Watching molecular motion at interfaces
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Citation for published version (APA):
Donovan, M. A. (2018). Watching molecular motion at interfaces
2. Experimental Methods

2.1 Time-Resolved SFG Spectrometer

The spectrometer is largely described in reference.\textsuperscript{42} An 80 MHz pulse train of 40 fs pulses from an 800 nm Titanium:Sapphire (Ti:Sa) oscillator (Mai Tai, Spectra Physics) is used to seed a regenerative amplifier pumped by a 30 W frequency doubled Q switched Nd:YLF laser. Subsequently, 2 mJ of the output from the 5 mJ, 1 kHz regenerative Ti:Sa amplifier (Spectra Physics Spitfire Pro) is divided evenly between two commercial optical parametric amplifiers (TOPAS, Light Conversion) the first of which generates broadband (~400 cm\textsuperscript{-1}) mid IR by collinear difference frequency mixing of the signal and idler waves inside of an internal AgGaS\textsubscript{2} crystal. Additionally, for the probe pulse pair, 1.5 mJ of broadband 800 nm light is frequency narrowed by a Fabry-Perot etalon to produce ~ 15 cm\textsuperscript{-1} bandwidth pulses for the VIS beam.

The idler wave from the second TOPAS is frequency doubled and mixed with 0.5 mJ from the fundamental 800 nm beam inside of a KTP crystal to generate intense mid IR pulses (~100 \textmu J) via optical parametric amplification and difference frequency mixing.\textsuperscript{43} The mid IR pump beam is then passed through a computerized delay stage (Physik Instrumente) before being mechanically chopped (by a Thorlabs chopper) at 500 Hz. Planoconvex CaF\textsubscript{2} lenses of $f = +5$ cm and $f = +15$ cm are used to focus the IR pump and probe into the sample plane, while an AR coated planoconvex $f = +20$ cm lens is used to focus the 800 nm beam. Spectra are acquired by first separating the pump-on to pump-off spectra via displacement by a galvano mirror moving synchronously with the laser, vibrating at 500 Hz. Signals are subsequently dispersed in an Acton Spectrometer (blaze 600 nm 1200 g/mm) and dispersed onto a Peltier-cooled EM CCD detector (Newton Andor). Labview software is used to control the delay stage and acquire the spectra. A generalized schematic of the time-resolved SFG spectrometer is shown in figure 2.1.
Furthermore, two separate sampling geometries are presented for experiments at the water/air interface and for the buried solid-liquid interface in figures 2.2 and 2.3.

**Figure 2.1** Schematic of the experimental setup used to perform TP-SFG experiments. Figures 2.2 and 2.3 respectively show detail about the sample geometry for the water/air and buried interface experiments, P: polarizer, Et: Fabry Perot etalon, BS: beamsplitter, λ/2: half wave plate,

The first sampling geometry involves the use of a bridge mirror in which the three incident beams first impinge upon a gold mirror before subsequently being overlapped at the surface. For this geometry, angles of incidence with respect to the surface normal amount to, respectively, 43, 53,
and 55 degrees for the IR probe, IR pump, and 800 nm beams. The beams are incident upon a rotating trough filled with liquid sample solution which is used to reduce laser heating by subsequent laser shots. To account for evaporation, the water level is replenished through a reservoir which keeps the surface level constant with the aid of a peristaltic pump. A visualization of this sample is shown in figure 2.1. After the sample, an iris spatially filters out the IR pump + 800 nm SFG signal and the resultant probe SFG beam is collimated by a +10 cm plano-convex lens before being further focused onto the detector by a +30 cm cylindrical lens. Shortly after the cylindrical lens, a vibrating mirror driven by a sinusoidal pulse at 500 Hz from a function generator triggered by the laser is used to spatially separate pumped and unpumped SFG signals. The signals are focused onto the spectrometer slit by a +5 cm cylindrical focusing lens. Labview software is then used to control the CCD settings. Pump-on and pump-off signals are acquired simultaneously by hard binning and integrating the signal at each individual delay time of the computer controlled stage.

Figure 2.2 Visualization of the sample stage with a rotating trough and liquid reservoir along with bridge mirrors. Courtesy of MJ van Zadel.
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The instrumental response time which is used to determine the temporal resolution of the experiment by measuring the third-order $\chi^{(3)}$ sum-frequency signal of infrared pump, infrared probe, and visible (IIV) beams which is readily detected at the sum of the three input frequencies. The time delay between the pump and probe pulses is scanned and the sum frequency signal emitted by the third-order coherence generated from the IR pump, the IR probe and the visible, is measured as a function of that delay time. This response is typically measured in the ppp polarization combination from a gold surface. Additionally, it may be measured from the sample surface. A Gaussian fit to the temporal shape of this IIV signal gives the instrumental response time. This is used to assess the instrument response from liquid surfaces in this thesis. Typical instrument response times measured in the time-resolved spectrometer range from 130 to 160 fs. The temporal resolution assuming a Gaussian pulse shape is then simply $T_{IIV}/\sqrt{2}$. For the buried silica interface, the instrumental response time is taking by fitting the rise of the transient SFG bleach signal from a thin layer of gold deposited on the hemisphere. The instrument response time is typically found to be have a Gaussian FWHM of 150 fs.

To measure SFG from a buried solid-liquid interface, we take advantage of the field enhancement provided by total internal reflection. For the SiO$_2$/H$_2$O interface, the angles of incidence were chosen to enhance the high-frequency end of the SFG spectrum in total internal reflection geometry. For this buried interface geometry, angles of incidence with respect to the surface normal amount to, respectively, 55, 41, and 71 degrees for the IR probe, IR pump, and 800 nm beams. The appendix in chapter 6 presents the local field corrections and enhancements encountered in an SFG experiment. A 10 cm diameter hemispherical fused silica substrate was used as a substrate. In order to reproducibly approach the surface of the hemisphere, a white light microscope was used. First, an iris is placed in the sample position. The microscope is then set such that the iris is in the focal plane of the white light microscope. The incident laser beams are subsequently overlapped with the help of the microscope and the iris. The scatter from the 800 nm beam can be readily detected from this position, and
this scatter is indicative of the correct sample height. Next, a standard alignment procedure with a gold coated SiO$_2$ hemisphere in the sample position is used. With the aid of the microscope, the surface of the gold coated hemisphere may be easily found, and from this surface, the overlap of the beams may be fine-tuned. Since there is some difficulty in detecting the IIV instrument response from this sample geometry, we measure the pump-probe SFG signal from gold directly. The rise of the bleach in such a measurement is fit to a Gaussian function, and the FWHM of this Gaussian function is taken to be the instrumental response function. FWHM instrument response times of 150 fs are found for the buried interface experiments.

![Figure 2.3](image)

**Figure 2.3** Top, visualization of the experimental geometry used to probe the buried liquid-solid interface with a hemispherical substrate. Bottom: Top view of the sample cell with the hemispherical substrate. Courtesy of MJ van Zadel
2.2 Data processing

A Matlab script written by Ruth Livingstone was used to plot the raw data acquired from the measurement. Typically, a plot of the raw data will appear as a bleach as shown in Figure 2.4. This example shows the transient population dynamics of taken under s-polarized pump excitation in the sps polarization combination. The pump spans the entire aliphatic stretching range. Of note, the bleach is centered at around 2958 cm$^{-1}$. Plotted is the difference between pump-on and pump-off signals. To plot a pump-probe trace, we instead use the same software to plot the ratio of pump-on to pump-off to determine the percent decrease the pump has on the signal. A frequency range is chosen over which there is a transient signal. An example of how the trace is built up is shown in Figure 2.5.

![Figure 2.4](image)

**Figure 2.4** Pump-probe transient showing the bleach over a wide frequency range at different delay times of the pump relative to the probe.
Figure 2.5 parallel-pumped SFG spectra at different delay times for ssp spectrum of acidic solution of L-leucine: Individual pumped and unpumped spectra taken at different stated delay times. Green traces show the spectrum of leucine which is excited by a pump pulse which spans the aliphatic range i.e., pump on, blue traces show the static spectrum which is not excited i.e. pump off Red shows the calculated difference between pump on and pump off i.e. the bleach.

In Figure 2.5, individual spectra of L-leucine in the ssp polarization acquired at different delay times between the pump and the probe pulse are shown. Spectra traced in blue show the static spectrum of L-leucine which is not affected by the pump pulse. Analogously, spectral traces shown in green show spectra of L-leucine which are excited by the pump pulse. A difference between the two spectra ($I_{on} - I_{off}$) is shown in red. This difference is known as the bleach. At very negative delay times, there is no apparent influence of the pump. At 200 fs, the bleach is maximum, and this is evidenced over the whole band. Again at 1.2 ps, there is still residual bleach of the signal left in the symmetric stretching mode. The signal has recovered to a heated ground state at 20 ps, and this is apparent if the reader
refers to Figure 2.6 because the bleach signal does not completely recover back to the level it is at at pump probe delay times \( t << 0 \) fs.

**Figure 2.6.** Different time ranges in an SFG pump-probe experiment. Blue represents pump-probe delay times \( t << 0 \), red shows delay times which lie within the instrumental response, and green shows a pump-probe delay time which corresponds to population dynamics. The trace shown is the pumped \( CH_3 \) symmetric stretch of \( L \)-leucine taken with the ssp probe polarization combination. Bleach is integrated from 2860 to 2900 cm\(^{-1}\). The inset shows the static ssp spectrum.

Figure 2.6 plots the ratio between the intensity of an SFG spectrum which is excited by mid IR light (pump on) and an SFG spectrum which is non-perturbed. As shown in Figure 2.6, there are typically three temporal ranges in a pump-probe SFG experiment. Signals at negative delay times which occur before the onset of the instrumental response are averaged such that the response at \( t << 0 \) fs is 1 i.e. the pump-pulse has not yet arrived. The red region shows the onset of the instrumental response, molecular signals are convoluted here with the instrument response. Delay times which occur after the instrumental response is over are shown in green. For the case of
the region highlighted in green the signal recovery occurs due to vibrational population dynamics. This bleach signal may or may not include the effects of molecular reorientation. The picture painted in figure 2.6 is oversimplified, and sometimes the onset of the signal may occur at times later than the instrumental response. At other times, the signal may not recover. To take the effects of molecular reorientation into account, comparison of orthogonally pumped transients is performed as shown at the end of chapter 1.

The subsequent chapters of this thesis all use the TP-SFG methods presented in chapters 1-2 to study the influence of molecular reorientation on the vibrationally pumped transient SFG signal. From these experiments, rates of molecular motion at interfaces are investigated and interpreted with the help of numerical modeling methods. Chapters 3, 4, and 6 investigate model surface active leucines as monomers and as side chains within LK peptides. Experiments are performed at the air-water interface for the adsorbed biological molecules, and molecular dynamics simulations help resolve the rates of molecular reorientation. Chapter 5 refers to experiments which measure the buried interface between silica and water. The experiments there take advantage of total internal reflection geometry and a hemispherical substrate for time resolved methods. Phase resolved experiments were additionally performed by J. Cyran to aid in the identification of the spectral species, and a brief overview of the phase resolved measurement is given in Chapter 6. The rest of this thesis presents surface SFG measurements which attempt to quantify the effect that molecular reorientation has on IR pump, SFG probe measurements.