Ultrafast dynamics of interfacial water
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Chapter 2
Experimental Techniques

In setups employed in conventional sum-frequency generation (SFG) spectroscopy, a visible (VIS) and a frequency-tunable infrared (IR) beam are temporally and spatially overlapped on the sample surface [13,18,38,39]. For water surfaces, when the IR frequency is tuned into resonance with the frequency of the OH stretching mode of water molecules, the SFG signals are strongly, resonantly enhanced. This one-dimensional spectral signal, the SFG intensity as a function of IR frequency, provides us with information on the structure and hydrogen-bonding strength of interfacial water molecules. To understand the structural and energetic dynamics of specifically surface molecules, time-resolved SFG approaches are required [23,24,29,40,41].

Here we present novel setups for IR-pump/SFG-probe time- and polarization-resolved vibration spectroscopy [26] and phase-sensitive time-resolved vibrational spectroscopy. These setups allow for experiments aimed at elucidating the energetic and structural dynamics of specifically interfacial water molecules. In the experiments, interfacial water molecules are excited with an intense IR-pump pulse which is resonant with the molecular O-H stretch vibrations. The excitation of the water molecules and the subsequent relaxation of the excess vibrational energy are monitored by probing the same vibration with an IR/VIS-probe pulse pair, which generates sum-frequency signals from the interface. The reorientational motion and vibrational relaxation of the interfacial water molecules are determined in one-color polarization-resolved SFG spectroscopy, while the vibrational coupling between different modes is determined in two-color SFG spectroscopy. The homogeneity and heterogeneity of interfacial water molecules can be addressed using two-dimensional (2D) time-resolved phase-sensitive SFG spectroscopy.

2.1 Introduction
In this chapter, the experimental setups for time- and polarization-resolved vibrational sum-frequency generation (TPR-SFG) spectroscopy and two-dimensional phase-sensitive time-resolved vibrational sum-frequency generation (2D-PS-SFG) spectroscopy are described in detail. The first section focuses on the one- and two-color experimental setups, the sample part where the SFG signals are generated, and the detection optics and electronics. In the
second section the data analysis is discussed. The setup is built based on reference [32]. The notation of optics and optomechanics in the figures is as follows: B: Beam splitter, DB: Dichroic beam splitter, F: Filter, P: Polarizer, $\lambda/2$: Half-wave plate, L: Lens, TS: translation stage, MTS: Motorized translation stage, C: Chopper, DP: Delay plate, CL: Cylindrical lens, M1: Dielectric mirror for 800 nm, M2: Dielectric mirror for 1100 nm, M3: Gold mirror, M4: Dielectric mirror for SFG signals, and M5: Gold concave mirror with focal length $f = 50$ mm.

2.2 TR-SFG setup

The experimental setups are composed of three different parts; the first part consists of the laser system and the corresponding optical components used to generate the intense IR pump, IR probe, and VIS probe pulses. The second part consists of a rotating trough and a motorized stage to alleviate the effects of the heat generated by the intense IR beam and to compensate evaporation of the samples from which the SFG signals are generated. The last is the detection part which consists of collimated optics, a galvano mirror, and a monochromator with a CCD.

2.2.1 One-color experiments

For one-color experiments, shown in Fig. 2.1, a Ti:sapphire oscillator (Mira 900; Coherent Inc.) pumped by a CW laser (Verdi; Coherent Inc.) is used to seed a regenerative/multipass amplifier (Titan; Quantronix) which is pumped by a high energy (18 W, 100 ns) Nd:YLF laser (DQ-527, Quantronix). The amplifier output is centered at 806 nm with full width half maximum of 12 nm and is 120 fs long. The repetition rate is 1 kHz and the energy is 3.5 mJ/pulse. 1.1 mJ of this pulse energy is used to pump a commercial optical parametric amplification unit (TOPAS; Light Conversion, Vilnius, Lithuania) to produce $\sim$ 300 µJ of signal ($\sim$ 1260 nm) and idler ($\sim$ 2200 nm) fields. The idler field is then frequency-doubled in a $\beta$-barium borate ($\text{BBO} \; 7\times7\times3 \text{ mm}^3, \phi = 90^\circ, \theta = 22.2^\circ$) crystal to generate $\sim$ 30 µJ of $\sim$ 1100 nm pulses. This doubled idler beam is then mixed with the remaining 2.3 mJ of the 806 nm Ti:sapphire output to generate the difference frequency in a KTiOPO$_4$ (KTP; $10\times10\times3 \text{ mm}^3, \phi = 0^\circ, \theta = 41.8^\circ$) crystal, leading to the production of pulses at a wavelength of $\sim$ 3 µm, of 150 fs length, full width half maximum of 100 cm$^{-1}$ and 100 µJ IR pulse energy. The generated IR is split, using an 80:20 beam splitter, with the larger portion used for the IR pump and the smaller for the IR probe, so we can only pump and probe with the same
wavelength. A chopper which is synchronized with the 1 kHz laser repetition rate is inserted in the IR pump beam, leading to a 500 Hz pump pulse repetition rate. The visible probe beam is formed from that portion of the amplifier output (0.1 mJ) not used previously. That is, the visible probe pulse is not spectrally narrowed and the length of the pulse is 120 fs. The polarizations of IR pump, IR probe and VIS probe are controlled by polarizers and $\lambda/2$ wave plates. The SFG-probe spectra are recorded under $ssp$ (SFG, VIS, IR probe) polarization conditions, while for the pump beam the $\lambda/2$ wave plate is motorized to allow the collection of alternate polarization pumped spectra. Positive lenses are used to focus each beam on the sample, with focal lengths of 100, 50 and 200 mm for IR pump, IR probe, and VIS probe, respectively.

![One-color time- and polarization-resolved SFG setup](image)

Fig. 2.1 One-color time- and polarization-resolved SFG setup.

### 2.2.2 Two-color experiments

The two-color experimental geometry is shown in Fig. 2.2. Since, in contrast to the one-color experiments, we need to pump and probe with different wavelengths, another optical parametric amplifier (TOPAS) is included to generate the broadband probe pulses. The laser system we use in the two-color experiment is a Ti:sapphire regenerative amplifier (Spitfire Ace, Spectra-Physics) seeded with an oscillator (Mai Tai, Spectra-Physics) and pumped with a diode-pumped green laser (Empower, Spectra-Physics). The amplifier is used to generate laser pulses centered at 800 nm with a full-width-at-half-maximum (FWHM) of 30 nm and a
pulse duration of 40 fs. The amplifier produces ~ 5 mJ of energy/pulse with a repetition rate of 1 kHz. Two commercial optical parametric amplifiers (TOPAS-C, Spectra-Physics) are each pumped with 1 mJ of the amplified 800 nm beam. For one TOPAS-C the signal and idler are used in a difference frequency mixing process in a silver gallium disulfide (AgGaS$_2$) crystal, resulting in 5 μJ IR pulses, tunable around a central wavelength of ~ 2940 nm (~ 3400 cm$^{-1}$) with a FWHM of 300 cm$^{-1}$, which are used as IR probe pulses. Another TOPAS-C is used to produce the IR pump with the same experimental scheme as in the one-color experiments. The bandwidth of the IR pump pulse is determined by the thickness of the KTP crystal (~ 6 mm), and amounts to approximately 100 cm$^{-1}$; the pump wavelength can be tuned by changing the angle of the KTP crystal. This tunable narrow-band IR pump pulse can be used to excite different OH groups with stretching frequencies determined by their specific hydrogen bond strength. The remaining 800 nm pulse (~ 1 mJ) of the laser output is narrowed by an etalon (SLS Optics Ltd) to 9 cm$^{-1}$ and is used for the VIS probe.

Fig. 2.2 Two-color time- and polarization-resolved SFG setup.

2.2.3 SFG generation and detection

The IR-pump/SFG-probe measurements at the air/water interface are made in reflection geometry, as schematically shown in Fig. 2.3. The IR pump, IR probe, and VIS probe beams
are arranged such that they are in a plane orthogonal to the air/water interface and have incident angles of ~ 55°, 46°, and 53°, respectively, with respect to the surface normal. At the interface, two SFG signals are generated: one is the IR pump/VIS SFG signal and the other is the IR probe/VIS SFG signal. If the IR pump and IR probe are both 3300 cm⁻¹ and the VIS beam is 806 nm, the IR pump/VIS (dashed purple line) and IR probe/VIS SFG (solid purple line) signals reflect from the interface are ~ 53.4° and 51.6°, respectively, with respect to the surface normal. Therefore the IR pump/VIS SFG signal can be spatially filtered out with a pin hole centered on the IR probe/VIS SFG signal. The band-pass filter after the collimating lens filters out other signals which have different wavelength form the SFG signals. The pulse energies of the IR pump, IR probe, and VIS probe at the sample for the one-color experiment are 24, 6, and 4 μJ/pulse, respectively, while for the two-color experiment they are 40, 1, and 4 μJ/pulse, respectively. The sample is distilled Millipore filtered water (18 MΩ-cm resistivity) in a homemade Teflon trough, which is rotated at 7.5 rpm to suppress the effect of heat from successive laser shots. To perform an experiment, the infrared pump pulse is variably delayed with respect to the probe pulse (τ) using a mechanical delay line.

![Fig. 2.3 Experimental geometry of time-resolved SFG setup at the sample.](image)

For the 2D-PS-SFG, as shown in Fig. 2.4, the IR/VIS probe pair is first focused onto a gold mirror to generate a non-resonant SFG signal, which is used as the local oscillator (LO). After passing through a 1-mm thick fused silica plate, which causes a delay of 1.7 ps relative to the IR/VIS probe pair, the LO is then refocused, together with the remaining IR/VIS probe pair, onto the sample by means of a gold-coated spherical mirror with a focal length of 50 mm. The incident angles of the IR pump, IR probe, and VIS probe beams are ~ 31°, 51°, and 40°, respectively, with respect to the surface normal. The sample signal and LO are collimated by a spherical lens. A height sensor (LK-G85, Keyence) with resolution of 200 nm
which is synchronized with a motorized z-direction translation stage (8MVT40-13-1, Standa) is used to compensate the height change caused by the evaporation of the water.

![Diagram of SFG setup](image)

**Fig. 2.4 Phase-sensitive time-resolved SFG setup at the sample.**

The SFG signals generated at the interface are collected and collimated by a 200 mm positive lens, as shown in Fig. 2.5. The signals are then focused into the monochromator with two cylindrical lenses. The first cylindrical lens (CL1) with a focal length of 300 mm is used to focus the signal in the vertical while the second one (CL2) with a focal length of 50 mm is used to focus the signal in the horizontal. With this geometry, the SFG signal is loosely focused vertically and tightly focused horizontally. Combined with the galvano mirror inserted after CL1, we can spatially separate different SFG signals vertically on the CCD chip. If the galvano mirror is synchronized (500 Hz) and phase-locked with the chopper, i.e., the angle of the galvano mirror is related to chopping of the IR pump pulse, we can see two spectra in the spectrometer. One of the spectra includes the effect of the IR pump excitation and one is recorded without the pump pulse. For each delay time point, four spectra are recorded - a spectrum following excitation with a $p$-polarized pump pulse, followed by a spectrum without the pump pulse present, followed by an $s$-polarized pumped spectrum, followed by an unpumped spectrum. The polarization of the IR pump pulse is controlled by a $\lambda/2$ plate mounted in a motorized rotation stage. If the polarization-resolved experiment is not performed, only the $p$-pumped and unpumped signals are recorded. The normalized (differential) IR-pump/VSF-probe signals are computed as the ratio (difference) between the signals with and without the pump for each pump polarization independently. For TR-SFG
experiments, the SFG signals are detected by an electron-multiplied charge coupled device camera (EMCCD, iXon 897, Andor) in the monochromator. For phase-sensitive experiments, the SFG signals interfere with the LO in the monochromator and are then detected by the EMCCD (Newton 971, Andor).

![Geometry of the detection optics.](image)

**Fig. 2.5 Geometry of the detection optics.**

### 2.3 Data analysis

![Data analysis](image)

**Fig. 2.6 A typical normalized IR-pump/SFG-probe signal of hydrogen-bonded OH groups at the air/water interface.**

A typical example of normalized, one-color IR-pump/SFG-probe data recorded from the air/water interface is shown in Fig. 2.6. These data are plotted as the pumped spectra divided by the unpumped spectra with various time delays following Eq. (1.23), therefore at sufficient negative time delays the ratio equals one. For this experiment, the IR pump and IR probe were both centered at 3350 cm\(^{-1}\), with a spectral width of approximately 100 cm\(^{-1}\). The normalized SFG signals show fast recovery after the pump-induced bleach followed by an additional, slower decrease. The shape of the signal reflecting vibrational relaxation of the H-bonded OH groups of interfacial water molecules can be understood in the following manner [42–44]: The initial bleach originates from the pump-induced excitation of the OH
stretching mode from the ground state \((v = 0)\) to the first excited state \((v = 1)\). Due to the large anharmonicity of the OH stretching vibration, the SFG signal generated from the excited state is shifted out of the probing window, causing the decrease in the SFG signal. The partial recovery of the signal indicates that the excited population is transferred with a time constant \(T_1\) to an intermediate level \(v^*\) through intramolecular vibrational relaxation (IVR). For pure \(\text{H}_2\text{O}\), \(v^*\) is composed of the HOH bending mode \((\sim 1650 \text{ cm}^{-1})\) and the \(\text{O}^−\text{H}···\text{O}\) hydrogen bond stretch mode \((\sim 300 \text{ cm}^{-1})\). Since the overtone of the bending mode is at \(\sim 3300 \text{ cm}^{-1}\), it can be the main recipient for the excess vibrational energy [45,46]. The long-time offset after the recovery is due to the sequential relaxation of the intermediate state to the “hot” ground state \((v' = 0)\), caused by the relaxation of the excess energy from the bending mode to the low frequency libration mode, which leads to a full thermalization of the subensemble of the water molecules. Accordingly, the signal can be reproduced with a four-level cascade system (Fig. 2.7(a)) [24]. \(T_1\) and \(\tau_{eq}\) denote the sequential relaxation rate from of the excess energy from \(v = 1\) to \(v^*\), then to \(v' = 0\). We describe the dynamics of the population changes of the states by using the following set of differential equations:

\[
\begin{align*}
\frac{\partial N_0}{\partial t} & = -\sigma I(t)[N_0 - N_1] \\
\frac{\partial N_1}{\partial t} & = \sigma I(t)[N_0 - N_1] - N_1 / T_1 \\
\frac{\partial N_{v^*}}{\partial t} & = N_1 / T_1 - N_{v^*} / \tau_{eq} \\
\frac{\partial N_{v'}}{\partial t} & = N_{v^*} / \tau_{eq}
\end{align*}
\]  

(2.1)

where \(N_0\), \(N_1\), \(N_{v^*}\), and \(N_{v'}\) denote the population of state \(v = 0\), \(v = 1\), \(v^*\), and \(v' = 0\), respectively. Here, the exponential decay of the cascading process is assumed for the vibrational relaxation from \(v = 1\) to \(v^*\) and from \(v^*\) to \(v' = 0\), while the pumping efficiency is determined by the population difference of the ground and excited states. \(\sigma\) is the absorption cross-section from the \(v = 0\) to \(v = 1\) transition and \(I(t)\) is the intensity of the time-dependent IR pump pulse. For conventional TR-SFG spectroscopy, the normalized SFG signal can be calculated as:

\[
I_S(t) = \frac{\chi_0[N_0(t) - N_1(t)] + \chi_{v^*}N_{v^*}(t) + \chi_{v'}N_{v'}(t)]^2}{[\chi_0N_0(t << 0)]^2}
\]  

(2.2)

In our analysis, we fit the time trace data by coupling Eqs. (2.1) and (2.2). The values of \(T_1\), \(\tau_{eq}\), \(\chi_0\), \(\chi_{v^*}\), and \(\chi_{v'}\) are free parameters taken from the fit to the data, where \(\chi_0\), \(\chi_{v^*}\),
and $\chi_v$ are the effective susceptibilities of the OH oscillators in the $v = 0$, $v^*$, and $v' = 0$ states, respectively. The trace that describes the data depicted in figure 2.6 was calculated using equation (2.2) with parameters fit to the data. Clearly, the description works very well, allowing us to extract information on the dynamics of the H-bonded OH stretching mode of interfacial water molecules from the data. However, the time-dependent SFG signal reflects not only the vibrational energy relaxation of molecules with the specific vibrational frequency excited by the pump pulse, but the signals are also affected by the reorientational motion of interfacial molecules: following vibrational excitation with the pump pulse, excited OH groups can reorient away from, and towards, the polarization axis of the probe, making those specific molecules contribute less, respectively more, to the signal.

Inversely, using an appropriate experimental scheme, the molecular reorientation motion can be revealed by time-resolved SFG experiments, specifically using pump pulses with different polarizations (TPR-SFG technique). Differently polarized pump pulses will excite OH groups of specific orientation with orientation-dependent efficiency: if the transition dipole moment of the OH group is oriented along the polarization axis of the pump pulse, excitation will be relatively efficient. Therefore, in addition to the lifetime of the OH groups, the reorientation motion of these OH groups can also be measured by using the time-resolved SFG technique; the recovery of the difference of the signals between SFG signals when IR pump and IR probe pulses are polarized parallel (both $p$-polarized) and those when IR pump and IR probe pulses are orthogonally polarized (IR pump is $s$-polarized and IR probe is $p$-polarized) will reveal the in-plane and out-of-plane motion of these OH groups [47]. The detailed description of how to calculate the TPR-SFG signal has been offered previously [27] and will be discussed in chapter 3.

On the other hand, TR-SFG can be combined with phase-sensitive detection approaches, which we have implemented in our 2D-PS-SFG spectroscopy scheme. 2D-PS-SFG spectroscopy is analogous to the 2D-IR technique, with the additional characteristic of being surface-specific. The differential 2D-PS-SFG signal eliminates the contribution of $\chi_{\text{sample}}^{(2)} (\omega_{\text{SFG}})$, which is shown in Eq. 1.50. Therefore, for the 2D-PS-SFG experiment, the differential $\text{Im}[\chi^{(2)}]$ calculated from the four-level model is

$$\Delta \text{Im}[\chi^{(2)}](t) = \chi_0[N_0(t) - N_1(t)] + \chi_{v^*}N_{v^*}(t) + \chi_vN_v(t) - \chi_0N_0(t) << 0 \quad (2.3)$$

The details of extracting the time constant of vibrational relaxation and spectral diffusion from the 2D-PS-SFG data will be described in chapter 5.
Fig. 2.7 (a) A 4-level system used to describe the energy flow pathway of hydrogen-bonded OH groups. \( v = 0, v = 1, v^*, \) and \( v' = 0 \) are the ground state, first excited state, intermediate state, and “hot” ground state, respectively. \( \sigma \) is the absorption cross-section from the \( v = 0 \) to \( v = 1 \). \( T_1 \) and \( \tau_{eq} \) denote the sequential relaxation rate from of the excess energy from \( v = 1 \) to \( v^* \), then to \( v' = 0 \). \( \chi_0, \chi_{v^*}, \) and \( \chi_{v'} \) are the effective susceptibilities of the OH oscillators in the \( v = 0, v^*, \) and \( v' = 0 \) states, respectively. (b) Time variations of the populations for each vibrational state obtained from fitting the data in Fig. 2.6 using Eq. (2.1).

The populations of each vibrational state are depicted as a function of pump-probe delay time in Fig. 2.7(b). We can see a decrease in the population in the ground state \( (v = 0) \) with a rapid increase in the first excited state \( (v = 1) \). This figure shows that the vibrational lifetime of the OH stretching mode \( (T_1 < 100 \text{ fs}) \) is very short, and the population of \( v = 1 \) is transferred to \( v^* \) state followed by the slow relaxation to the heated ground state \( (v' = 0) \).