe signal originates from the following mechanism. As shown in Figure 6.6, the IR pump pulse ramps up, heats the solution and creates a gradual shock front. The compression wave front propagates into the bulk solution and travels with acoustic velocity $v$. The VIS/IR probe pulses generate the probe SFG signal at the air/solution interface. Due to the refractive index mismatch, part of the SFG signal directly reflects from the surface (d-SFG) while the rest is transmitted into the bulk phase. The transmitted SFG signal is partially reflected from the compression pulse wave front (r-SFG) due to the density difference between the wave front and the surrounding environment. The oscillations in the SFG signal intensity can therefore be attributed to the interference of two SFG signals: the SFG signal directly originating from the interface (d-
SFG) and the one reflected from the compression wave (r-SFG). While theoretically an SFG signal could also be generated at the wavefront interface, this mechanism can be excluded, since the penetration depth of the infrared radiation into the bulk is very limited; in that case much stronger damping would be observed.

The optical path difference between d-SFG and r-SFG is $2Ln(\omega)\cos\theta$, where $L$ is the distance between the air/water interface and the shock wave front, $n(\omega)$ is the refractive index of water at frequency $\omega$, and $\theta$ is the angle of refraction of the SFG signal. $L= v\times t$, where $v$ is the acoustic velocity of the solution and $t$ is the time interval after the shock wave is launched. During one period of the acoustic oscillation, the optical path change of the probe SFG signal reflected by the sound pulse is equal to the wavelength of the probe SFG signal, so $\tau=\lambda/2vn\cos\theta$, where $\tau$ is the period of the oscillation signal and $\lambda$ is the wavelength of the SFG signal. With our experimental geometry, where the incident angles of IR probe = 44.6° and VIS probe = 50.4°, which leads to 34.8° of refractive angle of the SFG signal, and the wavelength of IR probe = 3350 cm$^{-1}$ and VIS probe = 806 nm, which leads to the SFG signal of 634.6 nm, and the acoustic velocity and the refractive index of H$_2$O are 1496 m/s and 1.33, respectively, the oscillation period of H$_2$O is calculated to be 194 ps. From Table 6.1 it is apparent that the period of each solution is approximately the same as calculated, while the phase shift differs from solution to solution. This phase shift is due to the initial phase difference between d-SFG and r-SFG at 0 fs, when the shock wave is launched. The NaI, NaBr, and pure water have phase shift around 0 rad, while the NaCl and NaF are around 2 rads. One possible explanation is that due to the higher surface activity of larger halide anions,
the local electric field created by layers of cations and anions is enhanced, and the bulk contribution (electric-quadrupole and magnetic-dipole contributions) is enlarged. Since the reflected and transmitted SFG signals are influenced by the electric-quadrupole and magnetic-dipole contributions [125], this could explain the phase shift differences between solutions.

6.4 Conclusion
We have shown that, with IR-pump/SFG-probe spectroscopy, we can elucidate the generation and propagation of shock waves at the interface. The oscillations of the normalized SFG signals originate from the interference of the reflective SFG signals from the air-liquid interface and the shock wave front. The period of these oscillations are proportional to the sound velocity of the aqueous solution, which is roughly the same for H₂O, NaF, NaCl, NaBr, and NaI solutions. The phase shift of the oscillation is attributed to originate from the electric-quadrupole and magnetic-dipole contributions of the bulk phase.