STRUCTURE AND DYNAMICS OF INTERFACIAL WATER AT SURFACES
WITH VARYING HYDROPHOBICITY

A Dissertation
Presented to the Faculty of the Graduate School
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In Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

by
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Aqueous interfaces are ubiquitous across atmospheric, biological, and technological processes. Interfacial water is thought to play an active role in many of these processes. For instance, hydrophobic coatings are used for anti-biofouling and the interaction between water molecules and the hydrophilic coatings is believed to inhibit protein adhesion. However, the precise role of water is not well understood. Interfacial water is also notoriously difficult to study experimentally since the number of water molecules at the interface is miniscule compared to the bulk and the ultrafast fluctuations of the hydrogen-bonding network require sub-picosecond time resolution. Sum-frequency generation (SFG) is a second-order nonlinear spectroscopy that is sensitive to only the vibrations of interfacial water due to the requirement of broken inversion symmetry within the dipole approximation. Using hydrophobic, hydrophilic and mixed hydrophobic/hydrophilic self-assembled monolayers, we examined the structure of the interfacial water with heterodyne-detected SFG (HD-SFG) to obtain the purely absorptive vibrational line shape. In order to probe the dynamics of the hydrogen-bonded interfacial water, we performed time resolved SFG experiments. The vibrational relaxation time was measured using IR pump- SFG probe experiments, and the spectral diffusion time was measured with interferometric 2D SFG.
BIOGRAPHICAL SKETCH

Stephanie Sanders earned a Bachelor of Arts degree in Chemistry and Mathematics from Albion College in 2015. While at Albion, she worked on the green synthesis of shaped palladium nanoparticles for catalysis with Professor Kevin Metz and traveled to Professor Paula Colavita’s laboratory at Trinity College Dublin to complete part of her research. She enrolled as a PhD student in Chemistry and Chemical Biology at Cornell University and joined the group of Professor Poul Petersen. In the beginning of 2019, she moved to Bochum, Germany to continue her dissertation under the supervision of Professor Petersen who accepted a new position at Ruhr-Universität Bochum.
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CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1 Motivation

Water is an active component in many natural and technological processes. The proper structure and function of biomolecules depends on their interactions with water, therefore the properties water form the basis for life on Earth.\textsuperscript{1-4} The unique properties of water stem from its highly flexible and dynamic hydrogen-bonded network.\textsuperscript{3} Thus, characterizing both the structure and ultrafast dynamics of the hydrogen-bonded network is essential to understanding water at the molecular level.

1.1.1 Interfacial Water

Aqueous interfaces exist in either the form of a molecular interface or an extended macroscopic interface, as illustrated in Figure 1.1. Inherently, processes with more than one component in an aqueous environment contain interfacial water. When water comes into contact with a surface, the bulk hydrogen-bonded network is terminated, and the water molecules reorient at the interface. The chemical and physical properties of the surface determine how the hydrogen-bonded network in the interfacial region restructures, and thus the unique properties of interfacial water. These interfacial regions provide environments for a wealth of chemical processes that depend on the interfacial water properties determined by a given surface.
Interfacial water is universal in biological systems. Thus, one way of viewing biological processes is as reactions at aqueous interfaces. Additionally, water is not merely a passive background in biology because without water, life cannot exist. Water plays an active role in the proper structure and function of biomolecules, such as protein folding based on hydrophobic interactions. Atmospheric chemistry also largely occurs at aqueous interfaces. The surfaces of aerosols provide reactive chemical environments for heterogenous atmospheric chemical reactions to occur. In addition to the abundance of interfacial water in natural processes, the unique reactivity of aqueous interfaces is employed in technical applications ranging from fuel cells to membrane filtration. For instance, the interaction between water and mixed hydrophobic/hydrophilic surfaces can promote proton transfer and deter protein aggregation and biofouling.

In order to understand the role of water in the wide range of systems described above, we need to begin by characterizing the structure and dynamics of interfacial water. However, biological and technological surfaces are complex, so simpler
interfaces are needed to elucidate the structure and dynamics of interfacial water as a function of surface composition. Self-assembled monolayers (SAMs) provide the ability to controllably tune the physical and chemical composition of the surfaces. Therefore, they provide a platform to probe the structure and dynamics of interfacial water as a function of surface chemistry on a molecular level. Additionally, interfacial water is notoriously difficult to study experimentally since the number of water molecules at the interface is miniscule compared to the bulk and the hydrogen-bonded network restructures on the sub-picosecond time scale. Sum-frequency generation (SFG) is an ideal spectroscopy for studying interfacial water because within the dipole approximation SFG signal only results from the interface where the inversion symmetry is broken. This dissertation aims to examine the structure and dynamics of interfacial water at SAMs with different chemical character using SFG.

1.2 Vibrational Spectroscopy of Water

The vibrational frequencies, and hence vibrational spectra, of the OH stretching modes of water are very sensitive to the local hydrogen-bonded network. The vibrational spectrum of liquid water has three main features: the water bending mode at ~1630 cm\(^{-1}\), a combination band at ~2100 cm\(^{-1}\), and the OH stretching mode at ~3300 cm\(^{-1}\), as observed in the spectrum in Figure 1.2 obtained using a Fourier Transform Infrared (FTIR) spectrometer in attenuated total reflection (ATR) geometry. Most characterization of water with vibrational spectroscopy has focused on the broad OH stretching mode since it is highly sensitive to the local hydrogen-bonded structure of water. There is clear correlation between stronger hydrogen bonds and lower vibrational
OH stretching frequencies in hydrogen-bonded systems. Hydrogen-bonding weakens the covalent OH bond causing a shift to lower vibrational frequency.\textsuperscript{16–18} Thus, the distribution of OH stretching frequencies in water is indicative of the distribution of local hydrogen-bonding environments within the sample. Comparing the spectral shape of the vibrational spectra of water at different interfaces to bulk water provides insight to how the hydrogen bonded structure changes due to interactions with the different interfaces. However due to the ultrafast fluctuations of the hydrogen-bonded network of water, the vibrational spectrum of water only probes an average hydrogen-bonded structure. Characterizing both the structure and ultrafast dynamics of the hydrogen-bonded network is necessary to understand water on a molecular level.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{vibrational_spectrum.png}
\caption{Vibrational spectrum of water measured with FTIR spectroscopy in ATR geometry.}
\end{figure}

1.2.1 Vibrational Spectroscopy of Bulk Water

Over the past few decades, time-resolved pump-probe and 2D infrared (IR) spectroscopy coupled with theoretical calculations and molecular dynamics (MD) have provided a detailed understanding of the structure and dynamics of the hydrogen-bonded network of bulk water.\textsuperscript{16,17,19–28} Early literature examining static vibrational
spectra of water often deconvoluted the OH stretching region into multiple Gaussian peaks representing specific hydrogen-bonding configurations, sometimes validated by the presence of isosbestic points. However, this interpretation gives a misleading, static picture of the hydrogen-bonded network. Time-resolved IR experiments and MD simulations have shown that liquid water contains a continuum of hydrogen-bonded configurations that rearrange on ultrafast time scales. Accordingly, there are no stable broken hydrogen-bonded species in bulk water and the OH stretching spectrum cannot be divided into distinct sub-populations since hydrogen-bonds interconvert on the sub-200 fs timescale. This sub-200 fs timescale governs the fluctuations of the hydrogen-bonded network. The timescale between successive hydrogen-breaking events as characterized by large angle jump-dynamics observed in MD simulations on the picosecond time scale. As a result, the ultrafast and in particular 2D IR methods not only provide insight into the dynamics of the hydrogen-bonded network but also change the way we understand the nature and structure of the liquid.

1.2.2 Vibrational Spectroscopy of Interfacial Water with Bulk Methods

Given the power of bulk methods to understand the structure and dynamics of bulk water, transient and 2D IR have been applied to more complex systems with both molecular interfaces and at extended interfaces through careful sample selection. The dynamics of water in the hydration shell of a series of salts and small molecules have been studied with bulk spectroscopies. When a solute is added to water, the hydrogen-bonded network rearranges around the molecules, which will change the vibrational dynamics. However, in order to observe significant deviations from bulk water dynamics, high solute concentrations (several molar) are needed. At high solute
concentrations, the water dynamics in the hydration shell are slowed down by less than an order of magnitude, indicating that the structure of the hydrogen-bonded network around small solutes is only slightly changed. Alternatively, samples that eliminate most of the bulk water can be prepared to study the dynamics of water in interfacial environments with transient and 2D IR. One way of excluding bulk water is to form “nanopools” of water in reverse micelles. Depending on the size of the reverse micelles formed, the ratio of surface-to-bulk water changes making it possible to isolate the interfacial contributions. Small reverse micelles exhibit water dynamics that are slower than the bulk by up to two orders of magnitude. Whereas, large reverse micelles have two distinct contributions to the dynamics: one similar to the small reverse micelles and one similar to the bulk. Therefore, the size dependent dynamics in reverse micelles reveal that the large micelles have an interfacial region surrounding a bulk-like core while the small micelles only have an interfacial water, and the dynamics of interfacial water in contact with the surfactant used to stabilize the reverse micelles are significantly slower than the bulk. Another way to eliminate most of the bulk water is by studying dehydrated samples, such as DNA, in a surfactant film, studying stacked lipid bilayers with a very small water content, or studying thin films of the fuel cell membrane Nafion. Vibrational probes sensitive to the dynamics of water can also be inserted to regions of interest to probe water dynamics at interfaces compared to the bulk. For example, metal carbonyls and nitrile probes have been inserted in biomolecules, such as lipid bilayers and proteins, to measure the dynamics of water in the hydration shell. Generally, water in the hydration shell of biomolecules is observed to slow down by a factor of 2 to 3 compared to bulk water. Lastly, third order
spectroscopies have recently been extended to the ATR geometry.\textsuperscript{51–54} In the ATR geometry, signal is only generated for a few micrometers from the surface so the surface-to-bulk ratio is much higher than in transmission experiments. The precise depth measured in the ATR depends on several factors including the wavelength, angle of incidence, and refractive indices of the ATR crystal and sample.

Therefore, it is possible to study the dynamics of water molecules confined at the solid-water interface or at interfaces labeled with vibrational probes with the inherently bulk-sensitive transient and 2D IR measurements. However, these methods cannot inherently separate the surface response from bulk, which makes it hard to study interfacial water directly through the OH vibrations. This dissertation aims to use surface-specific analogs to the bulk ultrafast vibrational spectroscopic methods to directly probe only the water molecules at the surface.

1.2.3 Vibrational Spectroscopy of Interfacial Water with Surface Specific Methods

Even order spectroscopies are, within the dipole approximation, surface-specific for liquids, such as water. As described in detail in Chapter 2, SFG is a second order nonlinear spectroscopy typically used to probe molecular vibrations by combining a resonant infrared pulse and a non-resonant visible or near-IR upconversion pulse focused at the interface. Since these are optical processes which only rely on the symmetry of the sample to distinguish the interface from the bulk, they can be applied to study any interface that can be accessed by the optical beams, including exposed air-solid and air-liquid interfaces, as well as buried liquid-liquid, solid-solid, and solid-liquid interfaces.
The water-air interface is perhaps the simplest interface to experimentally study. It is a soft, hydrophobic interface since water cannot form hydrogen-bonds with the air. The SFG spectrum of the air-water interface was first measured by Shen and coworkers in 1993.\textsuperscript{55} The SFG spectrum of the air-water interface without and with Fresnel coefficient correction, as measured by Richmond and coworkers, is shown in Figure 1.3a.\textsuperscript{56} The sharp peak at 3700 cm\textsuperscript{-1} in the SFG spectrum corresponds to the non-hydrogen-bonded OH, also referred to as the dangling or free-OH, which is oriented away from the interface into the air. The presence of a free-OH highlights the surface-specificity of SFG since the non-hydrogen-bonded waters inherently can only exist in the top water layer, yet the intensity is comparable to the intensity of the hydrogen-bonded water. The hydrogen-bonded region displays two main features peaked around 3200 and 3400 cm\textsuperscript{-1}. These two spectral features merge into a single broad feature when the strong intra- and inter-molecular couplings between the OH stretching modes of water are removed by isotopic dilution, as seen in Figure 1.3b measured by Bonn and coworkers.\textsuperscript{57} This spectral change reveals that these two hydrogen-bonded features at the water-air surface are not representative of two distinct hydrogen-bonded sub-populations but result from complex anharmonic couplings, including couplings between OH stretching modes and coupling of the OH stretch and bend forming a Fermi-resonance.\textsuperscript{45,58–60} Distinct sub-populations with unique hydrogen-bonding environments may exist for more complex surfaces. However, given the effect of the vibrational coupling on the observed spectrum, care must be taken when assigning features in the hydrogen-bonding region to specific sub-populations of water molecules,
but the overall spectral shape and intensity reflects on the distribution of hydrogen-bonding strengths at the interface.

A complication of conventional SFG, which will be discussed in further detail in Chapter 2, is that the measured intensity mixes the real and imaginary components of the signal. A variation of SFG, called Heterodyne-Detection SFG, can be used to separate the real and imaginary parts of the signal. The extracted imaginary component is comparable to linear vibrational spectra, such as FTIR and Raman spectroscopy, and also has sign information that can be used to distinguish relative orientation between vibrational modes. The heterodyne-detected SFG spectrum of the air-water interface has been measured by several groups. The spectrum as measured by Tahara and coworkers is shown in Figure 1.3c. The free-OH peak points away from the interface and is positive in the spectrum, where the hydrogen-bonded region is negative indicating that the net orientation of these OH bonds is downward. There has been some
controversy regarding a positive feature at low frequencies, which could result from complications with the phase reference.

1.3 Research Overview

Over the last decades, vibrational SFG has been employed to isolate the vibrational spectrum of interfacial water at a wide range of surfaces, including lipid monolayers, mineral surfaces, and polymer coatings.\textsuperscript{67–72} The chemical nature of the interface (hydrophobic or hydrophilic, neutral or charged) greatly affects the water structure. Hydrophobic interfaces typically display non-hydrogen-bonded OH (free-OH) bonds and strain the remaining interfacial water hydrogen-bonded network, while hydrophilic surfaces tend to interact more strongly with the interfacial water. When the interface is charged, the sign and location of the charge dictates the orientation of the surrounding water molecules causing a widening of the interfacial region. This dissertation aims to explore the difference in interfacial water structure and dynamics at self-assembled monolayers (SAMs) where the chemical structure is varied from hydrophobic to hydrophilic.

This chapter provided an introduction to the importance of interfacial water and the power of vibrational spectroscopy to characterize the structure and dynamics of water. Chapter 2 gives an overview of the surface-specific vibrational spectroscopic techniques used to probe the structure and dynamics of interfacial water. In Chapter 3, the structure of the interfacial water as determined by HD-SFG at hydrophobic, hydrophilic, and mixed hydrophilic/hydrophobic SAMs is discussed. The effect of surface charge and vibrational couplings on the HD-SFG spectra of water at the SAMs is examined in Chapter 4. In Chapter 5, the dynamics of water at SAMs measured with transient HD-
SFG and 2D HD-SFG are discussed. The phase errors in our HD-SFG spectrometer and the phase uncertainty in our HD-SFG analysis are presented in Chapter 6. An extension of our current HD-SFG design to directly measure the imaginary SFG spectrum and reduce phase uncertainty in the HD-SFG analysis is described in Chapter 7. In Chapter 8, a general overview of this dissertation and future directions are discussed.

1.4 References


(8) Casillas-Ituarte, N.; Callahan, K. Surface Organization of Aqueous MgCl2 and Application to Atmospheric Marine Aerosol Chemistry. Proc. ... 2010.


129 (46), 14311–14318.


(44) Kel, O.; Tamimi, A.; Fayer, M. D. Size-Dependent Ultrafast Structural Dynamics inside Phospholipid Vesicle Bilayers Measured with 2D IR Vibrational Echoes.


2.1 Theory of Sum Frequency Generation

When light interacts with a material, it induces a polarization resulting in a spectroscopic signal. The spectroscopic techniques can be ordered in terms of the number of interactions between the material and incident photons:

\[ \vec{P}(t) = \epsilon_0 [\chi^{(1)} \vec{E}(t) + \chi^{(2)} \vec{E}^2(t) + \chi^{(3)} \vec{E}^3(t) + \cdots] \]

\[ \equiv \vec{p}^{(1)}(t) + \vec{p}^{(2)}(t) + \vec{p}^{(3)}(t) + \cdots \]  \hspace{1cm} (2-1)

where \( \epsilon_0 \) is the permittivity of free space, \( \chi^{(n)} \) is the \( n \)th order susceptibility, and \( \vec{E}(t) \) is the incident electric field.\(^1\)\(^2\) Sum frequency generation (SFG) is a 2\(^{nd}\) order non-linear spectroscopy, so the induced polarization can be written as

\[ \vec{P}^{(2)}(t) = \epsilon_0 \chi^{(2)} \vec{E}_1(t) \vec{E}_2(t) \]  \hspace{1cm} (2-2)

where \( \vec{E}_1(t) \) and \( \vec{E}_2(t) \) are two different electric fields. Within the electric dipole approximation, all even order processes are forbidden in centrosymmetric media. Therefore, \( \chi^{(2)} \) is only nonzero if the system lacks inversion symmetry. This requirement of broken inversion symmetry can occur on both the molecular level (a molecule with a lack inversion symmetry acts as an emitter) and the macroscopic level (the system exhibits an asymmetric distribution of emitters resulting in an overall coherent signal). For isotropic media, such as liquids, the interface breaks the inversion symmetry and only the interfacial region contributes to the signal. Figure 2.1 illustrates how the air-water interface induces a net orientation at the surface. In the first layer of water molecules, there is a net orientation of the hydrogens pointing down. However,
away from the surface, for every water molecule with a given orientation there is a nearby water with the opposite orientation, which cancels the signal out. The thickness of the interfacial layer that contributes to the SFG signal is dependent on how much disorder is induced by the surface. By comparing experimental and theoretical results, the thickness probed by SFG at the air/water interface was determined to be 3.5 angstroms.\textsuperscript{3}

**Figure 2.1:** Illustration of SFG at the air/water interface adapted from reference 27. The arrows represent the transition moment of the water molecules. At the interface (black arrows), there is a net orientation resulting in an SFG signal. In the bulk (gray arrows), the orientation of the molecules is random, and the signals will cancel.

For vibrational SFG, an IR photon resonantly excites a vibrational transition of the molecule by a dipole transition, and the visible photon upconverts the signal to a virtual state and induces an anti-stokes Raman transition to produce a photon at the sum of the incident frequencies, as illustrated in Figure 2.2.
Therefore, the SFG cross-section is a product of the transition dipole moment ($\mu$) and the Raman polarizability ($\alpha$), which is another way of stating the requirement of broken inversion symmetry. The product of the transition dipole moment and Raman polarizability is the hyperpolarizability ($\beta$). The SFG molecular response depends on the second order non-linear susceptibility ($\chi^{(2)}$), which is the orientational average of the hyperpolarizability of all molecules in the system:

$$\chi^{(2)} = \sum \beta = \sum \mu \cdot \alpha \quad (2-3)$$

An SFG spectrum is measured by either scanning the IR frequency or by using a broadband IR pulse spanning the vibrational transitions of interest, while a narrowband visible pulse is held at a constant wavelength. The emitted SFG signal is detected at the sum to the two incident frequencies. However, SFG spectra are typically reported as a function of the IR frequency, which is calculated from the SFG detection axis and the known, constant visible frequency, to provide the surface vibrational spectrum.
2.1.1 Homodyne Detected Sum Frequency Generation

Conventional, homodyne detected SFG experiments measure the intensity of the produced SFG beam, which is proportional to the norm squared of the nonlinear susceptibility.

\[ I_{SFG} \propto |\chi_{eff}^{(2)}|^2 \]  

(2-4)

This means the complex phase of the nonlinear susceptibility is lost and the real (dispersive) and imaginary (absorptive) components of the response, including the non-resonant contribution, interfere, which can distort the spectral line shapes. To extract the purely absorptive spectrum, typically the effective nonlinear susceptibility is fitted to a sum of Lorentzian peaks and a non-resonant background, which may contain a phase factor:

\[ \chi_{eff}^{(2)} = \chi_{NR}^{(2)} e^{i\theta} + \sum_n A_n \frac{1}{\omega_n - \omega - i\Gamma_n} \]  

(2-5)

This approach has proven to be very successful in a wide range of different applications. However, water is notorious for exhibiting broad spectral lineshapes, which cannot be fit to Lorentzian lineshapes. To accurately describe the absorptive spectra for inhomogeneous systems, the complex second-order susceptibility needs to be measured directly with heterodyne detection (HD).

2.2 Heterodyne Detected Sum Frequency Generation

In heterodyne detected SFG (HD-SFG), a known, nonresonant SFG signal is interfered with the sample SFG signal.\textsuperscript{6,9,10} Through data processing and normalizing to a reference sample, the real and imaginary components of the non-linear susceptibility are obtained.
The imaginary component contains the absorptive, out-of-phase features, which can be compared to the linear FTIR and Raman spectra, while eliminating the dispersive, in-phase features originating from the real component. Obtaining the imaginary component also eliminates the need to fit the data with lineshape functions with explicit real and imaginary components, such as Lorentzian. Furthermore, the absolute sign of the imaginary susceptibility provides information on the relative (up vs. down) orientation of the non-linear transition moments, the product of the dipole moment and polarizability, with respect to the surface. Typically, the sign convention, where a positive OH feature points away from the bulk, corresponding to “up” for the air-water interface, is adopted. This is illustrated by the arrows in Figure 2.3 representing the nonlinear transition moments of three populations of molecules at the hydrophobic-water interface. Here the non-hydrogen bonded OH (green arrows) point up and on average the hydrogen-bonded OH groups (blue arrows) also point up, while the symmetric methyl group stretch (black arrows) point down, towards the bulk. In order to make these assignments, the sign of the nonlinear transition moment for the molecular functional group must be known. For instance, the symmetric CH stretching modes have a negative hyperpolarizability, thus a positive peak in the spectrum corresponds to a transition moment pointing towards the bulk. Correspondingly, the imaginary SFG spectra would have a positive features for the free OH mode, hydrogen-bonded OH stretching mode, and symmetric stretch CH modes.
2.2.1 Experimental Implementation

Although measuring the imaginary component of the nonlinear susceptibility provides the desired absorptive vibrational spectrum of the interface, HD-SFG has not been widely implemented due to the technical complexity. Heterodyne detected SFG requires high phase stability and spatial overlap between the local oscillator and sample signal. Two general types of heterodyne detection schemes have been implemented in the SFG community. The first, developed by the Shen group, is referred to as phase-sensitive SFG (PS-SFG), and is main implemented with narrowband picosecond (ps) infrared pulses.\textsuperscript{11,12} The second is interferometric, broadband HD-SFG that was first implemented by the Benderskii and Tahara groups.\textsuperscript{13-15} Our group developed a new experimental design for HD-SFG, Figure 2.4, with high phase stability and flexibility allowing for any surface in any polarization combination to be probed.\textsuperscript{10}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{orientation_vibrational_modes.png}
\caption{Orientation (up vs. down) of vibrational modes at a hydrophobic-water interface: methyl modes (black), free OH (green), hydrogen bonded OH (blue)}
\end{figure}
In our design, the local oscillator is generated in transmission in a thin film of ZnO on a CaF2 window. Then, the infrared, visible, and local oscillator are collimated between two off-axis parabolas before being focused at the sample. By collimating the beams after the local oscillator is generated, additional polarization optics can be placed in the local oscillator which allows for the option of implementing balanced detection, as seen in Figure 2.4, or the extension of HD-SFG to chiral samples. Additionally, by using shared optics for the local oscillator, infrared, and visible beams our geometry has a high phase stability. However, both PS-SFG and HD-SFG require an external phase reference in order to extract the phase of the sample. The accurate phasing of HD-SFG spectra is an ongoing issue in the field and will be discussed in detail in Chapter 6. Improving the experimental design of HD-SFG geometries is key to improving the phase stability, phase accuracy, and increasing the implementation of HD-SFG. Recently, the Shultz group introduced a design for a non-linear interferometer with high phase accuracy, but is complex to implement.\textsuperscript{16-18} Thämer et al. published a design for PS-SFG in a collinear geometry.\textsuperscript{19} The collinear geometry results in very high phase stability of the set-up. Taking inspiration from these designs and building on our current

**Figure 2.4:** Phase stable and flexible heterodyne SFG detection scheme allowing to probe any surface in any polarization combination. Reproduced from reference 28.
design, we implemented the use of a wedge pair in order to improve the phase accuracy of our design, which will be the focus of Chapter 7.

2.3 Time-Resolved Sum-Frequency Generation

Time-resolved spectroscopy measures the dynamics of a system by measuring spectra after an induced change. In order to accurately map out the dynamics, ultrafast, femtosecond (fs) laser pulses that are shorter than the processes of interest are used. The two main types of vibrational time-resolved, third-order, spectroscopies are transient or pump-probe and 2D IR. Transient IR measurements characterize the vibrational relaxation dynamics, providing information on the energy dissipation driven by couplings between modes.\textsuperscript{20,21} 2D experiments reveal the heterogeneous and homogeneous contributions to the linewidths and capture spectral diffusion dynamics, which inform on the number of stable species and the time-scale of their interchange, and indicate couplings between modes. Fourth-order spectroscopies are the surface specific analogs to third-order time-resolved spectroscopies. By combining IR pumps with our HD-SFG probe, we measure the vibrational dynamics of the molecules at the surface. The details of transient HD-SFG and 2D HD SFG are presented in sections 2.3.1 and 2.3.2 respectively.

2.3.1 Transient HD-SFG

Transient HD-SFG or IR pump – HD-SFG probe measurements reveal the interfacial vibrational relaxation dynamics. In transient SFG, part of the IR pulse used for the SFG process is split off with a KBr beamsplitter and used as a pump to excite the sample. The IR pump excites some of the molecules in the ground vibrational state into the first excited state resulting in a decreased population of the ground state and an increased
population in the first excited state. Then, later in time, the SFG probe (combination of IR and visible pulses) measures the surface vibrational spectrum of either the excited state or ground state, as seen in Figure 2.5a/b. Since vibrational potentials are anharmonic, the signal from molecules in the excited state appear at lower frequencies than the ground state. The time delay, $\tau_1$, between the IR pump and the HD-SFG probe is varied in order to measure the vibrational dynamics, Figure 2.5c. The absolute change induced by the pump is generally less than 10% of the signal so the unpumped, static HD-SFG spectrum is subtracted from the transient signal in order to highlight the changes in the spectrum versus time.

![Figure 2.5: For transient SFG, the energy levels for the excited state (a) and ground state (b) and the pulse timing and geometry (c).](image)
2.3.2 Two-dimensional HD-SFG

Two-dimensional HD-SFG can reveal vibrational couplings, energy transfer and frequency resolved vibrational dynamics. In a 2D HD SFG spectrum, the frequency dependence of the excitation on the transient signal is plotted in terms of the excitation ($\omega_1$) versus detection axis ($\omega_3$). Unlike 2D IR, the excitation and detection axes are not equivalent in 2D HD SFG. The pump pulses undergo twp dipole ($\mu$) transitions, whereas SFG is being detected so the detection axis depends on both the dipole ($\mu$) and polarizability ($\alpha$). Therefore, cross peaks are not equivalent, as seen in Figure 2.6.\(^\text{22}\)

![Diagram of 2D HD SFG]

**Figure 2.6:** The molecular transition type dependence for diagonal (1,2) and cross (3,4) peaks in 2D HD SFG. Reproduced from reference 22.

In 2D HD SFG, two different experimental methods have been implemented. The first uses narrowband excitation pulses to measure a transient spectrum for each excitation wavelength to build up a 2D spectrum.\(^{23,24}\) The second uses a broadband pump-pair, where the timing between the excitation pulses ($\tau_1$) is varied to interferometrically resolve the excitation axis in the 2D spectrum at a waiting time, $\tau_2$, as seen in the pulse
sequence in Figure 2.7.\textsuperscript{22,25,26} The advantage of the interferometric method is that the time and frequency resolution of the experiment is not restricted by the time-bandwidth product of the pump pulse.

![Pulse sequence used to measure 2D HD SFG.](image)

**Figure 2.7**: Pulse sequence used to measure 2D HD SFG.

For broad peaks like the OH stretching modes, the homogeneous and inhomogeneous broadening of the peak is of particular interest. The shape of the peaks along the diagonal in the 2D spectrum provides information on the peak broadening. Peaks that are homogenously broadened appear round and symmetric, whereas peaks that are inhomogenously broadened are elongated along the diagonal. Directly after excitation, an inhomogenously broadened peak will appear elongated because the excitation is isolated to the subpopulation that was directly excited, Figure 2.8a. However, as the time between the excitation and detection is increased, the molecules excited at a given frequency will sample all the possible configurations and become homogenously broadened, Figure 2.8b. The time it takes the system to evolve from inhomogenously to homogenously broadened via spectral diffusion is the correlation time, $\tau_c$.  

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Figure 2.8: An inhomogenous lineshape after excitation (a) that becomes homogenously broadened after the correlation time. Adapted from reference 29.

2.4 References


(5) Bonn, M.; Nagata, Y.; Backus, E. H. G. Molecular Structure and Dynamics of Water at the Water-Air Interface Studied with Surface-Specific Vibrational


(13) Stiopkin, I. V; Jayathilake, H. D.; Bordenyuk, A. N.; Benderskii, A. V.


(20) Hamm, P.; Zanni, M. *Concepts and Methods of 2D Infrared Spectroscopy*;


CHAPTER 3

HETERODYNE-DETECTED SUM FREQUENCY GENERATION OF WATER AT SURFACES WITH VARYING HYDROPHOBICITY*

* Adapted from S.E. Sanders and P.B. Petersen J. Chem. Phys. 2019, 150, 204708

3.1 Introduction

Aqueous interfaces are ubiquitously involved in natural and technological processes. The structure and function of biomolecules depend on their interactions with water.1–6 Technological advancements, such as proton transport in fuel cells and membrane filtration, depend on efficient processes at aqueous interfaces.7–10 When water comes into contact with a surface, the bulk hydrogen-bonding network is terminated and the interfacial water molecules restructure according to the surface chemistry of the interface. Given the complexity of both natural and technical interfaces, obtaining a detailed understanding of the dependence of the structure of interfacial water on the chemical and physical characteristics of the interface is a first step in elucidating the role of water at these interfaces. However, interfacial water is notoriously difficult to study experimentally since the number of water molecules at the interface is miniscule compared to the bulk.

Sum frequency generation (SFG) is a second order non-linear vibrational spectroscopy, which is forbidden in centrosymmetric media under the dipole approximation. As a result, only the interfacial water results in an SFG signal since the surface breaks the inversion symmetry that exists in bulk water. In recent years, SFG has been used to study interfacial water in a variety of different systems by probing the
OH stretch region, as overviewed in several review papers.\textsuperscript{11–16} However, the majority of SFG studies use conventional, homodyne-detected SFG, which measures the norm squared of the second-order nonlinear susceptibility ($|\chi^{(2)}|^2$). Although homodyne-detected SFG provides the vibrational spectrum of the interfacial water, the sign information of the nonlinear susceptibility is lost, and the spectrum is distorted by interferences between resonances and with the nonresonant background. Heterodyne-detected SFG (HD-SFG) is an interferometric method that allows the complex $\chi^{(2)}$ to be measured directly. The imaginary part of $\chi^{(2)}$ (Im $\chi^{(2)}$) is purely absorptive and is thus analogous to the bulk vibrational spectrum, while the sign of the spectrum provides information on the orientation of molecular species. The use of HD-SFG has aided the understanding the structure and orientation of water at the air-water and surfactant (or lipid)-water interfaces. At the air-water interface, the HD-SFG spectrum showed that the hydrogen-bonded water molecules have the opposite orientation than the free OH.\textsuperscript{17–22} For lipid-water interfaces, the comparison of homodyne-detected SFG and HD-SFG showed that the apparent red-shift of the hydrogen-bonded water peak for cationic lipids compared to anionic or zwitterionic lipids was skewed due to the real part of $\chi^{(2)}$, not from stronger hydrogen-bonded water.\textsuperscript{23} The sign information from HD-SFG also helped identify weakly hydrogen-bonded water molecules interacting with the carbonyl of the lipid headgroup.\textsuperscript{24} However, the use of HD-SFG to probe solid-water interfaces are still limited due to the added experimental complexity.\textsuperscript{25–27} We recently presented a new experimental geometry, which is robust, flexible and allows for the solid-water interface to be probed nearly as easily as the exposed surface.\textsuperscript{25}
The chemical composition of surfaces can be conveniently tuned using self-assembled monolayers (SAMs). Both thiol-based SAMs on gold and silane-based SAMs on silica have been studied with SFG.\textsuperscript{28–37} However, silane monolayers are simpler to implement for studying the interaction of water with SAMs since the interface can be accessed through the substrate. Fused silica substrates obstruct the high-frequency side of the OH stretch frequency due to silanol groups. In order to probe the entire OH stretch frequency, an infrared-grade fused silica window or calcium fluoride window coated with a thin layer of silica need to be used.\textsuperscript{32,38} Silica-coated calcium fluoride offers an additional advantage of being transparent in the OD stretch region as well. Hydrophobic monolayers, namely octadecyltrichlorosilane (OTS), have been studied by a number of groups. The overall structure of the water is similar to the hydrophobic air-water interface, but spectrum is dependent on experimental geometry and monolayer order.\textsuperscript{29,30} However, only a few studies examining water at hydrophilic or charged monolayers exist.\textsuperscript{33–35} By using different silanes, the surface character can be tuned from hydrophilic to hydrophobic. An ideal hydrophilic monolayer would be OH terminated, but the terminal hydroxyl group renders it incompatible with silane based SAMs. In this study, we use a commercially available silane containing the polyethylene glycol (PEG) repeating unit as the hydrophilic monolayer of interest. Monolayers with intermediate surface character can be made by using a silane with a head group of intermediate hydrophobicity, such as methoxy terminated,\textsuperscript{39} or by creating a mixed monolayer of a hydrophilic and a hydrophobic silane.\textsuperscript{40,41} Mixed monolayers are heterogeneous, chemically complex, and provide a controlled way to approach the natural heterogeneity of biological molecules. In this study, we employ
HD-SFG to probe water in contact with hydrophobic, hydrophilic, and mixed monolayers in order to elucidate how surface chemistry changes the hydrogen-bonding strength and structure at the interface.

3.2 Experimental Methods

3.2.1 Sample Preparation

Samples were prepared on 1 mm thick calcium fluoride windows (Crystran Ltd.) coated with 10 nm of silica. The silica was deposited using an Oxford Instruments ALD FlexAL atomic layer deposition system (110°C, plasma). After deposition of silica, a 150 nm thick gold reference spot with a 5 nm titanium adhesion layer was sputtered on to the substrates with a magnetron argon sputtering deposition system. The order of the silica and gold reference is important for achieving consistent interference with the local oscillator between the gold and the sample. The substrates were annealed at 800°C in a high-vacuum furnace before the synthesis of self-assembled monolayers.

Prior to self-assembled monolayer deposition, all glassware was cleaned for at least 30 minutes in a Nochromix solution prepared by dissolving Nochromix cleaning reagent (Godax Laboratories) in concentrated sulfuric acid (Fisher Scientific, certified ACS Plus) according to directions on the Nochromix packaging. All glassware was washed to neutral pH with ultrapure water (18.2 MΩ·cm resistivity at 25°C, 5 ppb TOC) generated with a Milli-Q Advantage A10 system (EMD Millipore) and dried in an oven at 150°C for an hour. The hydrophobic monolayer was synthesized according to a previously published procedure.32 Briefly, 15 µL of octadecyltrichlorosilane (OTS,
≥95%, Sigma-Aldrich) was added to 15 mL of hexanes (HPLC grade, Fisher Scientific). The substrates were submerged for 1.5 hours, then washed with hexanes and sonicated for 5 minutes in hexanes and 5 minutes in Milli-Q water. The OTS monolayer was dried with nitrogen and stored dry. A silane containing the PEG repeating unit, 2-[methoxy(polyethlyeneoxy)₆-₉propyl]trichlorosilane (Gelest), was used for the synthesis of the hydrophilic and mixed monolayers studied. The deposition of the hydrophilic and mixed monolayers were adapted from previously published procedures.⁴⁰,⁴¹ The hydrophilic monolayer, referred to as PEG, was synthesized by adding 1.5 mL of 2-[methoxy(polyethlyeneoxy)₆-₉propyl]trichlorosilane to 15 mL of toluene (HPLC grade) and submerging the substrates for 24 hours. After 24 hours, the substrates were washed with toluene and sonicated for 5 minutes in toluene and 5 minutes in Milli-Q water. The PEG monolayer was dried with nitrogen and stored in toluene. The mixed monolayer, referred to as OTS/PEG, was synthesized in a two-step process due to the large difference in deposition time for OTS and PEG. First, the substrate was submerged in a solution of 15 µL of OTS in 15 mL of toluene for 0.5 hours. The substrate was rinse with toluene and placed in a solution of 1.5 mL of PEG in 15 mL of toluene for 24 hours. Then, it was washed with toluene and sonicated for 5 minutes in toluene and 5 minutes in Milli-Q water. Finally, the OTS/PEG monolayer was dried with nitrogen and stored in toluene. In depositing the mixed monolayer, we aimed to create a monolayer with both OTS and PEG character. In addition, the mixed monolayer conditions used in this study, two other synthesis conditions were tested with contact angle goniometry. If OTS and PEG were deposited in a single step, the contact angles were very close to pure PEG for most spots. If a two-step procedure where OTS
was deposited for one hour instead of half an hour, the average contact angle was only slightly lower than pure OTS. The two-step monolayer deposition process with only a half an hour deposition of OTS resulted in a contact angle that is approximately halfway between the pure OTS and pure PEG monolayers and was thus chosen for the SFG studies. However, our experiments do not provide a way of measuring the monolayer composition precisely. Depositing the OTS monolayer from a solution in toluene was also investigated but led to more disordered monolayers. Accordingly, hexanes was used for the synthesis of OTS monolayers instead of maintaining a consistent solvent for all three monolayers.

3.2.2 Contact Angle Goniometry

The macroscopic surface character of the SAMs was determined using a home-built contact angle goniometer. A collimated white light source (tungsten-halogen lamp, ThorLabs QTH10) illuminates a stage, and a microscope objective (5x, Zeiss) focuses the image onto the camera (1280 x 1024 monochrome CMOS camera, ThorLabs DCC1545M). A neutral density filter (ND20, ThorLabs) and a blue dichroic filter (FD1B, ThorLabs) are placed between the microscope objective and camera to reduce the intensity of light into the sensor and increase the image resolution on the monochrome CMOS sensor by reducing the effect of chromatic aberration, respectively. The sample stage was cleaned with acetone before placing a substrate on the stage. Using a 25 µL syringe, 3 µL of Milli-Q water is deposited on the substrate. An image of the droplet is collected using UC480 Camera Manager and the contact angle is analyzed using the DropSnake plugin in ImageJ. Three droplets (six angles total) were analyzed for each monolayer to determine the average contact angle and distribution.
3.2.3 Sum Frequency Generation

The heterodyne-detected sum-frequency generation spectrometer has been described in detail elsewhere.25 Briefly, a Ti:sapphire amplifier (Coherent Legend Elite Duo) seeded by a Ti:sapphire oscillator (Coherent Micra-5) generates 25 fs, 800 nm, 5 mJ pulses at a 1 kHz repetition rate. The visible, upconversion pulse is generated by filtering 1 mJ of the output with a Fabry-Perot etalon (TecOptics, Inc.). The resonant IR beam is generated by converting 3 mJ of 800 nm light into tunable broadband IR pulses in a commercial optical parametric amplifier (Coherent OPerA Solo). The full-width-half-maximum bandwidth of the IR pulses generated with the OPA is approximately 250 cm\(^{-1}\). Henceforth, four OPA positions were used to cover the entire CH and OH stretch regions. Before the sample, the visible (central wavelength 792.8 nm, bandwidth 0.7 nm, pulse energy 10 µJ) and IR (central wavelength between ~3000 cm\(^{-1}\) and ~3600 cm\(^{-1}\), pulse energy 5 µJ) are focused into a 150 nm thin film of ZnO sputtered onto a 0.5 mm thick CaF\(_2\) window to generate the local oscillator. The three beams (SFG\(_{LO}\), visible, and IR) are collimated with a 90° off-axis parabolic mirror (ThorLabs, MPD269-P01) and the SFG\(_{LO}\) is delayed in time with respect to the visible and IR beams by a 2 mm thick CaF\(_2\) window placed in the collimated region. The beams are refocused with a 60° off-axis parabolic mirror (PIKE Technologies, 300-1246-51) onto the sample to generate SFG\(_{\text{reference}}\) or SFG\(_{\text{sample}}\). The spot size of the IR beam is ~450 µm at the sample position and the visible beam is slightly larger to ensure upconversion of all the excited vibrations. The sample cell consists of a PTFE coated o-ring sandwiched between the sample and a PTFE back plate with two holes, as illustrated in Figure 3.1. All the SFG data presented here is from the backside solid-air and solid-water interface.
To go from dry to wet monolayers, water was injected into the cell through PTFE tubing stuck in the holes of the PTFE back plate. The SFG signals are focused onto the slit of a polychromator (Princeton Instruments, Acton SP2500) where they are dispersed by a diffraction grating (600 grooves/mm, blazed at 500 nm), and the resulting signal was imaged on a liquid nitrogen cooled CCD camera (Princeton Instruments, model 7509-0001, 1340 x 400 pixels). To collect “homodyne-detected” data, the LO was blocked in the collimated region.

![Figure 3.1: Experimental setup for HD-SFG spectrometer and sample cell geometry.](image)

The phasing procedure for our HD-SFG experiments have been previously been described in detail. A gold spot is deposited on the silica coated CaF$_2$ in the same plane as the SAM monolayer and is used as an initial non-resonant reference for phasing our HD-SFG spectra. A 15 nm thin adhesion layer of titanium is used to fasten the gold. Prior to performing the heterodyne analysis, the data from each OPA position were summed together, as seen in Figure 3.2. Due to the high phase stability of our
experimental design\cite{ref25}, no phase drift between OPA positions was observed. Since the absolute phase of gold can change from sample to sample, the relative phase between the gold reference and the sample was adjusted after the initial phasing by a few tens of degrees such that the imaginary spectrum is zero where no molecular absorbances exist (i.e. the regions below the CH stretches and above the OH stretching frequencies). This procedure has previously been used successfully\cite{ref27,ref42}. The method only assumes that the phase from gold is constant across the spectrum, but does not rely on knowing the absolute phase of gold and corrects for small differences in the sample and reference position. We estimate our error in our phase to be better than ±20 degrees. Further details on the phasing procedure used are described in detail below.

\textbf{Figure 3.2:} HD-SFG fringes for individual OPA positions for Au (top) and OTS (bottom) in red, orange, green and blue and the sum of the fringes in black.
3.3 Results and Discussion

Contact angle goniometry and homodyne-detected SFG of the CH stretches were performed in order to characterize the chemical surface character and order of the synthesized SAMs. The contact angle is determined by the differences in the surface tension between the water-solid, water-air, and solid-air interfaces. A larger contact angle is indicative of a more hydrophobic surface. Contact angles can range from 0° (superhydrophilic, no drop) to 180° (superhydrophobic, drop only touches solid at a single point) with 90° being the turning point between hydrophilic and hydrophobic. By measuring multiple water droplets for each sample, the overall hydrophilicity/hydrophobicity and the uniformity of the SAMs using the average contact angle and standard deviation was determined. Representative contact angles for each of the monolayers are displayed in Figure 3.3. For the OTS monolayer synthesized in hexanes, the contact angle was 114.7° ± 2.4° indicating that the surface was hydrophobic and uniform. When the OTS monolayer was deposited in toluene instead, the contact angle was 102.9°. The lower contact angle corresponds to a less hydrophobic monolayer, which is one reason why we focused on the OTS monolayer deposited from hexanes in this study. The pure PEG monolayer was determined to be hydrophilic and uniform with a contact angle of 38.5° ± 2.9°. This PEG monolayer is less hydrophilic than freshly cleaned silica, which has a contact angle near 0°, due to the less hydrophilic nature of the PEG repeating unit compared to the silanol groups. As expected, the mixed OTS/PEG monolayer exhibited a contact angle between the two pure monolayers, 80.5° ± 10.7°, but closer to the pure hydrophobic monolayer. The standard deviation for OTS/PEG is significantly larger than the pure monolayers indicating that the surface is
not uniform, some regions have more OTS character and some regions have more PEG character. In depositing the mixed monolayer, we aimed to create a monolayer with both OTS and PEG character. In addition, the mixed monolayer conditions used in this study, two other synthesis conditions were tested with contact angle goniometry. If OTS and PEG were deposited in a single step, the contact angles were very close to pure PEG for most spots. If a two-step procedure where OTS was deposited for one hour instead of half an hour, the average contact angle was only slightly lower than pure OTS. Of the three synthesis conditions tried, we chose the mixed monolayer that was closest to 50/50 as determined by contact angle. However, our experiments do not provide a way of measuring the monolayer composition precisely.

Figure 3.3: Sketch of SAM structure (carbon atoms in black, hydrogen atoms in white, and oxygen atoms in red), representative contact angle droplet, and homodyne SFG spectra of the CH stretch spectral region of dry and wet monolayer for the three SAMs studied.
While the contact angles reflect macroscopic interactions, the SFG spectroscopic measurements probe microscopic interactions. In order to study the microscopic order of the SAMs and how it relates to the macroscopic order measured with the contact angles, we probed the CH stretches of the dry monolayers with SFG. Due to the symmetry requirements of SFG, it is highly sensitive to the order of the monolayers.\textsuperscript{30,32} Each of the monolayers exhibits two types of CH groups, the terminal methyl groups and the methylene groups in the chains. For a well-ordered monolayer, every other methylene group points in opposite directions and destructively interfere producing no overall SFG response from the methylene groups. Conversely, the terminal methyl groups point in the same direction and result in a strong signal. However, the introduction of gauche defects in the SAMs disrupts the perfect destructive interference of the methylene groups. Previously, our group studied the order of mixed length hydrophobic monolayers through the appearance of SFG signals from the methylene groups.\textsuperscript{32} Here, we use the relative intensity of methylene to methyl SFG signal to qualitatively investigate the order of the different SAMs. The dry OTS monolayer exhibits small amounts of methylene character, Figure 3.3. The two main peaks result from a methyl groups (the symmetric methyl stretch and the symmetric methyl stretch + fermi resonance), and the shoulders result from methylene groups not canceling perfectly. Accordingly, the dry SFG spectrum of OTS indicates that the monolayer is well ordered but contains a few gauche defects. When OTS was deposited from toluene instead of hexanes, the contact angle was approximately 5 degrees lower and exhibited a more distinct CH\textsubscript{2} peak at \textasciitilde2850 cm\textsuperscript{-1} indicating more disorder, Figure 3.4.
Unlike OTS, the PEG monolayer has significant methylene character and is consequently significantly more disordered. This is largely due to the variable chain length of the commercial silane (6-9 PEG units), which allows for longer chains to bend over shorter chains. While, Van der Waals interactions are responsible for keeping the chains ordered and extended, if a long chain is deposited next to a short chain, the end of the long chain is free to bend and introduce methylene character into the SFG spectrum. Even though there is disorder as a result of the variable chain length and the precise ratio of chain lengths is unknown, the SFG spectrum of the dry PEG monolayer is similar at multiple locations on the sample, as displayed in Figure 3.5, which confirms that the sample is uniform as predicted by contact angle measurements. The gauche defects from the mismatched chain lengths also exposes the oxygens in the PEG chain improving the hydrophilicity of the monolayer. The mixed OTS/PEG monolayer has the largest methylene peak relative to the methyl peak and is accordingly the most disordered monolayer. This is a result of the inherent disorder of the PEG monolayer.

**Figure 3.4:** CH stretching modes for the dry OTS monolayers synthesized from hexanes and toluene. Monolayer deposited from toluene has more distinct CH\textsubscript{2} modes indicating disorder.
with different chain lengths, as well as disorder and defects created by mixing OTS and PEG. As expected from the large standard deviation of contact angles, the mixed OTS/PEG monolayer is not uniform as indicated by different CH stretch spectra at different regions of the sample, as shown in Figure 3.6. Our SFG spectrometer does not provide enough spatial resolution to specially resolve the composition and patterning of the sample region. The sample position resulting in the spectrum displayed in Figure 3.3 was chosen for studying the interaction of water with the mixed monolayer since it had the largest methyl peaks confirming the presence of hydrophobic chains. Furthermore, the methylene peaks at this spot line up with the methylene peaks of pure OTS and pure PEG and accordingly both hydrophobic and hydrophilic moieties exist within the probe area.

![SFG spectra of the CH stretch modes for three different spots on the PEG sample exhibiting similar spectral shapes and intensities.](image)

**Figure 3.5:** SFG spectra of the CH stretch modes for three different spots on the PEG sample exhibiting similar spectral shapes and intensities.
Upon the addition of Milli-Q water, we first examined how the CH stretch region changed after interacting with water using homodyne-detected SFG. The hydrophobic, OTS monolayer does not strongly interact with the water and the CH stretch region retains the two strong peaks resulting from the terminal methyl groups. However, the PEG containing monolayers change in shape because the water can strongly interact with the oxygens within the PEG chains. The PEG containing monolayers also exhibit a relative decrease in intensity, which is most dramatic in the pure PEG monolayer since the entire monolayer can hydrogen bond with the water. Whereas, the mixed OTS/PEG monolayer maintains some of its structure due to the hydrophobic OTS chains. The examination of the CH stretch region is useful in comparing the relative interactions and flexibility of the monolayers, however, the OH stretching region provides a more direct comparison of the strength and orientation of water molecules at the various monolayers.

![SFG spectra of the CH stretch modes for four different spots on the OTS/PEG sample with varying spectral shape and intensity.](image)

**Figure 3.6:** SFG spectra of the CH stretch modes for four different spots on the OTS/PEG sample with varying spectral shape and intensity.
The OH stretch region in both homodyne-detected and HD-SFG spectroscopy is shown in Figure 3.7. The OH region of water in contact with all three monolayers exhibits the double peaked structure, which has been seen in the SFG spectra of water at a variety of interfaces and is caused by the intra- and inter-molecular coupling between the OH groups.\textsuperscript{11–16} However, the relative intensity of the two peaks differs between the samples with the PEG containing monolayers producing a stronger relative water signal. The OTS spectrum additionally contains the free OH at \( \sim3680 \text{ cm}^{-1} \) that is characteristic of water in contact with the hydrophobic surface. Water in contact with OTS has been studied by a number of groups.\textsuperscript{30,44–46} Overall, the present homodyne detected spectrum of OTS, Figure 3.7, is comparable to the spectra in the literature. The free OH peak, predominant methyl stretches, and large contact angle confirm the hydrophobicity of our OTS monolayer. Differences in the hydrogen-bonded region of water at OTS likely result from differences in monolayer order and experimental geometry.\textsuperscript{28,30} Tyrode and coworkers explored the relation between the intensity of the hydrogen bonded OH stretch region of water and the monolayer order, and suggested that the hydrogen bonded OH stretching intensity is dominated by direct silica-water interactions from water in cracks in the monolayer. Previous atomic force microscopy measurements have quantified the amount of cracks in OTS monolayers to be only a few percent of the surface area.\textsuperscript{32,46} If water molecules inside defects in the monolayer covering a few percent of the surface area would dominate the hydrogen bonded water signal, they would have to be highly aligned, which seems unlikely. Furthermore, the fact that we observe spectral differences between the three different monolayers directly shows that the hydrogen-bonded region is not solely due to water molecules in contact
with silica. While it is difficult to estimate the contribution of such trapped water molecules, the study by Tyrode and coworkers clearly shows that the hydrogen-bonded region can vary significantly depending on the monolayer order, which presents some uncertainty in quantifying the spectrum of monolayer-water interfaces.

![Graphical representation of the SFG spectra and imaginary component](Figure 3.7: Homodyne-detected SFG spectra (top) and the imaginary component of $\chi^{(2)}$ (bottom), measured by HD-SFG, of water in contact with the three SAMs. Dashed vertical line indicates the shift in peak frequency between the homodyne-detected spectra and $\text{Im}(\chi^{(2)})$.

Since homodyne-detected SFG measures the norm squared of $\chi^{(2)}$, which results the complex mixing of the real and imaginary components, we performed HD-SFG of water at each interface to extract the purely absorptive imaginary component and dispersive real component of $\chi^{(2)}$ for each monolayer, Figure 3.8. Although the general peak structure of the hydrogen-bonded OH stretching region is maintained, there is a red shift of about 50 cm$^{-1}$ compared to the homodyne-detected spectrum, Figure 3.7. This
The frequency shift is consistent between the three monolayers, which were independently phased, and remains significant within our phase accuracy of +/-20°, which is discussed further in Chapter 6, confirming that the frequency shift is not an artifact of phasing. This red shift of the OH stretch peak could result from the real part of the $\chi^{(2)}$ skewing the spectrum or interferences between peaks of opposing signs and was previously observed in HD-SFG spectra of lipid-water interfaces. Since the 50 cm$^{-1}$ shift is consistent for all three monolayers, while OTS does not have a negative hydrogen-bonding OH stretch peak, the red shift in the double peaked spectral feature results from the real part of $\chi^{(2)}$. Often SFG spectra of water are used to describe the hydrogen bonding strength of interfacial water since the OH stretching frequency correlates to hydrogen bonding strength. However, due to the real part of $\chi^{(2)}$ skewing the spectrum, using homodyne-detected SFG can lead to an inaccurate picture of the hydrogen bonding strength of interfacial water.

Figure 3.8: Real (blue) and imaginary (red) components of the entire spectrum recovered from summed HD-SFG spectra, and the measured homodyne-detected SFG (black) spectra for all three monolayers.
By performing HD-SFG, the sign of the $\text{Im}(\chi^{(2)})$ spectrum is also recovered, which provides information on the relative orientation of the dipoles. This additional sign information furthermore makes it easier to identify weak spectral features. For example, in the homodyne-detected SFG spectrum of OTS, Figure 3.7, only two main CH stretching peaks are apparent. However, in the HD-SFG spectrum, the $\text{Im}(\chi^{(2)})$ has two positive peaks and two negative peaks in the CH stretching region. These peaks have previously been identified as the CH$_3$ symmetric stretch ($r^+$), the CH$_2$ asymmetric stretch ($d^-$), the CH$_3$ Fermi resonance of the bending overtone with $r^+$ ($r^+$FR), and the CH$_3$ asymmetric stretch ($r^-$). The fit analysis of the CH stretching region of OTS, Table 1, is in good agreement with previous analyses of the imaginary spectrum of OTS. The OTS/PEG and PEG monolayers have similar CH stretching peaks with alternating signs. Even though the peaks corresponding to the terminal methyl symmetric stretching vibrations are positive, the methyl group is pointing down since the hyperpolarizability of the CH stretch is negative. As expected, the free OH and the methyl stretch in OTS have opposite orientations, indicating the free OH points toward the hydrophobic interface. However, the the hydrogen bonded water and the free OH have the same sign and orientation. This finding agrees with previous measurements of the OTS-water interface, but differs from the air-water interface, which has been shown to have the free OH in the opposite orientation of the hydrogen-bonded water. The hydrogen-bonded region in the imaginary spectrum of water in contact with OTS, Figure 3.7, differs to some extent from that measured by Shen and coworkers. However, both the CH peaks and free OH match well. From homodyne SFG, it is known that monolayer order has a large effect on the hydrogen bonded OH stretch resonse,
which could potentially explain the discrepancy in the imaginary spectra. Additionally, Shen and coworkers phased their spectrum with quartz, which has since been shown to result in a peak not related to a vibrational resonance at the water-air interface around 3000 cm$^{-1}$ and problematic as a phase reference for the buried surfaces due to difference in propagation media, which could be another possible reason for the discrepancy. Roke and coworkers have also presented an imaginary spectrum of OTS that has the same sign and general structure of the imaginary spectrum of OTS in Figure 3.7. By using the sign information from the HD-SFG spectrum of the OTS, a snapshot of the average water orientation at the interface can be built up, as illustrated in Figure 3.9.

![Illustration of interfacial water interacting with the three SAMs. Black arrows illustrate the terminal methyl stretches pointed toward the water. Blue arrows illustrate the hydrogen-bonded OH stretches with an overall orientation towards the monolayer. Green arrows illustrate water molecules interacting directly with the SAMs: the free OH for OTS and the strongly hydrogen-bonded water interacting with the PEG chains for OTS/PEG and PEG.](image-url)

**Figure 3.9:** Illustration of interfacial water interacting with the three SAMs. Black arrows illustrate the terminal methyl stretches pointed toward the water. Blue arrows illustrate the hydrogen-bonded OH stretches with an overall orientation towards the monolayer. Green arrows illustrate water molecules interacting directly with the SAMs: the free OH for OTS and the strongly hydrogen-bonded water interacting with the PEG chains for OTS/PEG and PEG.
The SAMs were assembled on a thin layer of silica. All the experiments described here were performed under neat water with approximately pH 5.6 due to adsorbed CO₂. At this pH, the underlying silica layer would be negatively charged. Studies of water at the bare silica surface have shown a large Eisenthal $\chi^{(3)}$ effect due to the negative charge of silica at neutral and basic pH values. Accordingly, a negative charge on the silica under the SAMs would create a static electric field that is likely contributing to a net orientation of the hydrogen-bonded water molecules towards the interface. Previous homodyne-detected SFG studies of the OTS-water interface showed a spectral dependence on the pH and ionic strength, confirming an Eisenthal $\chi^{(3)}$ effect due to the underlying silica. However, the spectral differences between the monolayers show that the chemical interactions between the monolayer and the water cause distinct spectral shapes independent of the charge on the silica. By screening the charge from the silica surface with salt, the overall intensity of the water spectrum would be expected to decrease. In order to determine the full extent of the silica’s effect on the spectrum, further studies varying the pH and ionic strength are needed, as described in Chapter 4.

As described above, HD-SFG allowed for the identification of additional CH stretching peaks based on differences in sign. Similarly, distinct spectral features in the OH stretch region of water can be identified and fitted in the spectra for PEG containing monolayers based on the spectral sign. For both the mixed OTS/PEG monolayer and the PEG monolayer, there is a broad negative peak between the CH stretching region and the dominant, positive double-humped OH structure, Figure 3.7. Since this strongly hydrogen-bonded water only exists for the PEG containing monolayers, it likely results from water hydrogen bonding with the oxygens in the PEG chains, as illustrated in
Figure 3.9. With the lack of free OH and the presence of the negative strongly hydrogen bonded peak, the structure of the interfacial water at the mixed OTS/PEG monolayer is dominated by the PEG chains.

A more detailed comparison of the hydrogen bonded region can be achieved by fitting the imaginary spectra. Typically, SFG data is fit with Lorentzians since they explicitly contain real and imaginary components,\(^\text{59-62}\) where a few studies have used Voigt profiles to describe the inhomogeneous broadening while maintaining explicit real and imaginary components.\(^\text{63-65}\) Fitting with Lorentzian line shapes has been effective in fitting homogenously broadened peaks, such as CH stretches, but is not ideal for fitting inhomogenously broadened peaks, like that of hydrogen-bonded water. Obtaining the imaginary component of the nonlinear susceptibility allows the absorptive spectrum to be fit by peaks with any lineshape function, such as Gaussians to quantify the spectral features. Since the CH stretching peaks are expected to be homogenously broadened, they were fit with the imaginary component of a Lorentzian lineshape, whereas the water peaks are fit with Gaussian lineshapes. The imaginary component was fit with five Lorentzians for the CH stretches and three or four Gaussians for the water peaks.

\[
\text{Im} \left( \chi_{\text{HD-SFG}}^{(2)}(w_{\text{IR}}) \right) = \sum_{j=1}^{5} A_j \frac{(w_j - w_{\text{IR}})}{(w_j - w_{\text{IR}})^2 + \Gamma_j^2} + \sum_{k=1}^{3/4} A_k e^{-\frac{(w_{\text{IR}} - w_k)^2}{2 \sigma^2}} \tag{3-1}
\]

where \(A\) is the amplitude, \(\omega\) is the peak frequency, \(\Gamma\) is the Lorentzian linewidth and \(\sigma^2\) is the variance of the Gaussian function. The fitted peaks and the total fit compared to the experimental spectra for all three SAMs are shown in Figure 3.10. The total fits are in good agreement with the data, as illustrated by the bold, black curves (fits)
overlapping the bold, red curves (experiments) well across the entire spectrum. The full set of fit parameters can be found in Table 3.1. Each spectrum was fit with a total of eight or nine total peaks. The number of resonances included in the fit was chosen based on the minimum number that still yielded a reasonable fit, as based on the residuals, and guided by previous assignments in the literature. The CH region was fit with 5 Lorentzians corresponding to different CH$_3$ and CH$_2$ stretching modes, and the OH stretch region was fit with up to 4 Gaussians for each spectrum.

**Figure 3.10:** Experimental data (red, bold) and Fit (black, bold) for all three SAMs. The 5 Lorentzians for the CHs are in red, red-orange, orange, green, and light blue. The Gaussians for the hydrogen bonded water are in purple and magenta. The Gaussian for the free OH (for OTS) or negative, strongly hydrogen-bonded peak (for OTS/PEG and PEG) is in dark blue. The final Gaussian for OTS is in aqua.
Table 3.1: The fit parameters for all three monolayers. Each Lorentzian has an amplitude, linewidth (Γ), and center frequency (ω). Each Gaussian has an amplitude, standard deviation (σ), and center frequency (ω). The ratio of the two hydrogen-bonded peaks (Gaussian 2 and Gaussian 3) for all monolayers was also calculated as a measure of relative hydrogen bonding strength.
For the pure OTS monolayer, the observed CH resonances are comparable to those obtained in previous experiments.\textsuperscript{25,47,48} Lorentzians 1-5 used to fit the CH stretching modes correspond to d\(^+\) (CH\(_2\) symmetric), r\(^+\) (CH\(_3\) symmetric), d\(^-\) (CH\(_2\) asymmetric), r\(^+\)FR (CH\(_3\) symmetric + Fermi Resonance), and r\(^-\) (CH\(_3\) asymmetric) respectively. To our knowledge, no prior SFG studies exist for similar PEG monolayers and we do not attempt to further assign the CH resonances here. Qualitatively, the CH resonances for the PEG containing monolayers are similar to OTS and were thus fit to the same CH stretching modes. However, the CH resonances for the pure PEG monolayer generally exhibit broader linewidths compared to the pure OTS monolayer reflecting the larger disorder caused by the distribution of chain lengths. The mixed monolayer could exhibit a number of resonances observed in either pure monolayer. For simplicity, we also fit CH region of the mixed monolayer to 5 Lorentzians since this was sufficient to obtain a reasonable fit. For the mixed monolayer, the linewidths lie in between those for the two pure monolayers. We note that the resolution of the heterodyne-detected experiment is not fine enough to resolve separate peaks for the OTS and PEG components for each CH mode.

The OH stretching region was fit with 4 Gaussians for the pure OTS and 3 Gaussians for OTS/PEG and PEG. These Gaussians are numbered 1 through 5 by increasing frequency, with Gaussian 1 only existing for the PEG containing monolayers and Gaussians 4 and 5 only existing for the pure OTS monolayer. For all three monolayers, Gaussians 2 and 3 are the hydrogen-bonded OH stretch modes that make up the double peaked feature typically observed around 3200 and 3400 cm\(^{-1}\) for H\(_2\)O surfaces and result from the inter- and intra-molecular couplings between the OH modes. Gaussian
4 around 3600 cm⁻¹ is only present in the sample of the pure OTS monolayer and was added to improve the fit. It has a similar frequency to a silica peak recently observed with SFG, and likely results from the silica coated CaF₂. This peak is not always present but has been observed on multiple samples. Gaussian 5 is the free OH. For the mixed OTS/PEG and pure PEG monolayers, Gaussian 1 of opposite sign as Gaussians 2 and 3 was added to improve the fit. We attribute these features to water molecules that are hydrogen-bonded to the PEG chains more strongly that the rest of the water populations. Similar peaks with signs opposite to the main hydrogen-bonding peaks have previously been seen at the lipid-water interface.²⁴ Fitting the water resonances with Lorentzians instead of Gaussians led to significantly poorer fit, as shown in Figure 3.11. The inaccuracy of Lorentzian lineshapes reproducing the imaginary spectrum of water highlights that the OH spectrum of water is inhomogeneous broadened and that obtaining the purely absorptive lineshape is needed to accurately fit the water spectrum. In order to fit the homodyne-detected spectrum of water, an algorithm to extract the imaginary component, such as the Maximum Entropy Method, or a more complex lineshape, such as a Voigt profile, must be used. However, while fitting the imaginary susceptibility allows for quantifying the spectral features, care must to taken in assigning them to specific sub-populations of water given the spectral distortions caused by inter- and intra-molecular couplings. In order to fully understand the sub-populations of water interacting with monolayers, isotope dilution experiments are needed to remove the inter- and intra-molecular couplings.
Without assigning the hydrogen-bonded water peaks to specific populations at the interface, the spectral fits allows for quantifying of the relative hydrogen-bonding...
strengths between monolayers by calculating the ratio of the amplitudes of the two peaks that comprise the double-peak structure. The ratios of the stronger hydrogen-bonded peak to the weaker hydrogen-bonded peak are 1.16, 1.5, and 1.67 for OTS, OTS/PEG, and PEG respectively. This indicates that on average the hydrogen-bonding strength of the interfacial water in contact with PEG is the strongest and that the ratio for the mixed OTS/PEG monolayer is between the two pure monolayers, as expected given its composition, but closer to that of the pure PEG monolayer. Overall the HD-SFG spectroscopic data shows that the molecular hydrogen-bonded structure of water in contact with the mixed monolayer is closer to that of water in contact with the pure PEG monolayer, where the macroscopic properties as captured in the contact angle measurement as closer to the pure OTS monolayer.

3.4 Comparing the Norm Squared Spectra to Homodyne Detected Spectra

In conventional SFG, the measured SFG intensity is

\[ I_{\text{SFG}} \propto |E_{\text{sample}}|^2 \propto |\chi^{(2)}|^2 \]  

(3-2)

where \( E_{\text{sample}} \) is the electric field of the SFG from the sample and \( \chi^{(2)} \) is the second-order nonlinear susceptibility. In HD-SFG, a LO with a given time delay is interfered with the sample SFG signal, resulting in the measured intensity:

\[ I_{\text{HD-SFG}} \propto |E_{\text{LO}}(t)e^{i\omega\Delta t} + E_{\text{sample}}(t)|^2 \]

\[ = |E_{\text{LO}}|^2 + |E_{\text{sample}}|^2 + E_{\text{LO}}E_{\text{sample}}^*e^{i\omega\Delta t} + E_{\text{LO}}^*E_{\text{sample}}e^{-i\omega\Delta t} \]  

(3-3)
where $E_{LO}$ is the electric field of the LO and $\Delta \tau$ is the time delay between the sample and LO electric fields. After Fourier transforming the measured HD-SFG intensity, the $E_{LO}^*E_{\text{sample}}^*e^{i\omega \Delta \tau}$ term is windowed out and the real and imaginary parts of $\chi^{(2)}$ can be extracted. The imaginary component has a purely absorptive lineshape that is comparable to bulk IR measurements. However, the real and imaginary parts of $\chi^{(2)}$ can also be used to simulate the homodyne detected spectra $|\chi^{(2)}|^2$:

$$|\chi^{(2)}|^2 = |\text{Re}(\chi^{(2)}) + i \text{Im}(\chi^{(2)})|^2$$  \hspace{1cm} (3-4)

The comparison of the calculated norm squared, $|\chi^{(2)}|^2$, from the HD-SFG experiment, to the measured homodyne-detected SFG spectra, act as a quality check of the Fourier transform analysis and windowing procedures in the HD-SFG processing. There is good agreement between the norm squared and homodyne signal for all three monolayers, as shown in Figure 3.12. The CH signal for OTS, is slightly lower in the norm squared spectra as some of the CH stretch free induction decay was cut to limit the noise in the spectrum. For the mixed OTS/PEG and PEG monolayers, there is slightly lower intensity in the norm squared spectra on the high frequency side due to inconsistent LO overlap across different IR wavelengths.
3.5 Conclusion

In this study we have obtained homodyne-detected and HD-SFG spectra of water in contact with monolayers with tunable chemical functionality. Analyzing the HD-SFG spectra of water in contact with the monolayers revealed a red shift of the hydrogen-bonded water feature for all monolayers illustrating that the interfacial water is not as strongly hydrogen-bonded, as previous homodyne SFG spectra have suggested. While

![Graph showing comparison of homodyne SFG spectra (red) and norm squared calculated from HD-SFG (black) for all three monolayers.](image)

**Figure 3.12:** Comparison of homodyne SFG spectra (red) and norm squared calculated from HD-SFG (black) for all three monolayers.
the charged silica surface under the monolayers potentially contributed to the net ordering of the interfacial water, the distinct spectral differences between the monolayers indicates that the chemical structure of the SAMs effects the interfacial water orientation and allow for an analysis of the microscopic water structure in contact with the monolayers.

We observe that although the contact angle of the mixed monolayer is closer to the pure hydrophobic monolayer; the HD-SFG spectrum of the mixed monolayer is closer to that of the hydrophilic monolayer. This indicates that the macroscopic chemical properties of the surface are dominated by the hydrophobic parts of the monolayer, but that the molecular hydrogen-bonded water structure of the interfacial water is dominated by the hydrophilic parts of the monolayer. The study thus highlights the need for spectroscopic measurements to understand molecular-level structures since these are not easily extracted from macroscopic measurements. However, care must be taken to not assign peaks in the spectra of isotopic pure water to specific sub-populations due to the complicated inter- and intra- molecular couplings in water, warranting further studies with isotopic dilutions.

3.6 References


(31) Hopkins, A. J.; Richmond, G. L. The Water–Hydrophobic Interface: Neutral and


CHAPTER 4

MEASURING THE WATER STRUCTURE AT SAMS: ELIMINATING THE DIFFUSE LAYER CONTRIBUTION AND VIBRATIONAL COUPLINGS

4.1 Introduction

Oxide surfaces, such as silica, accumulate surface charges when in contact with water due to the protonation/deprotonation equilibrium of surface hydroxyl groups. The equilibrium between protonated and deprotonated surface hydroxyl groups depends on the pH of the solution and the pH where the number of protonated and deprotonated surface hydroxyl groups are equal is the point of zero charge (PZC). In the case of silica, the PZC is at a pH of 2, so the surface is negatively charged at a neutral pH.\textsuperscript{1,2} The surface charge creates a static electric field which propagates into the solution at a length scale of the Debye length. This electric field orients water molecules, giving rise to an increase in the second order susceptibility proportional to the Debye length of the field and further causes a true third order response with the static electric field acting as one of the involved fields. Both these effects can be described as contributing to the second order response by an effective third order susceptibility ($\chi_{\text{eff}}^{(3)}$) times the surface potential.\textsuperscript{3,4} Therefore, the resulting SFG signal for charged surfaces can be described by two regions: the binding interfacial layer (BIL) and the diffuse layer (DL).\textsuperscript{5} The BIL are the water molecules that are perturbed directly by the surface chemistry and structure of the interface, whereas the DL are the water molecules within the Debye length that are oriented by the surface charge.\textsuperscript{5–7}
Several groups have investigated the pH\textsuperscript{8-11} and specific salt effects\textsuperscript{9,10,12-17} on the SFG spectrum of the silica-water interface. These experiments showed that there exist two types of deprotonable OH groups at the silica surface with different pKa values and that specific ion interactions significantly affect the net surface charge at this complex interface. Tyrode and coworkers furthermore showed that the SFG spectrum strongly depends on the surface pretreatment.\textsuperscript{9} Recently the spectral dependence of the interfacial electric field have been examined, showing that the intensity in the 3200 cm\textsuperscript{-1} region is due to water molecules orientated in the field and the 3400 cm\textsuperscript{-1} region is due to water molecules within the Stern layer, the tightly bound layer of ions at the interface.\textsuperscript{18} Despite the simple chemical composition of silica, the molecular interactions with water at the interface has been found to be highly dependent on sample conditions.\textsuperscript{9}

The SAMs investigated in Chapter 3 were deposited on a thin layer (~10 nm) of silica, which could add a DL contribution to the SFG signal. To eliminate the contribution from the underlying silica, two approaches are taken. The first is adding salt to the solution to screen out the surface charges. The second is to change the surface charge by changing the pH. Previous studies of the octadecyltrichrolosilane (OTS)-water interface showed changing the pH led to changes in both the spectral intensity and shape indicating that some underlying silanol groups remain unreacted and can be deprotonated similarly to the bare silica-water interface.\textsuperscript{19-21} As discussed in Chapter 3, there are spectral differences between the hydrophobic-water and hydrophilic-water interfaces, thus there are distinct spectral features from SAM-water interactions. By performing a series of salt and pH dependence experiments to remove the DL
contribution a more accurate structure of water at the interface will be measured. Furthermore, it is well known that water vibrational spectra are significantly affected by inter- and intramolecular couplings. These inter- and intramolecular couplings complicate the analysis of the water spectrum but can be removed by isotopic dilution. To obtain a detailed picture of the structure of the interfacial water, the effects of surface charge and vibrational coupling need to be removed.

4.2 Experimental Methods

4.2.1 Sample Preparation

Self-assembled monolayers used for the SFG experiments were prepared using the same method as described in Chapter 3. The hydrophobic monolayer (OTS) was deposited on a 1 mm thick window and the hydrophilic monolayer (2-[methoxy(polyethylenoxy)₆₉propyl]trichlorosilane, PEG) was deposited on a hemicylindrical prism (10x10mm diameter, Crystran Limited). The infrasil (IR grade fused silica) used was cleaned with NoChromix in sulfuric acid and rinsed with ultrapure water before use.

All the solutions used were made using glassware that was cleaned with NoChromix in sulfuric acid and rinsed to neutral pH with ultrapure water. Prior to making the solutions, sodium chloride (NaCl, Sigma Aldrich) and potassium chloride (KCl, Sigma Aldrich) were baked in a 200°C oven for 3 hours to remove any impurities. Concentrated hydrochloric acid (HCl, Sigma Aldrich), potassium hydroxide (KOH, Sigma Aldrich), and deuterium oxide (D₂O, 99.96%, Cambridge Isotope Laboratories)
were used as received. The highest concentration solutions were made by dissolving the solute (NaCl, KCl, HCl, or KOH) in ultrapure water. Lower salt concentrations were prepared by serial dilution. For the isotopically diluted water, ultrapure water and D$_2$O were mixed in a ratio of 1:3 to obtain predominantly HOD in D$_2$O ($H_2O$:HOD:D$_2$O = 1:6:9).

4.2.2 Heterodyne-Detected Sum-Frequency Generation

The experimental set-up for heterodyne-detected SFG was described in Chapter 3. Some of the data presented in this chapter was collected after the Ti:sapphire amplifier (Coherent Legend Elite Duo) was upgraded and a new nonlinear crystal (Potassium titanyle arsenate) was used to generate the mid-IR in the optical parametric amplifier (OPA). Previously, the visible, upconversion pulse filtered with a Fabry-Perot etalon had a bandwidth of 0.7 nm and the IR pulses had a bandwidth of approximately 250 cm$^{-1}$. After the upgrades, the visible, upconversion pulse filtered with a Fabry-Perot etalon had a bandwidth of 1 nm and the IR pulses had a bandwidth of approximately 350 cm$^{-1}$. Therefore, the resolution of the two experiments differs slightly. The sample cell for the hemicylindrical prism is similar to the sandwich cell used for the windows described in Chapter 3. However, a custom PTFE adapter was used to hold the prism, while the back plate was a silica window, which mean that the cell had to be filled before beginning the experiment.
4.3 Results and Discussion

Silica is naturally abundant and accordingly the silica-water interface is relevant to many geochemical applications. At neutral pH values the surface is negatively charged orienting water molecules within the Debye length due to the Eisenthal $\chi^{(3)}$ effect generating a large SFG signal. Several groups have investigated the pH$^{8-11}$ and specific salt effects$^{9,10,12-17}$ on the SFG spectrum. In the context of this dissertation, understanding the SFG response of the silica-water interface is important as the SAMs are deposited on silica and the underlying silica can result in the alignment of water molecules in the diffuse layer. Therefore, characterizing the silica-water interface can provide insight on the spectra of the SAM-water interfaces. For pure water (~pH 5.6), the SFG response of the water at the silica interface exhibits a broad, double peak, as seen in Figure 4.1. This broad, double peak also dominates the imaginary spectrum, and the positive sign indicates that the water molecules are pointed towards the silica as expected for a negatively charged surface. However, when salt is added to screen the surface charge or the pH is reduced to eliminate the surface charge, the spectral intensity is greatly reduced, the broad, double humped spectral shape is less distinct, and a small peak around 3600 cm$^{-1}$ emerges, Figure 4.1. This small peak at 3600 cm$^{-1}$ has been previously identified for the silica-water interface and was determined to be water molecules bound to siloxane bridges on the surface.$^{22}$ Both adding salt and changing the pH also changes the water orientation at the surface, as seen in the imaginary spectra in Figure 4.1. The water molecules are no longer pointing mainly toward the surface, due to the negative charge. Instead the majority of the hydrogen-bonded water molecules point away from the surface, while the water hydrogen bonding to the siloxane bridges point towards the surface. The measured imaginary spectra for the silica-water interface
are also in agreement with previously published data. Based on the results from the SFG of water at silica, both 200 mM NaCl and 0.1 M HCl (pH2) are effective at removing the diffuse layer contribution of the SFG signal.

![Homodyne-detected SFG spectra](image)

**Figure 4.1**: Homodyne-detected SFG spectra (top) and the imaginary component of $\chi^{(2)}$ (bottom), measured by HD-SFG, of the silica surface in contact with pure water (pH 5.6), 200 mM NaCl, and 0.1 M HCl (pH 2).

To classify the contribution of the diffuse layer from the underlying silica to the SFG spectra of water at the SAMs discussed in Chapter 3, the ionic strength and the pH of the solution was varied at the different SAMs. Based on the results for the silica-water interface, adding 200 mM NaCl or reducing the pH to 2 should effectively remove the diffuse layer contribution. Upon the addition of salt, the homodyne-detected SFG signal at the OTS interface is significantly reduced, indicating that the underlying silica does induce order leading to a diffuse layer contribution, Figure 4.2. Note that there is no observed free-OH in Figure 4.2 for the water-OTS interface because it is outside of
the frequency range that was probed in this experiment. Unlike the silica interface, the spectral shape of the imaginary component for the hydrogen-bonded water molecules at the OTS interface is similar with and without salt, as seen in Figure 4.2. The largest difference is the overall intensity reduction by eliminating the DL contribution with the salt. This suggests that the net orientation of the water towards the OTS was not only due to the diffuse layer contribution, but also the direct restructuring from OTS terminating the hydrogen-bond network. Although the DL will always have the same spectrum, the ratio of the BIL to the DL for OTS will be higher than for fused silica because some of the surface silanol groups are used to bind the OTS monolayer to the surface, thus the overall surface charge will be lower.

Figure 4.2: Homodyne-detected SFG spectra (top) and the imaginary component of $\chi^{(2)}$ (bottom), measured by HD-SFG, of the OTS surface in contact with pure water and 200 mM NaCl.
Unlike the silica-water interface, the 200mM salt and pH 2 results are not similar at the OTS interface. When the pH is reduced to pH 2, there is little to no water signal apparent in the homodyne-detected SFG spectra. The imaginary spectrum for pH 2 at the OTS interface also has two different signs of hydrogen-bonded water, as shown in Figure 4.3, similar to the pH 2 solution at the silica interface. Recently, we performed HD-SFG experiments at additional concentrations of salt using KCl at the OTS interface, but the results still need to be analyzed. Additional concentrations will help determine if 200 mM of salt is sufficient for screening the surface charge at the monolayer surface. Our ongoing collaboration with the Gaigeot group to simulate the SFG response of OTS with salt will further aid in understanding the specific contributions of the interfacial water.

Figure 4.3: Homodyne-detected SFG spectra (top) and the imaginary component of $\chi^{(2)}$ (bottom), measured by HD-SFG, of the OTS surface in contact with pure water (pH 5.6) and 0.1 M HCl (pH 2).
As mentioned earlier, the strong inter- and intramolecular couplings in water also significantly affect the spectral shape of the water and need to be removed to better characterize the structure of water. The broad, double humped feature present in many SFG spectra of water is a result of these strong vibrational couplings. Isotopic dilution removes the inter- and intramolecular couplings. For both the air-water and silica-water interface, the broad, double humped feature becomes one peak upon isotopic dilution.\textsuperscript{23–25} This confirms that the double humped spectral feature does not indicate two distinct water structures, but can be attributed to strong inter- and intramolecular couplings. As illustrated in Figure 4.4, the broad, double humped feature for OTS also becomes one peak upon isotopic dilution so the spectral shape is dominated by the strong inter- and intramolecular couplings. The spectral intensity is also reduced since there are less oscillators. The free OH peak is lost for HOD due to the lower number of OH groups at the surface, but a small peak corresponding to the free OD appears at \(~2750\text{ cm}^{-1}\). For pure \(\text{D}_2\text{O}\), the OH stretching region is completely flat and the free OD is slightly larger than in HOD, Figure 4.4. Therefore, both the diffuse layer from the charge of the underlying silica and vibrational couplings significantly contribute to the spectral shape of the SFG spectra. Thus far, the two contributions have only been removed independently, but removing both at the same time is necessary to measure the most accurate spectrum of water at OTS.

Since all the SAMs were deposited on the same silica coated CaF\(_2\), the effect of adding salt or changing the pH to eliminate the diffuse layer contribution was expected to be similar. However, the PEG chains had a strong interaction with the NaCl. After adding only 20 mM NaCl to the PEG SAM, there was a large change in the spectral
shape across the entire frequency range, as shown in Figure 4.5. In contact with water, the PEG SAM exhibits a broad feature in the OH stretching region and small, nondescript CH stretching peaks attributed to large disorder in the chain orientation. Once a small amount of salt was added, the CH peaks feature prominently in the spectrum. The SFG intensity is proportional to the number of oscillators and their net order, since the number of CH bonds at the interface did not change, the increased CH
stretch intensity indicates that the salt is interacting with the monolayer and structuring the PEG monolayer. Unlike OTS, where adding salt did not change the spectral shape of OH stretching region, Figure 4.2, the spectral shape of the OH stretching region at PEG changes when salt is added. In the presence of salt, the spectrum of water at the PEG surface appears to narrow at lower frequencies and increase in intensity around 3600 cm\(^{-1}\), Figure 4.5. This change in the monolayer order and water spectrum is reversible. As shown in Figure 4.5, if the monolayer is rinsed and put in contact with water again after being in contact with salt, the original spectral shape is observed. Previous work in our group on PEG based anti-biofouling membranes observed a strong influences of a sodium phosphate buffer on the water structure.\(^{26}\) The spectral shape of the water in contact with PEG in the presence of salt does not change as a function of concentration. Figure 4.6 shows that as the concentration of salt is increased, the CH

![Graph showing spectral shape changes](image)

**Figure 4.5:** Homodyne-detected SFG spectra of the PEG surface in contact with water, 20 mM NaCl, and water after being in contact with salt.
stretching modes only exhibit small changes and the OH stretching region has a similar spectral shape with a reduction in overall intensity. The reduction in intensity with increasing salt concentration follows the expectation for salt screening the surface charge.

In addition to the structural change in the PEG monolayer observed directly after the addition of NaCl, there was a second observed spectral change that occurred on the order of hours in contact with the NaCl solution. After days of the sample cell being assembled, the orientation of the water flips from towards PEG to away from PEG. The orientation change of the water between the initial data collection and second data collection is observed by the CH stretches being 90° out of phase in the homodyne-detected spectrum and the same CH orientation, but opposite OH stretching orientation in the imaginary spectrum, Figure 4.7a. The CH stretches for both data collection time 1 and 2 are not aligned with the CH stretches for the dry monolayer in the homodyne-

**Figure 4.6:** Homodyne-detected SFG spectra of the PEG surface in contact with water, 20 mM NaCl, 50 mM NaCl, and 500 mM NaCl.

In addition to the structural change in the PEG monolayer observed directly after the addition of NaCl, there was a second observed spectral change that occurred on the order of hours in contact with the NaCl solution. After days of the sample cell being assembled, the orientation of the water flips from towards PEG to away from PEG. The orientation change of the water between the initial data collection and second data collection is observed by the CH stretches being 90° out of phase in the homodyne-detected spectrum and the same CH orientation, but opposite OH stretching orientation in the imaginary spectrum, Figure 4.7a. The CH stretches for both data collection time 1 and 2 are not aligned with the CH stretches for the dry monolayer in the homodyne-
detected spectra due to interference with the broad OH stretching modes, but are aligned in the heterodyne-detected spectra indicating a consistent orientation. Additionally, the OH stretches have the opposite orientation for the two data collection times indicating that the net water orientation flipped, Figure 4.7b. The precise timescale of the reorientation is not known but occurred within 2 days of the sample cell being assembled. The final orientation with the water pointing towards the bulk appears to be the equilibrium orientation of the system as additional data was collected for days and no other spectral change was observed.

Figure 4.7: Homodyne-detected SFG spectra (top) and the imaginary component of $\chi^{(2)}$ (bottom), measured by HD-SFG, of the PEG surface in contact with water and NaCl at multiple collection times: (a) CH stretching region with the CH stretches of the dry monolayer for reference, and (b) the full frequency range.

We attempted to measure the time scale of the flip in the water orientation later by examining the CH stretching modes. Using a higher concentration of salt (2 M), we observed the appearance of CH peaks for when PEG was in contact with the salt
solution. However, we did not observe a change in the CH stretching modes as seen in Figure 4.7, and the CH stretching modes in contact with 2 M NaCl, Figure 4.8, do not resemble either of the previously observed spectra. This may be a result of the high salt concentration, and a more careful examination of PEG in contact with lower concentrations of NaCl could elucidate the timescale of this reorientation. Surprisingly, the addition of KCl instead of NaCl does not structure the PEG chains, as indicated by the lack of pronounced CH peaks in Figure 4.8. Therefore, KCl could be used to screen the surface charge of silica without changing the structure of the surface.

![Graph](image)

**Figure 4.8:** Homodyne-detected SFG spectra of the PEG surface in contact with 2M NaCl and 0.1M KCl.

### 4.4 Conclusions

Although there were spectral differences in the SFG signals of water at the hydrophobic (OTS), hydrophilic (PEG), and mixed (OTS/PEG) monolayers, as
described in Chapter 3. The changes to the OTS-water spectrum upon the addition of salt or with decreased pH indicate there is a significant diffuse layer contribution to the SFG signal from the surface charge of the underlying silica. Therefore, eliminating the effect of the surface charge of silica is important in classifying the structure and orientation of the water molecules in the bound interfacial layer. Adding salt or changing the pH has shown to be an effective method for OTS. However, PEG interacts with NaCl so the salt restructures the monolayer and water in addition to screening the surface charge. Initial experiments with a KCl solution in contact with PEG suggest that the same monolayer restructuring does not occur, so KCl may be able to effectively screen the surface charge for the PEG containing monolayers. Possible methods for removing the effect of surface charge without adding salt would be to deposit the SAMs on Al₂O₃, which has no surface charge at a pH of 6,²⁷,²⁸ or capping all the unreacted silanol groups with a small silane molecule.²⁹,³⁰ These possibilities will be discussed in more detail in Chapter 8.

In Chapter 3, the importance of HD-SFG when analyzing the SFG response of interfacial water as the mixing of the real and imaginary components skews the spectral shape was discussed. Likewise, the spectral shape of interfacial water is distorted by the combination of the bound interfacial layer and the diffuse layer, as well as by the strong inter- and intramolecular couplings of water. To measure the most accurate SFG response of interfacial water, the response of isotopically diluted water with the diffuse layer eliminated needs to be measured with HD-SFG.
4.5 References


(27) Zhang, L.; Tian, C.; Waychunas, G. A.; Shen, Y. R. Structures and Charging of α-Alumina (0001)/Water Interfaces Studied by Sum-Frequency Vibrational


5.1 Introduction

Over the last few decades, SFG spectroscopy has been a powerful method for studying the interfacial water structure due to the inherent surface specificity of the technique.\textsuperscript{1–7} However, the hydrogen-bonded network of water is highly flexible and dynamic so characterizing the ultrafast dynamics of the hydrogen-bonded network is essential to understanding water at the molecular level. The combination of transient IR and 2D IR spectroscopies with MD simulations has been integral in obtaining a detailed understanding not only of the ultrafast dynamics of the hydrogen-bonded network of bulk water, but also the “true structure” of the liquid, i.e. whether multiple stable hydrogen-bonded species exist.\textsuperscript{8–19} In order to fully understand interfacial water, analogous surface-specific fourth-order time-resolved methods are needed. Several pump-SFG probe and 2D SFG measurements of aqueous interfaces have been performed,\textsuperscript{20–38} as described in a recent review.\textsuperscript{39} IR Pump - SFG probe measurements characterize the vibrational relaxation dynamics, providing information on the energy dissipation driven by couplings between the OH modes in the interfacial layer. 2D experiments reveal the heterogeneous and homogeneous contributions to the linewidths and capture spectral diffusion dynamics, which inform on the number of stable species in the interfacial region and the time-scale of their interchange.
Time-resolved SFG and 2D SFG experiments have shown that both the vibrational relaxation and spectral diffusion dynamics of water at the air-water interfaces is slower compared to the bulk due to a lower molecular density at the interface.\textsuperscript{23,40} In particular, the dynamics of the free-OH, at both the air-water and OTS-water interfaces, is significantly slower compared to the hydrogen-bonded region due to the vibrational decoupling in both frequency and space. Adding charged or zwitterionic surfactants or lipids to the air-water interfaces leads to complex dynamics that depend on the charge distribution and hydrogen-bonding of the head group, while charged solid-water interfaces exhibit dynamics ranging from comparable to bulk water to slower than the air-water interface, depending on the surface charge. Time-resolved SFG experiments have also investigated the silica-water interface, which has been found to exhibit charge (pH) dependent dynamics.\textsuperscript{36,41,42} Under neutral and basic conditions, the water dynamics at the silica-water interface are comparable to bulk water, but near the point of zero charge (pH=2-3) the water dynamics are ~3 times slower.\textsuperscript{36,41,42} Conversely, despite exhibiting charge (pH) dependent static SFG spectra, the dynamics of the alumina-water interface had minimal pH dependence for two different crystal faces.\textsuperscript{38,43} The water dynamics at the $\alpha$-Al$_2$O$_3$(1120) interface are approximately twice as fast as bulk water and constant within experimental error from pH 2 to 12.\textsuperscript{38} However, the $\alpha$-Al$_2$O$_3$(0001) interface shows a slight pH dependence with water dynamics similar to bulk water near the point of zero charge, but the same as $\alpha$-Al$_2$O$_3$(1120) otherwise.\textsuperscript{43}

The previous 2D SFG experiments of the OH and OD stretching vibrations of water have all been performed in the narrowband pump geometry,\textsuperscript{39,44} which is one of
two general ways of performing 2D experiments. The narrowband pump geometry combines a series of wavelength-dependent pump-probe experiments, utilizing a narrowband pump pulse that is scanned across the frequency range of interest to generate the excitation axis in a 2D spectrum with the probe axis as the other axis. This method is technically simpler, involving a single pump pulse that does not have to be phase stable with the probe. However, the method exhibits limited time and frequency resolution as determined by the time-bandwidth product of the pump pulse, typically around 150 fs and 150 cm$^{-1}$ for the experiments on water. The second method utilizes two broad-band pump pulses between which the time delay is scanned to produce an interferogram. The excitation axis is generated upon Fourier transformation. This method requires two phase stable excitation pulses with an accurately controlled time delay and is thus technically more difficult but exhibits increased time and frequency resolution.$^{45,46}$ Here the frequency resolution along the excitation axis is set by the number of time points along the pump-pump delay, and the time-resolution is set by the shorter broadband-pulses compared to the longer narrowband excitation pulse. In both cases, heterodyne detection is needed to obtain the phase of the emitted signal. Interferometric 2D SFG experiments were first demonstrated for molecules on gold surfaces.$^{47-49}$ Recently, a new design for interferometric 2D HD SFG experiments utilizing an external local oscillator was demonstrated facilitating studying transparent substrates,$^{50}$ thus paving the way for interferometric 2D HD SFG measurements with high spectral and temporal time resolution probing the ultrafast dynamics of interfacial water at tunable surfaces.
5.2 Experimental Methods

5.2.1 Sample Preparation

The preparation of the SAMs was described in Chapter 3. For the time-resolved HD-SFG experiments, only OTS and PEG were studied. The SAMs were deposited on CaF$_2$ hemicylindrical prisms (10x10mm diameter, Crystran Limited) with a 10 nm SiO$_2$ layer deposited through atomic layer deposition with one half of the prism coated with a 150 nm layer of gold. Hemicylindrical prisms are used for the time-resolved experiments as they have result in a signal intensity increase of approximately 4 times compared to flat windows due to the Fresnel Factors.

All the solutions used were made using glassware that was cleaned with NoChromix in sulfuric acid and rinsed to neutral pH with ultrapure water. Prior to making the solutions, sodium chloride (NaCl, Sigma Aldrich) was baked in a 200°C oven for 3 hours to remove any impurities. Ultrapure water (Millipore MilliQ, 18.2 MΩ•cm, ≤ 5 ppb total organic carbon) was used throughout the experiment.

5.2.2 Transient HD-SFG and Interferometric 2D HD SFG

The HD-SFG experimental set-up was previously described in Chapter 3. The experimental setup for the transient HD-SFG and 2D HD SFG is shown in Figure 5.1. The IR pulses generated in the optical parametric amplifier are split with a KBr beamsplitter. One part is used as the probe for the HD-SFG. The other part is used as the pump. The pump pulse is further split into two pulse pairs with a Mach-Zehnder interferometer. One pulse pair is focused onto the sample with an off-axis parabolic
mirror (f=101mm, ThorLabs). For the time-resolved HD-SFG experiments, the visible, IR probe, and IR pump pair were focused on the sample with off-axis parabolic mirrors at 55°, 65°, and 50° with respect to the surface normal. The IR pulses were centered at 3220 cm\(^{-1}\) with a bandwidth of 300 cm\(^{-1}\).

For the transient HD-SFG experiments, the stationary arm of the interferometer was blocked so only one pump pulse from the pump pair is used to excite the sample, and the time between the IR pump and HD-SFG probe, \(\tau_2\), is varied. At each value of \(\tau_2\), a HD-SFG spectrum is collected. The frequency resolution in the probe axis is 10 cm\(^{-1}\), determined by the visible upconversion pulse, and the temporal resolution in \(\tau_2\) is 85 fs, determined by the third-order IR\(_{\text{pump}}\)-IR\(_{\text{probe}}\)-visible cross-correlation on Au.

**Figure 5.1:** Experimental setup for 2D HD SFG spectrometer reproduced from reference 55.
For 2D HD SFG, the relative IR pump pulse timing, $\tau_1$, was scanned from -150 fs to 400 fs in step sizes of 2 fs resulting in an interferogram in the pump axis at $\tau_2 = 0$ fs. At each value of $\tau_1$, a HD-SFG spectrum is collected. After Fourier transforming both axes, a 2-dimensional surface is generated. The frequency resolution in the probe, $\omega_3$, axis is the same as in the transient experiment. The frequency resolution of the pump, $\omega_1$, axis is $60 \text{ cm}^{-1}$, determined by the step size and distance scanned between the pump pulses.

To correct for laser fluctuations, the moving pump was synchronized with an optical chopper triggered at 500 Hz, therefore every other pulse was blocked by the chopper. A galvanometric mirror was also synchronized to the laser trigger at 500 Hz which spatially separated every other laser shot on the CCD. For transient HD-SFG, one region contained the static, unpumped SFG signal and the other region contained the pumped SFG signal. Therefore, laser fluctuations could be normalized out. Similarly, for 2D HD SFG, one region contained the singly pumped SFG signal and the other contained the signal with two interfering pumps.

5.3 Results and Discussion

In Chapter 3, the structure of the interfacial water at hydrophobic and hydrophilic monolayers was probed with HD-SFG. In the hydrogen-bonding region, the interfacial water spectrum was dominated by a broad, positive two peaked structure for both monolayers. However, the relative intensity between the two peaks depended on the chemical nature of the surface. To further characterize the interfacial water at the
hydrophobic and hydrophilic SAMs, we performed transient HD-SFG and 2D HD SFG of water centered at the broad two peaked spectral feature.

5.3.1 Transient HD-SFG

Broadband IR-pump – HD-SFG probe experiments examine the interfacial vibrational relaxation dynamics. Figure 5.2a shows the SFG response at OTS as a function of the time delay, $\tau_2$, between the IR pump and the HD-SFG probe. At 0 fs, there is a broad bleach across most of the spectrum. As the time delay increases, the maximum of the bleach shifts from 3250 cm$^{-1}$ to 3150 cm$^{-1}$. At long time delays, there is a broad induced feature at higher frequencies and a broad bleach at lower frequencies, which is indicative of the “hot ground state”. This feature is spectrally similar to the difference between hot and room temperature water, as increasing the temperature weakens hydrogen-bonding and results in a shift to higher frequencies. However, in the transient experiments it is not a true thermal state due to the rapid time scale. Bulk measurements attributed the “hot ground state” to strong coupling between the OH stretching and low-frequency intermolecular modes in water.$^{19}$

**Figure 5.2:** (a) IR pump – HD-SFG probe spectrum of the OTS-water interface and (b) the averaged pump-probe regions (open circles) and their corresponding fits (solid lines) to extract the vibrational relaxation dynamics.
To extract the time scales of the vibrational dynamics, the lower frequency signal (centered around the bleach) between 3150 and 3250 cm\(^{-1}\) and the higher frequency signal between 3300 and 3400 cm\(^{-1}\) were averaged. Then, the averages for the two regions were fit with exponentials resulting in the fits show in Figure 5.2b. The bleach displayed single exponential relaxation dynamics of 295 \(\pm\) 20 fs. A single exponential fit of the “hot ground state” (higher frequencies) resulted in a fit of 380 \(\pm\) 40 fs. However, as seen in the contour plot in Figure 5.2a, there is a bleach component at early times that recovers before the “hot ground state” grows in. Therefore, it was fit to two timescales with a biexponential. If the first ultrafast timescale was constrained to the timescale from the fit of the black, the longer intermolecular coupling relaxation timescale resulted in a non-physical result so it could not be accurately fit with the time delays measured in the experiment. The timescale of the ultrafast vibrational relaxation at the OTS-water interface was observed to be slightly slower than bulk water (275 fs),\(^{51}\) but faster than the air-water interface (400 fs).\(^{24}\) The air-water interface is also hydrophobic, but the vibrational relaxation time of the OTS-water interface is closer to bulk water than the air-water interface so the interfacial vibrational relaxation dynamics depend on more than surface chemistry. The air-water interface is a soft, hydrophobic surface and has a reduces water density at the interface, whereas the OTS-water interface is a solid, hydrophobic interface and has a region of higher density near the surface that could account for the difference in vibrational relaxation time. The OTS-water interface also has a diffuse layer contribution, which could have a different time scale than the bound interfacial water. However, further time-resolved experiments of
OTS in contact with salt solutions are needed to separate out the vibrational relaxation
time of the bound interfacial layer from the diffuse layer.

Transient HD-SFG was also performed for the PEG SAM with and without salt. As shown in Chapter 4, upon addition of NaCl the PEG monolayer changed structure and eventually flipped sign. The static, imaginary spectra for the PEG in contact with pure water and salt solution prior to the time-resolved experiments are shown in Figure 5.3. Overall, the spectra are both very broad, but have opposite signs.

The pump-induced difference in the SFG response of water and salt at PEG as a function of time delay between the IR pump and HD-SFG probe are shown in Figure 5.4a-b. Both exhibit a bleach around zero time delay. However, the bleach for the PEG-water interface, Figure 5.4a, is largely obscured by the initial coherent artifact during pump and probe pulse overlap. The bleach for the PEG-salt solution interface, Figure 5.4b, is a positive because the static spectrum is negative, thus a positive feature.
indicates that the absolute intensity of the signal is reduced. Given the low signal to noise for the PEG-water interface, the attempts to fit the data to extract the vibrational relaxation time were unsuccessful. The single exponential fit of the bleach for the PEG-salt solution interface yielded a vibrational relaxation time of 170±40 fs. Since this timescale is faster than both bulk water and the water-OTS interface, it suggests efficient energy transfer from the water to the PEG. Additionally, fitting timescale of the higher frequency induced feature growing in for the PEG-salt interface to a single exponential resulted in a timescale of 380±70fs. Therefore, both the timescale for the vibrational relaxation and the growth of the “hot ground state” are approximately twice as fast at the PEG-salt solution interface than in the bulk.

Figure 5.4 IR pump – HD-SFG probe spectrum of (a) the PEG-water interface and (b) the PEG-salt solution interface, and (c) the averaged pump-probe regions and their corresponding fits to extract the vibrational relaxation dynamics.
The “hot ground state” for PEG in contact with the salt solution is also reversed compared to bulk water and the hydrophobic-water interface. Typically, the “hot ground state” has a reduced intensity at low frequencies and an increased intensity at high frequencies as increasing the temperature weakens the overall hydrogen-bonding strength. As the peak for the PEG-salt solution interface is negative, the long-time spectra have a reduced intensity at high frequencies and an increased intensity at low frequencies. Water is known to bind more strongly to ethylene oxide groups than itself,\textsuperscript{52–54} which results in the negative, low frequency band attributed to water molecules bound to PEG in the imaginary component of the SFG spectrum. Within the signal to noise, the “hot ground state” for the PEG-water interface appears to have the normal sign, overall weakened hydrogen-bonded structure, so the inverted “hot ground state” seems to be related to the added salt and not the PEG monolayer specifically. However, the reason for the strengthened hydrogen bonds at long times is unknown and needs to be investigated further. Temperature dependent spectra of the PEG-water interface or mixtures of polyethylene glycol and water with and without salt could help identify the origin of the strengthening of the hydrogen bonds for the PEG-salt solution interface.

\textbf{5.3.2 2D HD SFG}

Two-dimensional IR experiments of bulk water exhibit strong intra- and intermolecular coupling, resulting in the excitation being delocalized over several water molecules and efficient spectral diffusion.\textsuperscript{19} Molecular dynamics simulations and 2D SFG experiments in the scanning pump geometry found that the water-air interface exhibits slower spectra diffusion than the bulk attributed to the reduced density at the
The 2D SFG experiments also suggested that the higher frequencies exhibited an even slower spectral diffusion time than the lower frequencies.

Interferometric 2D HD SFG measurements for pure water in contact with OTS and PEG at $\tau_2=0$ fs are shown in Figure 5.5b-c. The static spectra for the two interfaces are similar in the spectral region probed in the experiment, as seen in Figure 5.5a, but there are differences in the relative intensities of the two positive, hydrogen-bonded peaks, which was discussed in more detail in Chapter 3. For both monolayers, the 2D surface is dominated by a broad bleach along the diagonal. However, at $\tau_2=0$ fs, the water at

![Figure 5.5](image)

**Figure 5.5** Water at OTS (hydrophobic) and PEG (hydrophilic) SAMs: (a) static, imaginary spectra for both SAMs in the probed spectral range, and the 2D surfaces at a waiting time of $\tau_2=0$ fs for (b) the water-OTS interface and (c) the water-PEG interface.
PEG is more inhomogeneous than water at OTS as observed by the centerline slope. This suggests that the spectral diffusion is faster for OTS than PEG. Furthermore, the PEG sample exhibits larger inhomogeneity resulting from the chemical structure of the monolayer. In order to determine the exact spectral diffusion dynamics, additional waiting times are needed, but the ultrafast vibrational relaxation at the interface and low signal to noise have limited the current experiment to a waiting time of τ_2=0 fs. Additionally, there is a hint of multiple species, as indicated by multiple local maxima along the diagonal. The separation of the low frequency peak centered at ~3200 cm^{-1} and a small peak at ~3400 cm^{-1} is consistent with the multiple time scales observed at the water-air interface.

5.4 Conclusions

A series of time-resolved HD-SFG experiments were performed on hydrophobic and hydrophilic SAMs to understand the vibrational dynamics of the interfacial water at these interfaces. The IR pump – HD-SFG probe experiments at the OTS-water interface revealed a vibrational relaxation time similar to bulk water, but faster than the air-water interface. The reason the vibrational relaxation is slower at the air-water interface is due to the lower density of molecules at the surface. However, at the solid interface, the density of water molecules is close to the bulk value, accordingly the vibrational dynamics are not reduced. Additionally, the IR pump – HD-SFG probe experiments at the PEG-salt solution revealed vibrational relaxation times faster than the bulk. The difference between the relaxation times at OTS and PEG could result from
the effective delocalization of the energy into the PEG monolayer or the removal of the diffuse layer contribution by adding salt.

Interferometric 2D HD SFG also showed differences in the inhomogeneity of water at OTS and PEG for a waiting time of 0 fs, suggesting a slower spectral diffusion time and larger inhomogeneity at the PEG monolayer. Additional waiting times are needed to fully characterize the spectral diffusion dynamics. To obtain a detailed molecular-level understanding of the vibrational dynamics of interfacial water at SAMs with different surface chemistry, the diffuse layer contribution, and the intra- and intermolecular couplings also need to be removed. These contributions can be removed by performing the experiments described above as a function of salt concentration and isotopic dilution. The current results were limited significantly by signal-to-noise, but the technical innovations in SFG spectroscopy should make the needed experiments possible.

5.5 References


(4) Shultz, M. J.; Baldelli, S. Aqueous Solution/air Interfaces Probed with Sum


(38) Tuladhar, A.; Dewan, S.; Kubicki, J. D.; Borguet, E. Spectroscopy and Ultrafast


(45) Cervetto, V.; Helbing, J.; Bredenbeck, J.; Hamm, P. Double-Resonance versus


(51) Ramasesha, K.; De Marco, L.; Mandal, A.; Tokmakoff, A. Water Vibrations


CHAPTER 6

PHASE UNCERTAINTY IN HETERODYNE-DETECTED SUM-FREQUENCY GENERATION

* Section 6.3.5 was adapted from S.E. Sanders and P.B. Petersen J. Chem. Phys. 2019, 150, 204708

6.1 Introduction

The accurate phasing of HD-SFG spectra is an ongoing problem in the field. Sun et al. explored the absolute phase of various potential phase references and noted the importance of the wave propagation phase effect in determining the phase of the reference.¹ Quartz has traditionally been used as a phase reference because z-cut quartz has a well-defined phase of 0° or 180°. As the SFG signal from quartz originates from the bulk phase of the crystal, the phase is inherently 90° shifted from the phase of the surface SFG signal emitted from the sample, therefore the effective phase of quartz is 90°. However, the optimum phase reference has been debated.²⁻⁴ Non-resonant second harmonic generation (SHG) experiments of the air-water interface versus z-cut Quartz measured an additional 25 ± 15° phase shift on top of the intrinsic 90° surface versus bulk shift.⁵ This shift was attributed to the dispersion within the coherence length in the quartz crystal compared to the molecularly thin air-water interface. Recently, Thämer et al. performed a quantitative determination of the nonlinear bulk and surface response from quartz, which showed that surface contribution is not as small as often assumed so it can have a considerable impact on the phase causing deviations from 90°.⁶ Tahara and coworkers argued that the positive band around 3000 cm⁻¹ in the imaginary spectrum of
the air-water (H₂O) normalized to quartz also exists in the air-D₂O spectrum and is an artifact of phasing.⁷

Studying buried surfaces adds an additional complication since the phase reference and the sample need to have the same propagation medium. While quartz is a good phase reference for exposed surface since it has a well-defined phase, it is not a viable phase reference for buried surfaces.⁸ Therefore, gold, which can be deposited directly on part of the sample, has been used in a number of HD-SFG studies of buried surfaces.⁹–¹³ A drawback of using gold as a phase reference is that the absolute phase of gold can vary depending on preparation. Recently, the Shultz group measured the absolute phase of gold (Au) with a 532nm visible, upconversion pulse to be -222°.¹⁴ The visible wavelength used for the upconversion pulse will affect the phase since the SFG response from Au originates from surface electronic states and Au has electronic resonances near both the visible and SFG wavelengths. In an SFG experiment, the visible wavelength is held constant and the IR is varied so the phase from Au is flat across the IR frequencies probed since there are no IR resonances.¹⁵,¹⁶ Therefore, the phase of Au in our spectrometer will be different from the phase measured by the Shultz group because our visible, upconversion pulse is at 792.5 nm. Instead of determining the absolute phase of our gold reference, we vary the relative phase between the gold and sample to satisfy the condition that the imaginary component of χ(2) is zero when there are no molecular vibrational resonances. This phasing procedure assumes that the phase of gold is constant across the spectral region studied but is not sensitive to the absolute phase of gold.
Small differences in sample placement and beam propagation can introduce phase shifts in the data. In this chapter, the phase shifts as a function of sample position, reproducibility in sample placement, and polarization for non-resonant samples will be measured with our HD-SFG spectrometer to determine the phase uncertainty in the set-up. The effect of varying the relative phase between Au and OTS during the phasing procedure will also be examined.

6.2 Experimental Methods

The details of our HD-SFG spectrometer were described in Chapter 3. For the phase uncertainty experiments, the LO was generated by either y-cut quartz (0.5 mm thick, MTI crystal) or ZnO (150 nm thick) sputtered on CaF$_2$ (0.5 mm thick). The samples used were Au (Thor Labs, PF10-03-M03) and ZnO (150 nm thick) sputtered on CaF$_2$ (1 mm thick).

In order to examine the inherent phase uncertainty and error in our HD-SFG spectrometer, non-resonant SFG signals were measured under several conditions. First,

![Figure 6.1](image)

**Figure 6.1:** Top down view of the HD-SFG set-up indicating the x and y directions of the sample stage.
the effect of sample position on the phase was examined. The sample is mounted on an xyz translation stage so the position of the sample can be finely adjusted with micrometers. Translation in the z-direction corresponds to changing the height of the sample. The x and y directions are indicated with arrows in Figure 6.1. Both the effect of adjusting the x-position and z-position were investigated. The effect of adjusting the y-position was not investigated since it is equivalent to adjusting the z-position for a flat sample in the reflection geometry. Second, the effect of removing the sample and putting it back in was examined. Lastly, the effect of changing the visible polarization was examined. The error in our data analysis and phasing procedure was also examined using the data for the OTS-water interface from Chapter 3.

6.3 Results and Discussion

The phase and frequency of the fringes resulting from the interference between the LO and the sample are sensitive to the time delay between the LO and the sample as well as the inherent phase of the material. In each of the controls, the materials of the LO and sample are held constant to eliminate the effect of the material phase. In order to determine the relative phase as one parameter is varied, the imaginary part of the signal was multiplied by a factor of $e^{i\phi}$, where the phase ($\phi$) is varied until it matches the originally optimized signal.

6.3.1 Varying X-position

By adjusting the x-position, the sample is moved in and out of the focus where the visible and IR beams are overlapped. In order to position the sample surface at the
focus, the x-position is varied until the SFG signal from the Au surface is maximized, then this position is defined as 0.00 mm. As the x-position is varied from -0.06 mm to 0.07 mm, the signal from the Au is lower than at 0.00 mm confirming the sample was optimized at the focus (0.00 mm), Figure 6.2a. However, the LO is generated before the sample so absolute amount of LO generated should be consistent within the laser noise. The observed differences in LO intensity on the CCD, Figure 6.2b, occur from the small differences in pointing of the reflected LO into the CCD. The larger LO intensity at 0.01 mm compared to the optimized 0.00 mm is what results in the higher intensity in the LO + Au spectrum for 0.01 mm, Figure 6.2c. When zooming in on the LO + Au fringes, the absolute fringe depth is similar between all the traces, but there is a small frequency (phase) shift between ±0.01 mm (blue and red) and 0.00 mm (black), Figure 6.2c.

**Figure 6.2:** SFG spectra of y-cut quartz LO versus Au with varying the x-position of the sample: (a) only the Au sample, (b) only the y-cut quartz LO, (c) interference between the LO and Au for the whole spectrum and zoomed in on the peak.
Similar phase shifts in the LO + Au fringes were observed for the other x-positions, but were omitted from the plot for clarity.

To quantify the observed phase shifts in Figure 6.2c, our standard heterodyne-detection analysis was performed comparing the spectra for each x-position from -0.06 mm to 0.07 mm to 0.00 mm. If no phase factor (phase = 0°) is added to the imaginary spectra for ±0.01 mm, there is a noticeable frequency shift between ±0.01 mm (light blue and light red) and 0.00 mm (black), Figure 6.3a. However, when the imaginary spectra for ±0.01 mm are multiplied by a phase factor of 40°, the imaginary spectra for ±0.01 mm (blue and red) and 0.00 mm (black) fall directly on top of each other with only small intensity differences at the fringes, Figure 6.3a. By dividing the phased spectra for ±0.01 mm by the spectrum for 0.00 mm, a constant value of zero is observed over the entire frequency range indicating that the phase is flat over the frequency range, Figure 6.3b. The unphased spectra normalized to the 0.00 mm spectrum are also flat, as seen in Figure 6.3b, but they have a non-zero constant value due to the phase shift between the spectra. By performing the same phasing analysis for the other x-positions, the relative phase compared to the optimized signal at x=0.00 mm varies significantly over the position range studied. As shown in Figure 6.3c, the phase can vary by 260° by translating the sample 0.13 mm. Therefore, in order to maintain phase stability within an experiment, it is important to maintain the position of the sample surface in relation to the focus as much as possible.
6.3.2 Varying Z-position

By adjusting the z-position, the height of the sample is changed. If the sample is perfectly perpendicular to the beams, the sample position relative to the beam focus and therefore the phase should not change. However, small deviations from the sample not being positioned perfectly perpendicular to the beams or not sitting flat in the mount will introduce small shifts in the surface position relative to the focus. In a normal experiment, the z-position is adjusted to translate from the Au reference to the sample. The signal from the ZnO sample and overlap with the y-cut quartz LO was optimized with the z-position at 0 mm. When the z-position was adjusted by 5 mm (blue) or 10 mm (red), there is a small observed frequency shift in the LO + ZnO interference compared to 0 mm (black), Figure 6.4a, similar to when the x-position is varied. This phase shift is maintained in the unphased imaginary spectra, Figure 6.4b. However,
when the imaginary spectra for 5 mm (blue) is multiplied by a phase factor of -10° and the imaginary spectra for 10 mm (red) is multiplied by a phase factor of -55° all the imaginary spectra in the bottom plot of Figure 6.4b have the same phase. Compared to varying the x-position, the phase error accumulated by adjusting the z-position is smaller. Typically, the z-position is adjusted by around 5 mm or less when performing experiments, so the phase error accumulated in adjusting the z-position is minimal.

![Graphs showing SFG signal intensity with varying z-position](image)

**Figure 6.4:** Heterodyne-detected SFG of y-cut quartz LO versus ZnO with varying the z-position of the sample: (a) interference between the LO and Au for the whole spectrum and zoomed in on the peak, (b) unphased (phase 0) imaginary spectra (top) and phased imaginary spectra (bottom).

### 6.3.3 Reproducibility in Sample Placement

In the collection beam path, the horizontal and vertical are flipped with a periscope. Therefore, the vertical position on the CCD chip (y-strip) is an indication of the horizontal pointing leaving the sample so matching the y-strip is used when replacing the sample to reproduce the sample position. The SFG signal from Au and the
overlap with the y-cut quartz LO was optimized and collected. Then, the sample was physically removed from the set-up, and immediately put back in and repositioned so the y-strip on the CCD matched the originally optimized signal. As seen in Figure 6.5a-b, the intensity and spectral shape are different for both the Au and the LO. The most likely reason for this is that the vertical tilt (perpendicularity of the sample relative to

![Graphs showing SFG intensity and spectral shape comparison](image)

**Figure 6.5:** Heterodyne-detected SFG of y-cut quartz LO versus Au with removing the sample and repositioning it to match the y-strip on the CCD: (a) only the Au sample, (b), only the y-cut quartz LO, (c) interference between the LO and Au for the whole spectrum and zoomed in on the peak, (d) unphased (phase 0) imaginary spectra (light blue) and phased imaginary spectra (dark blue) compared with the originally optimized (red).
the beams) was slightly different since this cannot be accounted for by matching the y-strip. Slight vertical shifts off of the sample would result in horizontal shifts going into the monochromator, so the signal was possibly clipped on the entrance slit. The LO + Au interference has a large intensity difference due to the difference in the LO intensity and appears to have a slight phase shift, Figure 6.5c. Upon performing the heterodyne-detection analysis and phasing the y-strip matched data by -20°, there is good agreement between the original data and the y-strip matched data, as shown in Figure 6.5d. This agreement is very good considering the spectral differences and could possibly be improved if the slit into the monochromator was opened more. However, it is important to note that y-strip matching can only be used for references and samples that have the same propagation media. Using y-strip matching for a buried interface compared to front side Au will not work due to the dispersion in the window in probing a buried interface.

6.3.4 Polarization Dependence

In our set-up, the polarization of the visible beam can be rotated with a waveplate and a polarizer and the polarization of the detected SFG is determined by a polarizer before the CCD. Typically, the SFG of water experiments are collected in the ssp (SFG – s, visible – s, IR – p) polarization combination. However, the Au used as a reference only produces a strong signal in the ppp (SFG – p, visible – p, IR – p) polarization combination so the polarization must be changed in between the reference and sample. In order to explore the polarization dependence of the phase, ZnO was used as the sample since it produces a strong nonresonant signal in both ssp and ppp, Figure
6.6a. However, the reflection of the LO off ZnO is very weak in p-polarization compared to s-polarization as indicated by the order of magnitude lower signal in ppp compared to ssp for the LO and LO + ZnO, Figure 6.6b-c. The shape of the LO is also skewed to lower frequencies for the weaker, p-polarized LO. The small interference fringes seen in Figure 6.6b are a result of the sample signal from the ZnO not fully being

![Image](image.png)

**Figure 6.6:** Heterodyne-detected SFG of ZnO LO versus ZnO is ssp and ppp polarization combinations: (a) only the ZnO sample, (b), only the ZnO LO, (c) interference between the LO and ZnO for the whole spectrum and zoomed in on the peak, (d) unphased (phase 0) imaginary spectra (light blue) and phased imaginary spectra (dark blue) for ppp compared with the imaginary spectra for ssp (red).
blocked when the spectrum of the reflected LO was collected. There is a large phase shift between the two polarization combinations. The ppp spectra needed to be multiplied by a phase of $-130^\circ$ to compensate for the phase difference, Figure 6.6d. Ideally, the reference would be collected in the same polarization as the sample. Previously, ZnO was attempted to be used as a reference instead of Au for HD-SFG of water experiments, but the ZnO quickly dissolves in water so it is not a viable option without an additional protective layer. For now, using the Au reference in ppp is the best option, but the polarization dependence of the phase and the potential errors need to be considered.

6.3.5 Phasing Procedure

In order to assess the uncertainty in our phasing procedure, we adjusted the relative phase by $\pm 20$ degrees and $\pm 40$ degrees to see the effects on the spectrum for OTS in contact with water, Figure 6.7. With a phase of 20 degrees, the methyl stretches are aligned well with the frequency in the homodyne spectrum, Figure 6.7a, which is expected for an isolated peak. However, at this phase, the high frequency region above the free-OH and the region below the CH peaks is not approaching zero, as required, Figure 6.7b. Furthermore, while peak positions in the amplitude of the imaginary component and the intensity spectrum (homodyne) should exhibit the same frequency for an isolated peak, overlap between Lorentzian peaks or their interference with the non-resonant background cause a shift between the peak positions in amplitude and intensity spectra. Overlap between the positive and negative peaks in the CH region causes the peak in the amplitude spectrum to not perfectly coincide with the intensity
spectrum. Given that adjusting the phase with ±20 degrees causes a significant positive or negative amplitude above and below spectral features, which is erroneous, we set the phase accuracy to be better than ±20 degrees.

6.4 Conclusions

Given the variation in phase when varying the sample position, replacing the sample and matching the y-strip on the CCD, and adjusting the polarization it is important to acknowledge the potential phase errors in the HD-SFG spectrometer and minimize the variations made between reference and sample in an experiment. Characterizing the phase dependence on the physical manipulations of the sample is

Figure 6.7: Comparison of the imaginary component of the OTS spectrum with different phases. (a) only CH stretching region, (b) entire spectrum.
important for understanding the phase in the experiment. However, since our phasing procedure does not require an absolute, known phase for the reference small changes in phase due to sample position are removed by adjusting the relative phase between the sample and reference to achieve an imaginary spectrum that goes to zero away from the resonances. The phase uncertainty in our final spectra is determined by the phasing procedure, which is generally better than the uncertainty introduced by physical changes in the spectrometer.

Creating an easy to implement, phase stable and phase accurate HD-SFG spectrometer is still an ongoing goal. Our HD-SFG design is easy to implement and phase stable but requires the post-processing phasing procedure to obtain good phase accuracy. Conversely, the nonlinear interferometer design from the Shultz group has very high phase stability and accuracy, but is experimentally complex.\textsuperscript{17} In Chapter 7, our recent efforts to improve our phase accuracy of our HD-SFG spectrometer by directly measuring the imaginary spectrum are discussed.

### 6.5 References


144 (24), 244711.


(9) Vanselous, H.; Petersen, P. B. Extending the Capabilities of Heterodyne-Detected Sum-Frequency Generation Spectroscopy: Probing Any Interface in


CHAPTER 7

NEW EXPERIMENTAL DESIGN FOR PHASE STABLE AND PHASE ACCURATE HETERODYNE-DETECTED SUM-FREQUENCY GENERATION

7.1 Introduction

Over the past few decades, SFG has proven to be a powerful tool for studying interfaces because it is surface specific within the dipole approximation.\(^1\)\(^-\)\(^5\) However, SFG is a second-order nonlinear spectroscopy, where the emitted SFG signal is proportional to the square modulus of the second-order nonlinear susceptibility, \(|\chi^{(2)}|^2\). Therefore, the complex phase of the nonlinear susceptibility is lost. Measuring the intensity of the emitted SFG signal results in the mixing of the real (dispersive) and imaginary (absorptive) components of the response, including the non-resonant contribution, which can distort the spectral line shapes. This measurement also has a quadratic dependence on concentration, thus making measuring SFG responses at low concentrations more difficult. Heterodyne detection address both the issues described above, but HD-SFG has not been widely implemented due to complex experimental setups. In addition to the technical challenges, the analysis of heterodyne detected data is complicated due to the phase uncertainties discussed in Chapter 6.

Two general approaches are employed to extract the complex phase in SFG: scanning time domain approaches (narrowband and broadband versions),\(^6\)\(^-\)\(^8\) often referred to as phase-sensitive SFG (PS-SFG), and broadband multiplexed frequency domain approaches,\(^9\)\(^-\)\(^12\) often referred to as HD-SFG. In time domain approaches, the
relative time delay between the LO and the sample SFG is scanned and the modulated intensity is measured as a function of time delay. In frequency domain approaches, the LO is delayed by a few picoseconds with respect to the sample SFG and the spectral interference between them after being dispersed on camera with a monochromator is measured. Our previous experimental HD-SFG design extended the frequency domain approach of Tahara and coworkers, by replacing the one spherical mirror in between generating the LO and the sample with two off-axis parabolas. Adding an additional mirror creates a collimated region where the timing and polarization of the IR, visible, and LO beams can be manipulated in between generating the LO and the sample. The design is extremely phase stable and versatile, expanding the types of sample and polarizations accessible in HD-SFG.

In both methods, the imaginary spectrum of the sample is extracted by comparing the sample of interest to a phase reference. Therefore, small shifts in the sample position relative to the reference can lead to phase error, as discussed in detail in Chapter 6. Recently, new experimental designs from the Thämer et al. and the Shultz group with improved phase accuracy have been reported. The design from the Thämer et al. combines the frequency multiplexing of HD-SFG with the high phase stability of a collinear geometry. The precise timing control is achieved by splitting the IR with a beam splitter, then using one portion of the IR to generate the LO collinearly before filtering out the IR from the LO and visible beams and coupling in the second portion of the IR after the LO and visible travel through a translation stage, but before the sample. In this geometry, the LO and visible have a fixed time delay, but the visible timing with respect to the IR is varied resulting in changes of the sample SFG intensity.
The Shultz group implemented a nonlinear interferometer with an embedded linear Mach-Zehnder (MZ) interferometer. The embedded MZ interferometer enables reproducible sample positioning which improves the absolute phase accuracy. Coupling white light into the interferometer can precisely determine the path length differences between the two arms as a function of the sample position. Therefore, the absolute time zero between the two arms (LO and sample SFG) can be determined. Time zero corresponds to the dispersive, real component so by shifting the two arms by 90° the absorptive, imaginary component can be directly measured. However, the design of the interferometer is more experimentally complex and less flexible than our current HD-SFG setup and relies on actively stabilizing the interferometer arms. Taking inspiration from both the designs described above, we expanded the control of the relative timing between the LO and sample SFG in our current HD-SFG setup using a wedge pair. The wedge pair is a compact way of precisely varying the time delay. Therefore, instead of delaying the LO by a few picoseconds with respect to the sample SFG, the time delay between the LO and sample SFG can be precisely set and the sample amplitude and phase can be directly measured.

### 7.2 Experimental Methods

The new experimental design builds upon our current HD-SFG spectrometer, which was described in Chapter 3. The main difference is that additional material is added to all three beams in the collimated region to improve the control of the time delay between the LO and the sample SFG. An overview of the experimental design is shown in Figure 7.1. The sample SFG is delayed by a fixed amount relative to the LO by adding delay plates to the IR and visible. The thickness of the delay plates added to
the IR and visible were chosen to maintain the temporal overlap of the IR and visible beams at the sample. Initially, 3.3 mm thick CaF$_2$ and 3 mm thick CaF$_2$ were added to the IR and visible respectively. However, due to the high dispersion of CaF$_2$ in the IR, the delay plates were changed to 2 mm thick KBr and 2.3 mm thick fused silica for the IR and visible respectively. A CaF$_2$ wedge pair (Laser Quantum, 35 x 20 x 1.4 mm (middle), 4° wedge) was inserted into the LO so the relative time delay of the LO could be changed without changing the beam pointing. One wedge was set at a fixed height, while the height of the other wedge was scanned using a motorized stage (25 mm stage travel, ThorLabs, MTS25-Z8). As the stage was scanned, moving one wedge up or down, the thickness of CaF$_2$ that the LO travels through and correspondingly the time delay of the LO relative to the sample is varied. If the stage is moved by a step size of $dx$, the corresponding change in thickness of CaF$_2$ that the LO travels through is defined by

$$dT = \tan(4^\circ) \times dx$$

(7- 1)

where 4° is the wedge angle. The change in thickness, $dT$, can then be converted to a time delay, $dt$, with the refractive indices of CaF$_2$ ($n_{CaF2}(\lambda)$) and air ($n_{air}$), and the speed of light, $c$,

$$dt = \frac{dT(n_{CaF2}(\lambda) - n_{air})}{c}$$

(7- 2)

The precise time delay depends on wavelength due to the wavelength dependent refractive index of CaF$_2$. For SFG wavelengths near 640 nm, 1 mm of stage travel corresponds to roughly 100 fs. Therefore, a range of approximately 2.5 ps can be covered by scanning the moving wedge height.
By adding material to all three beams, there are three possible cases for the relative time delay as outlined in Figure 7.2. In Case 1, the LO goes through the thin edge of the wedge and arrives at the sample before the IR and visible. In Case 2, the LO, IR, and visible all arrive at the sample at the same time so there is no time delay between the LO and sample SFG. In Case 3, the LO goes through a thicker region of the wedge and arrives at the sample after the IR and visible. The height of the stationary wedge is set so case 2 occurs near the middle of the stage travel and the time delay between the LO and sample SFG can be scanned to cover all 3 cases.

Figure 7.1: Top: HD-SFG setup with delay plates in the IR (red) and visible (green) beams, and a wedge pair in the LO (orange). Inset shows image from CCD and region to be binned outlined in green. Bottom: Cross polarized heterodyne-detected SFG setup for balanced detection. Polarizations represented with arrows of the corresponding beam color: horizontal arrows are p-polarized and vertical arrows are s-polarized. The polarization of the LO is rotated by pol1 (45° polarizer) and pol2 (90° polarizer). The LO and sample SFG have opposite polarizations so an achromatic waveplate (AW) rotates the polarizations by 45° and a beam displacer (BD) separates the positive and negative interference between the LO and sample in two regions on the CCD. Figure is adapted from reference 12.
To improve the signal-to-noise ratio, a balanced detection scheme using cross polarized heterodyne-detected sum-frequency generation (XP-HD-SFG) was implemented, as shown in Figure 7.1 (bottom). In XP-HD-SFG, the sample SFG is interfered with the orthogonally polarized LO. The LO is generated in the same polarization as the sample, but the LO polarization is rotated by 90° with two thin polarizing films (Edmund Optics, 0.1 mm thick each). The first polarizer set at 45° and the second polarizer set at 90° with respect to the original LO polarization rotates the LO polarization from ‘p’ to ‘s’ (or ‘s’ to ‘p’) at the expense of losing more than ¾ of the light. Therefore, the polarization of the LO and sample SFG are orthogonal. An achromatic λ/2 waveplate (Eksma, 450-680 nm) rotates the two orthogonal beams by 45°, and a calcite beam displacer (ThorLabs) spatially separates the ‘s’ and ‘p’

Figure 7.2: Three cases for the relative timing between the LO and sample SFG when scanning the height of the moving wedge in the LO. Case 1: LO arrives before the IR/visible ($\Delta\tau < 0$), Case 2: LO and IR/visible arrive at the same time ($\Delta\tau = 0$), and Case 3: LO arrives after the IR/visible ($\Delta\tau > 0$).
components of the signals in the vertical dimension on the CCD, which can be binned into two separate regions of interest (ROI). One ROI contains the LO + sample SFG signal, while the other ROI contains the LO – sample SFG signal.

Initially, the time delay between the LO and the sample was scanned in steps of 0.1 mm over the entire stage travel to identify the approximate zero time delay. Once the approximate zero time delay was identified, the time delay was scanned in 0.001-0.002 mm steps for 3-4 mm around zero time delay with integration times from 0.5-2 s for non-resonant samples. A shorter range of time delays were scanned for the resonant OTS sample as integration times of 10-20 s were required.

The stage being used to scan the moving wedge has a homing accuracy of ±4.0 µm, a backlash of <6 µm, and bidirectional repeatability of 1.6 µm. Stage homing was only preformed when the stage was initially connected to the computer and not between experiments to remove potential error from homing. Additionally, quadrature detection, Figure 7.3, was implemented to account for position errors from backlash and incremental movement. A green diode laser (Laser Fuchs, LFD532-1), set to ‘s’ polarized relative to the wedge surface with a thin polarizing film (Edmund Optics, 0.1 mm thick), was split into two beams with a beam splitter (CVI, 50/50 visible). The transmitted beam was rotated by a ¼ wave with a thin λ/4 waveplate film (Edmund Optics, 0.1 mm thick) to circularly polarize the light. The reflected beam was reflected by a Si mirror through the wedge pair between the LO and IR, then reflected by another Si mirror and rotated by a ½ wave with a thin λ/2 waveplate film (Edmund Optics, 0.1 mm thick) before being recombined with the transmitted, circularly polarized beam in a second beam splitter (ThorLabs, 50/50 visible). Neutral density filters (ThorLabs,
reflective) were used to attenuate the intensity so interference could be observed by eye. Both arms were detected with Si photodiode detectors (ThorLabs, 400-1000 nm) with bandpass filters (ThorLabs, 360-580 nm) to remove stray light. However, the two arms were detected in orthogonal polarizations, which were selected using thin polarizing films (Edmund Optics, 0.3 mm thick).

**Figure 7.3:** Top: Schematic of the interferometer of green photodiode with one beam rotated by a thin film $\lambda/4$ waveplate (TF $\lambda/4$ wp), and the other beam rotated by a thin film $\lambda/2$ waveplate (TF $\lambda/2$ wp) after traveling through the wedge pair. The two arms of the interferometer are detected on silicon photodetectors (Si PD) in orthogonal polarizations selected by thin film polarizers (TF pol). Bottom: Normalized response of the PD in each arm. The response from PD2 is shifted by a quarter wave with respect to the response from PD1.
7.3 Results and Discussion

Scanning the time delay between the LO and the sample SFG varies the phase shift between the pulses. Therefore, at each frequency, the interference between the two signals varies from positive to negative interference at the SFG frequency corresponding to a period of approximately 2 fs. As discussed in Chapter 6, every material has an inherent phase. If the LO and sample are the same material, for instance ZnO, the frequency dependent phase of the material is the same and there should be no phase difference at time zero. However, in our geometry, the LO is reflected off the sample resulting in a 180° phase flip in the LO for exposed surfaces. Therefore, the phase difference between the LO and sample at time zero should be 180°. Additionally, if the response at each time point is summed over all frequencies (integrated SFG), we observe an interferogram corresponding to the single element detector response. Since the LO and sample for ZnO versus ZnO are 180° out of phase, time zero should correspond to the maximum negative interference in the integrated SFG.

7.3.1 Material of IR Delay Plate

Initially, CaF$_2$ delay plates were added to the visible and IR to compensate for the material added to the LO by the wedge pair. The moving wedge in the LO was scanned over 4 mm of stage travel (~400 fs). In the integrated SFG of ZnO versus ZnO, the interferogram is very asymmetric, Figure 7.4a, which indicates that the interference at $\pm dt$ are not equivalent. Examining the frequency resolved data around time zero provides insight into the origin of the asymmetry. The minimum interference in the integrated SFG occurs when the stage is at approximately 12.5 mm, which should
correspond to time zero. In the frequency resolved data near 12.5 mm, Figure 7.4b, the interference fringes are very curved. The fringes appear to be getting more vertical at lower stage positions (<12.5 mm) for the higher frequencies, whereas the fringes appear to be getting more vertical at higher stage positions (>12.5 mm) for the lower frequencies. Therefore, there is not a single time zero across all frequencies. This effect is due to the dispersion in the materials added to all three beams between generating the LO and the sample SFG. Unlike the designs from Thämer et al. and the Shultz group, where the timing between the LO and sample SFG is varied by changing the path length, our design uses material to vary the time delay between the LO and the sample SFG. Therefore, the delay plates in the visible and IR, and the wedge pair add dispersion to the beams due to the wavelength dependent refractive indices.

Figure 7.4: SFG response for ZnO (LO) versus ZnO (sample) with CaF$_2$ delay plate in the IR as a function of stage position: (a) integrated over all frequencies, and (b) frequency resolved.
The dispersion in the visible beam is insignificant as the spectral bandwidth is only 1 nm. However, both the LO and IR are broadband so the refractive index of CaF$_2$, and thus the time delay, will be significantly different across the spectrum. Figure 7.5a shows the time delays induced by the IR traveling through 3.3 mm of CaF$_2$ and the LO traveling through enough CaF$_2$ to match the delay of the IR at 3200 cm$^{-1}$. The time delays across the IR frequencies differ by roughly 90 fs and the time delays for the corresponding SFG frequencies differ by roughly 10 fs. The difference in the dispersion between the LO and IR is approximately 80 fs for IR frequencies from 2600 cm$^{-1}$ to 3800 cm$^{-1}$, Figure 7.5c. Therefore, the absolute zero time will vary across the spectrum. This explains why the fringes in Figure 7.4b, appear more vertical at lower stage positions for the higher frequencies and more vertical at higher stage positions for the lower frequencies. In order to minimize the dispersion, the 3.3 mm CaF$_2$ delay plate was replaced with a 2 mm KBr delay plate because the refractive index of KBr is less wavelength dependent in the IR than the refractive index of CaF$_2$. Repeating similar time delay calculations with the KBr delay plate, Figure 7.5b, the time delays of the IR across all IR frequencies differs by less than 10 fs, and the difference between the dispersion in the LO and IR is roughly 2 fs for IR frequencies ranging from 2600 cm$^{-1}$ to 3800 cm$^{-1}$. Thus, the dispersion effects should be much smaller for with the KBr delay plate. Even with the low dispersion of KBr in the IR, the IR is still slightly more dispersed than the LO traveling through the CaF$_2$. Therefore, the addition of more dispersive media, such as the thin polarizing films for balanced detection, to the LO may improve the dispersion matching between the LO and IR.
After replacing IR delay plate with KBr, the visible delay plate was also replaced to maintain the temporal overlap between the visible and IR at the sample. When the wedge position was scanned by roughly 4 mm, the curvature near time zero is significantly reduced. In Figure 7.6a, the frequency resolved SFG as function of the stage position has the expected inverted ‘v’ shape. At time zero, at approximately 12.2 mm, the fringes are roughly vertical. At stage positions left of time zero, the fringes are tilted to the right, and at stage positions right of time zero, the fringes are tilted to the left. This shape reflects the fact that the higher frequencies oscillate faster. The integrated SFG of ZnO versus ZnO with the KBr delay plate, Figure 7.6b, is also more symmetric than with the CaF₂ delay plate. However, there is still some asymmetry due to slight dispersion differences between the LO and IR.

Figure 7.5: Time delays of the IR (red) due to the delay plate in the IR and the LO (orange) due to the wedges thickness need for the LO to match the IR time delay at 3200 cm⁻¹ for a (a) 3.3 mm CaF₂ delay plate in the IR and (b) 2 mm KBr delay plate in the IR. (c) The difference in the LO and IR time delays for the CaF₂ (blue) and the KBr (black) delay plates.
Figure 7.6: SFG response for ZnO (LO) versus ZnO (sample) with KBr delay plate in the IR as a function of stage position: (a) frequency resolved, and (b) integrated over all frequencies.
From the integrated SFG, we identified time zero to be near 12.2 mm and the region around 12.2 mm was examined more carefully in the frequency resolved data. Figure 7.7 shows the frequency resolved SFG zoomed in around time zero. The time zero fringe should be the most vertical fringe. By finding the positions of the local maxima/minima in the region near time zero for each frequency, the slope of fringes close to time zero could be examined, Figure 7.7. The fringes near zero still have a slight curvature. However, the local maxima/minima for every frequency form nearly perfect lines, only deviating by one position step (0.001 mm) at the maximum. By switching the delay plate material from CaF$_2$ to KBr, the dispersion effects have been largely eliminated. Although, to measure the accurate phase of resonant samples, the precise phase variation of the spectrometer at time zero needs to be characterized.

**Figure 7.7:** Frequency resolved SFG response for ZnO (LO) versus ZnO (sample) with KBr delay plate in the IR as a function of stage position near zero. The black dots in the zoomed in region represent local maxima/minima showing there is little to no slope for the fringes near time zero.
7.3.2 Quadrature Detection

In order to accurately characterize the phase of our spectrometer and samples, the position of the stage at time zero needs to be known and consistent between experiments to 1 µm. However, the bidirectional repeatability of the stage used is worse than 1 µm and we noticed an accumulating error in the position read out. To account for any errors in the stage movement, we implemented quadrature detection using a laser interferometer.17

The experimental set-up used for the quadrature detection was described above and shown in Figure 7.3. By converting one arm of the interferometer used for quadrature detection to circularly polarized light, there is a 90° phase shift between the ‘s’ and ‘p’ polarization components. Additionally, there is a phase shift between the two arms defined by the path length difference. The measured interference between the two arms in one polarization is the sine of the phase shift between the two arms, and the other is the cosine, or sine with an added 90° phase. Therefore, the signals measured by the two Si photodiode detectors (PD) are sine waves shifted by a quarter wave, as seen in Figure 7.8a. Because the response of the two detectors should be the sine and cosine, the response of PD1 versus the response of PD2 should form a perfect circle. However, the graph of the measured response of PD1 versus the measured response of PD2 is slightly elongated along the diagonal, Figure 7.8b. Thus, the two detected signals are not exactly 90° out of phase stemming from the rotation of the thin ¼ waveplate film not being optimal.18
Figure 7.8: Quadrature Detection (QD) of a diode laser interferometer with one arm traveling through the wedge pair: (a) response of the two photodiode detectors (PD) as a function of stage travel normalized to 1, (b) correlation between the response in PD1 and PD2, each circle is at a different stage position, (c) number of wave periods of the diode laser calculated from QD versus the readout stage position shifted to be centered around zero, (d) time delay calculated from QD versus the readout stage position shifted to be centered around zero, (e) stage position calculated from QD versus the readout stage position shifted to be centered around zero, and (f) the difference between the readout stage position and QD calculated position (red) and the difference between the readout stage positions and smoothed QD calculated position (black).
To extract the phase between the two arms, the inverse tangent of the ratio between the intensity of PD1 and the intensity of PD2 is calculated.

\[
\varphi = \tan^{-1} \left( \frac{I_{PD1}}{I_{PD2}} \right)
\]  

(7- 3)

The extracted phase will vary from -180° to 180° with the period of the diode laser. Therefore, the extracted phase can be converted to the number waves detected as shown in Figure 7.8c. The green diode laser used has a wavelength of 532 nm, so the number of waves can be converted to time delay by multiplying the number of waves by the period of the laser. The time delays determined by quadrature detection versus the readout stage positions are shown in Figure 7.8d. Finally, the calculated time delays from quadrature detection are converted to stage position using the refractive index of CaF₂ using the inverse of equations 7-1 and 7-2:

\[
dx = \frac{dt \cdot c}{\tan(4°) \cdot (n_{CaF2(532nm)} - n_{air})}
\]  

(7- 4)

Over the 4 mm of measured stage travel, the correlation between the readout stage position and the stage position calculated by quadrature detection is roughly linear, Figure 7.8e. However, taking the difference between the readout and calculated stage position highlights the deviations between them. Figure 7.8f shows that the error in the readout stage position varies significantly, roughly 0.03 mm, over 4 mm of stage travel. On average the readout stage position is correct, but there are fluctuations of rough 0.01 mm over 0.5 mm of stage travel. The smaller fluctuations in the red trace of Figure 7.8f
are noise due to the imperfect quadrature and are smoothed over in the final calculated position axis from quadrature detection.

With quadrature detection, the position accuracy of the stage was improved, allowing for data at the same stage position between multiple scans to be compared. Using the readout stage position for multiple loops, the response of PD1 for each loop does not match over the entire range, as seen in Figure 7.9a. This indicates that the absolute stage position is not the same despite the readout values being the same. If the position axis calculated by quadrature detection for each loop is used instead, the response of PD1 for each loop matches over the entire range, Figure 7.9b. Therefore, the implementation of quadrature detection enables multiple loops for the same sample.

Figure 7.9: Response of photodiode 1 for two loops (loop 1 - red, loop 2 – blue) versus the stage position with (a) the readout stage position and (b) the stage position calculated with quadrature detection.
to be averaged together or data at the same stage position to be compared between a
reference and resonant sample.

### 7.3.3 Characterizing the Spectrometer Phase

Assuming the absolute phase of the ZnO LO generator and the ZnO sample are
equivalent, their phase difference at time zero will be $180^\circ$ due to the phase flip of the
LO upon reflection. Therefore, by comparing the frequency dependent phase of ZnO
versus ZnO at time zero, the deviations from $180^\circ$ characterize the spectrometer phase.
Due to the slight differences in dispersion of KBr for the IR wavelengths and CaF$_2$ for
the SFG wavelengths, the phase is expected to vary slightly over the spectrum.

Using balanced detection, the norm squared contributions can be separated from
the real and imaginary components. In balanced detection, the constructive interference
between the LO and sample SFG is measured in one region of interest, and the
destructive interference between the LO and sample SFG is measured in the other region
of interest. Thus, the intensity measured in the two regions of interest are

\[
I_{roi1} = \left| E_{LO} e^{i\omega \Delta \tau} + E_{samp} \right|^2 = \left| E_{LO} \right|^2 + \left| E_{samp} \right|^2 + E_{LO}^* E_{samp}^* e^{i\omega \Delta \tau} + E_{LO}^* E_{samp} e^{-i\omega \Delta \tau} \quad (7-5)
\]

\[
I_{roi2} = \left| E_{LO} e^{i\omega \Delta \tau} - E_{samp} \right|^2 = \left| E_{LO} \right|^2 + \left| E_{samp} \right|^2 - E_{LO}^* E_{samp}^* e^{i\omega \Delta \tau} - E_{LO}^* E_{samp} e^{-i\omega \Delta \tau} \quad (7-6)
\]

where $\Delta \tau$ is the time delay between the LO and sample. By taking the difference between
the two regions, the norm squared contributions are eliminated, whereas the sum of the
two regions eliminates the cross terms.
\[ I_{roi1} - I_{roi2} = 2E_{LO}^*E_{samp}^*e^{i\omega \Delta \tau} + 2E_{LO}^*E_{samp}e^{-i\omega \Delta \tau} \]  \hspace{1cm} (7-7)

\[ I_{roi1} + I_{roi2} = 2|E_{LO}|^2 + 2|E_{samp}|^2 \]  \hspace{1cm} (7-8)

For ZnO versus ZnO, the integrated SFG response is relatively symmetric with time 
zero occurring between -0.1 and -0.2 mm, Figure 7.10. The difference between the two
regions of interest alternates between positive and negative interference depending on
the precise time delay, Figure 7.11a. According to equation 7-8, the sum of the two
regions should not depend on the time delay between the LO and sample. Slight
variations in intensity as a function of time delay are observed in Figure 7.11b due to
laser fluctuations. Therefore, the sum between the two regions can be used to normalize
out the laser fluctuations in the difference spectrum.

![Figure 7.10](image)

**Figure 7.10:** Integrated SFG response for ZnO (LO) versus ZnO (sample) over all
frequencies as a function of stage position with balanced detection.
Figure 7.11: SFG response for ZnO (LO) versus ZnO (sample) as a function of stage position with balanced detection for (a) the difference and (b) the sum between the two regions of interest.
By examining the slopes of the fringes in Figure 7.11a, time zero was defined as a stage position of -0.1991 mm. The stage position axis was converted to time delay using equations 7-1 and 7-2 with -0.1991 mm defined as a time delay of 0 fs and the refractive index of CaF$_2$ at the SFG wavelength corresponding to an IR frequency of 3000 cm$^{-1}$. The time delay axis for each frequency will be slightly different. However, over 2 mm of stage travel the difference in time delay between 2900 cm$^{-1}$ and 3150 cm$^{-1}$ is only 0.1 fs, which is negligible near zero. Near time zero, the fringes appear very vertical for the center frequencies with only slight phase shifts away from zero, Figure 7.12a. Normalizing out the IR envelope by dividing by the maximum intensity at each frequency, Figure 7.12b, highlights the slight ‘s’ shape of the fringes near zero due to the slight phase differences across the spectrum. The phase at each point can also be calculated as the interference at each IR frequency forms a sine wave with a frequency of the detected SFG wavelength. At each frequency, the phase smoothly varies from 0° to 360° before repeating the cycle, as seen in Figure 7.12c. Away from zero both the fringes from the interference between the LO and the sample and the calculated phase slant towards the center. Although the fringe at 0 fs appears to be the most vertical, the fringe at ~10 fs is the most symmetric around 3000 cm$^{-1}$.

Time slices of the data and the calculated phase were taken near both 0 fs and 10 fs. In the current experiment, time steps of 0.001 mm were taken corresponding to roughly 21 time points per fringe (or 360°). Therefore, on average there is only data every 17°, so there is not necessarily a data point at exactly 180°. The time slices at -0.5779 fs and 9.933 fs correspond to the closest data point to the node nearest to 0 fs and 10 fs.
At time zero (0 fs), there is a broad negative response that has a similar shape to the IR envelope, as seen in the blue trace in Figure 7.13a. Whereas, the red trace in Figure 7.13a, corresponding to a cut at -0.579 fs or approximate 90° out-of-phase from

**Figure 7.12:** The difference of constructive and destructive interference between ZnO (LO) and ZnO (sample) as a function of stage position near time zero: (a) frequency resolved, (b) normalized to the maximum intensity at each frequency, and (c) converted to phase.
0 fs, is relatively flat over the spectral range. The slight slope of the data for the cut at -0.579 fs is consequence of the slight dispersion mismatch between the LO and the IR, and the three small peaks between 2900 cm\(^{-1}\) and 3050 cm\(^{-1}\) are a result of the CH stretches of hydrocarbons from the atmosphere absorbed to the LO and sample. The time slice near 10 fs, is significantly less flat than the slice at -0.579 fs in Figure 7.13a.

Time cuts of the phase, instead of time cuts of the data, are shown in Figure 7.13b. The phase is center at approximately 180° for both the time cut at -0.579 fs and 9.933 fs. The total deviation in phase is slightly smaller for the slice at 9.933 fs, but the phase of the slice varies by less than 5 degrees between 2900 cm\(^{-1}\) and 3150 cm\(^{-1}\) where the overlap between the LO and the sample is the best. By taking both the cuts of the data and the calculated phase into account, the current defined time zero is the flattest for this system. However, the phase for spectrometer has been characterized at every time point so the phase of the SFG response for another material could be calculated at any stage position by comparing it to the ZnO versus ZnO response as long as the setup of the spectrometer remains unchanged. SFG data as a function of time delay between the LO and sample have been collected for various combinations of LO (ZnO and y-cut
Comparing the ZnO LO to a ZnO sample, characterized the spectrometer phase, but did not characterize the absolute phase of ZnO. By comparing ZnO with Quartz, which has a known phase, the phase of ZnO can be determined. Then, the phase of Au can be determined by comparing Quartz with Au or ZnO with Au. Data analysis for all the combinations of LO and sample materials is still in progress.

### 7.3.4 Application to Resonant SFG with OTS

In order to measure the phase of a resonant sample, the stage position corresponding to time zero needs to be determined on a nonresonant sample first. The Au dot sputtered on the OTS sample was used to find the stage position corresponding to time zero with a similar procedure to the data analysis performed for the ZnO versus ZnO data outlined in section 7.3.3. Unlike with ZnO as the sample, the phase of the LO does not flip by 180° for Au because the refractive index of Au is lower than air for the SFG wavelengths.

Similar to the ZnO versus ZnO, the integrated SFG response of ZnO versus Au is fairly symmetric, Figure 7.14. However, there was a large intensity change and slight frequency shift of the signal at approximately 6.55 mm, which skewed the integrated SFG signal for stage positions above 6.5 mm. The intensity fluctuations were normalized out of the difference between the constructive and destructive interference using the sum of them. By examining the slope of the fringes in Figure 7.15a, the most vertical fringe was identified at the stage position of 5.847 mm. The fringe identified as time zero for the Au sample is a positive fringe, whereas the fringe identified as time zero for the Au sample is a positive fringe.
zero for the ZnO sample is a negative fringe. This is consistent with the 180° phase difference in the LO reflected off of Au compared to ZnO.

![Graph](image)

**Figure 7.14:** Integrated SFG response for ZnO (LO) versus Au (sample) over all frequencies as a function of stage position with balanced detection.

The time dependent response is similar for Au and ZnO near time zero. The Au also exhibits fairly vertical fringes near time zero, as shown in Figure 7.16a, and the slight ‘s’ shape of the fringes due to the dispersion in the spectrometer is highlighted in Figure 7.16b after the IR envelope is normalized out. The calculated phase is also relatively flat near time zero, Figure 7.16c. Therefore, the choice of the stage position of 5.847 mm as time zero seems reasonable.
Figure 7.15: SFG response for ZnO (LO) versus Au (sample) as a function of stage position with balanced detection for (a) the difference and (b) the sum between the two regions of interest.
At the node nearest to zero, the phase of Au exhibits a similar range of phases as ZnO near zero. Figure 7.17a compares the phase of Au and the phase of ZnO versus a LO generated in ZnO near time zero. The phase for ZnO has been shifted by 180° so the two phases are both centered near 0°. Overall, the shapes of the phase for the two materials are similar but shifted in frequency due to slightly different IR envelopes. A careful examination of the frequency dependence of the ‘s’ shape has not been

Figure 7.16: The difference of constructive and destructive interference between ZnO (LO) and Au (sample) as a function of stage position near time zero: (a) frequency resolved, (b) normalized to the maximum intensity at each frequency, and (c) converted to phase.
performed in detail but characterizing the phase across for IR frequencies from 2600 cm\(^{-1}\) to 3800 cm\(^{-1}\) is necessary before using this geometry to measure water at surfaces. Time slices of the data for ZnO versus Au at -0.5 fs and 0.0 fs, Figure 7.17b, have a relatively small signal and a broad feature consistent with the IR envelope, respectively.

![Figure 7.17: Time cuts of ZnO (LO) versus Au (sample) with balanced detection at the node (-0.5 fs) and peak (0 fs) for (a) the calculated phase of Au compared to ZnO versus ZnO and (b) difference between the constructive and destructive LO/sample interference](image)

The phase of resonant samples, such as OTS, can be measured by taking time slice at the same stage position of Au. Without quadrature detection, the readout stage position for the sample differed by up to \(\frac{1}{4}\) wave, as shown with the response of photodiode 1 for Au versus OTS in Figure 7.18a. This corresponds to the difference between the real and imaginary components. By measuring the stage position with quadrature detection, the response for photodiode 1 is almost identical for Au and OTS in the region scanned, Figure 7.18b. Therefore, the phase at time cuts can be compared between Au and OTS.
The sum of the constructive and destructive interference for OTS in the ppp polarization combination is dominated by the norm squared response of the LO and significantly varies over time due to laser fluctuations, Figure 7.19a. Unlike the nonresonant signals, the difference between the constructive and destructive interference is does not have straight fringes across the spectrum. There is a twist in the fringes at \( \sim 2970 \text{ cm}^{-1} \) due to the CH resonance, Figure 7.19b. Converting the intensity to phase, Figure 7.19c, the phase is flat above and below the CH resonances but exhibits a phase shift at the resonant frequencies.

**Figure 7.18:** Response of photodiode 1 for OTS in ppp data (red) with (a) the readout stage position and (b) the stage position calculated with quadrature detection compared to the response of photodiode 1 for the Au (black) data with the stage position calculated with quadrature detection.
The time slices of OTS in ppp for the same time delays as Au are relatively flat over the frequency range but have a dispersive line shape (-0.5 fs) or a peak (0 fs) at ~2970 cm⁻¹ where there is a strong CH resonance, Figure 7.20. However, the signals are very small due to the large intensity fluctuations and the strength of the LO being much larger than the sample. To convert these time slices to the real and imaginary

**Figure 7.19:** SFG response for ZnO (LO) versus OTS (sample) in ppp polarization combination as a function of stage position with balanced detection for (a) the sum and (b) the difference between the two regions of interest. The frequency dependent phase as a function of time delay (c) exhibiting a phase shift at the CH stretching frequency.
components, we need to correct for the phase of the spectrometer and the Au reference used to define the time zero. Using the amplitude and phase shown in Figure 7.19b-c, the real and imaginary components of the spectrum can be precisely determined. However, this analysis is still in progress.

**Figure 7.20:** Time cuts of ZnO (LO) versus OTS (sample) in ppp polarization with balanced detection at the node (-0.5 fs) and peak (0 fs) in the ZnO versus Au for difference between the constructive and destructive LO/sample interference

The data for ZnO versus OTS in ssp polarization combination had better signal to noise because the LO and sample had more comparable intensities as illustrated by the prominence of two CH stretching peaks in the sum between the two regions of interest, Figure 7.21a. Similar to OTS in ppp, there are phase shifts around the CH peaks for OTS in ssp at ~2875 cm\(^{-1}\) and ~2950 cm\(^{-1}\) in the difference spectra as a function of time delay, Figure 7.21b. However, the polarizers in the LO had to be switched out in between the Au and OTS in ssp data so the time delay at a given stage position are no longer the same. Other methods for determining time zero without the need for a nonresonant sample are currently being explored.
7.4 Conclusion

We have demonstrated a new experimental geometry for HD-SFG using a wedge pair to finely control the time delay between the LO and sample SFG. With low dispersion materials, there is only a slight frequency dependent phase shift of the non-resonant ZnO signal at time zero. Quadrature detection was implemented in order to accurately determine the stage position. The comparison of ZnO (LO) and ZnO sample was used to characterize the spectrometer phase. Further analysis still needs to be performed to characterize the phase of other nonresonant materials, such as Au and Quartz. Preliminary analysis of a resonant sample, OTS, is promising for directly
measuring the phase of the emitted SFG signal. However, the spectrometer phase and phase of reference at position of the time slice of resonant data still need to be corrected for in order to get the purely imaginary spectrum.

7.5 References


(7) Ji, N.; Ostroverkhov, V.; Chen, C. Y.; Shen, Y. R. Phase-Sensitive Sum-


CHAPTER 8

CONCLUSIONS AND FUTURE DIRECTIONS

8.1 General Summary

Most chemical processes in aqueous environments occur at an aqueous interface, either in solvation shells around chemical species or at extended surfaces. The surface perturbs the hydrogen-bonding network, and the hydrogen-bonded network of water rearranges due to the chemical nature of the interface. In order to obtain a detailed molecular understanding of technological and biological interfacial chemical processes, we need to have a detailed understanding of the structure and dynamics of water in interfacial regions. Due to its inherent surface-specificity, SFG has been a powerful technique for studying interfacial water.

Furthermore, since the properties depend on the surface chemistry, we need to understand water as a function of the surface chemistry. Here, hydrophobic, hydrophilic, and mixed hydrophobic/hydrophilic SAMs were used to vary the surface chemistry. Despite the macroscopic hydrophobicity of the mixed SAM falling in between the two pure monolayers, HD-SFG experiments showed that on the molecular level the interfacial water interactions are dominated by the hydrophilic PEG chains. However, we also saw a large diffuse layer contribution to the interfacial water SFG signal due to the surface charge of the silica under the monolayers, and intra- and intermolecular couplings between water molecules at the interface. These effects need to be removed in order to measure an accurate vibrational spectrum of the bound interfacial water layer. One way of removing the diffuse layer contribution is to add salt to screen the surface...
charge. In the case of the PEG monolayer, adding NaCl induced ordering of the monolayer. Therefore, adding salt will screen the surface charge, but can also change the interfacial structure in unexpected ways. Adding other salts that do not interact with the monolayer, such as KCl, to screen the surface charge or varying the surface charge by changing the pH can be utilized to remove the diffuse layer contribution.

Since the hydrogen-bonded network of water is highly dynamic, the ultrafast dynamics of the interfacial water also need to be measured to obtain the true structure of interfacial water as a function of surface chemistry. Preliminary transient HD-SFG and interferometric 2D HD SFG were conducted to probe the dynamics of interfacial water at hydrophobic and hydrophilic SAMs. Based on initial fits to the transient HD-SFG data for the OH stretch at OTS, the vibrational relaxation is slightly longer than bulk water, but faster than the air-water interface. This is because the density of water at the solid hydrophobic interface is close to the bulk unlike the lower density at the air-water interface. The 2D HD SFG experiments suggest that PEG, the hydrophilic SAM, may be more heterogenous than OTS. However, more waiting times still need to be collected to fully characterize the static heterogeneity and spectral diffusion dynamics.

The proper phasing and phase accuracy in HD-SFG is still an ongoing problem in the SFG community. Taking inspiration from recent developments from other groups, we extended our existing HD-SFG experimental geometry to scan the time delay between the LO and the sample signal using a wedge pair. By carefully adjusting the timing between the LO and sample, it is possible to set the time delay to directly measure the real or imaginary component on the SFG signal. This design has the potential to address the phase uncertainties in our current HD-SFG design.
8.2 Future Directions

8.2.1 Variations in Self-Assembled Monolayer Deposition

As discussed in Chapter 4, silica has a negative surface charge at neutral pH due to the protonation/deprotonation equilibrium of the surface silanol groups. The surface charge of silica leads to a net orientation of water molecules in the diffuse layer that contribute to the overall SFG signal. By varying the pH and ionic strength of the solution, we effectively eliminated the contribution from the diffuse layer. However, it is also possible to remove the effect of the surface charge by adjusting the deposition conditions. The general process for SAMs deposition on silica results from the silane groups reacting with the OH group on the surface of silica. Therefore, the deposition of silanes to form SAMs can occur on any oxide surface. Sapphire (Al₂O₃) is an ideal candidate for replacing silica as the substrate for studying water at SAMs because it has a no surface charge at pH of 6-8.¹² Unlike for SAMs on silica there should be little to no diffuse layer contribution to the SFG of water signal at SAMs on sapphire. Another possibility is to use a small silane molecule, trimethylchlorosilane, to cap the unreacted surface silanol groups and prevent deprotonation and surface charging.³⁴

8.2.2 Additional Hydrophilic Monolayers

In this dissertation, the difference between water at a hydrophobic (OTS) SAM and a hydrophilic (PEG) SAM was explored with HD-SFG. However, there is no reason to expect the PEG SAM studied to be representative of all hydrophilic monolayers. Studying the PEG SAM initially was chosen since the silane is commercially available and PEG based materials are used in technical applications, such as anti-biofouling materials.⁵ The oxygens in the PEG backbone can accept hydrogen bonds, but the SAM
cannot donate any hydrogen bonds. Comparing water at hydrophilic SAMs with
different hydrogen bond acceptors and donors would elucidate the role of hydrophilicity
versus the specific role of the PEG SAM structure in the structure and dynamics of water
at the interface. Azide terminated SAMs would be a good candidate for another
hydrophilic SAM to study. Our group previously made azide terminated SAMs for
attaching DNA to the surface. I also performed preliminary experiments depositing an
azide terminated alkyl chain to glass slides. The contact angle for the azide terminated
alkyl SAM was approximately 75°, so although it is hydrophilic is it is significantly less
hydrophilic than the PEG SAM examined in this dissertation. Based on the peak at
approximately 2100 cm\(^{-1}\) in the FTIR, Figure 8.1, there is an azide on the surface.

![Figure 8.1: Vibrational spectrum of azide terminated alkyl SAM.](image)

It would also be interesting to look at SAMs with hydrogen bond donors and
acceptors, such as amine and OH terminated SAMs. These SAMs would have their own
signal in the OH stretching region, which would complicate analysis. Preliminary SFG
experiments of an amine terminated SAM, Figure 8.2, show a broad signal around 3500
cm\(^{-1}\) for the dry SAM. There is also a broad signal below the frequency of the CHs when the in contact with water, Figure 8.2, which is likely the water hydrogen bound to the amine group. The ideal SAM would be OH terminated, but since silanes react with OH groups the OH groups on the silane need to be protected before deposition or the OH groups need to be created after the deposition of the SAM on the surface.

![SFG spectra of amine terminated SAM dry and in contact with water.](image)

**Figure 8.2:** SFG spectra of amine terminated SAM dry and in contact with water.

### 8.2.3 Self-Assembled Monolayer with Metal Carbonyl

As mentioned in Chapter 1, vibrational probes have been used in transient IR and 2D IR to measure the dynamics of water around biomolecules.\(^7\)\(^-\)\(^9\) The vibrational probes are often metal carbonyls because they have a strong IR signal. Metal carbonyls on the surface also have a strong SFG signal and our 2D HD SFG experiment was originally setup with metal carbonyls on TiO\(_2\).\(^10\) By attaching a metal carbonyl to an azide terminated SAM via click chemistry, the metal carbonyl on the surface could be used
as a vibrational probe to examine the dynamics of water at the interface with transient HD-SFG and 2D HD SFG with better signal to noise than measuring the water directly. The structure of the water at this interface could still be measured with HD-SFG of the OH stretching region.

8.2.4 Time-Resolved Sum Frequency Generation of Water

Time-Resolved SFG experiments of water are currently limited by the signal to noise and ultrafast relaxation time of water. In order to measure the spectral diffusion dynamics of water at the different SAMs, the 2D HD SFG experiments need to be performed with isotopically diluted water so the vibrational relaxation is slower allowing for more waiting times to be measured. However, isotopic dilution also reduces the signal strength since the number of oscillators is reduced. Currently, it takes between 24 and 28 hours to collect 4 averages of one 2D surface. Using a higher repetition rate laser would make it possible to collect more averages to improve the signal-to-noise ratio.

Another way to measure the spectral diffusion dynamics would be to adjust the current 2D HD-SFG set-up to measure the SFG photon echo. Photon echo experiments are used to determine the spectral diffusion. For bulk water, photon echo spectroscopy was used to measure the spectral diffusion dynamics of water before 2D IR spectra of water were measured.\textsuperscript{11–13} Surface (SFG) photon echoes were first described in the early 1990s, but have not been applied to interfacial water.\textsuperscript{14,15} In a three-pulse photon echo experiment, the dephasing (or spectral diffusion) time is measured without any frequency information. However, within the current frequency bandwidth of our 2D HD SFG experiments of water, a broad bleach around the center frequency dominates the
signal so a surface specific analog to the three-pulse photon echo experiment could be implemented to measure the interfacial spectral diffusion with a better signal-to-noise ratio than the current 2D HD SFG experiments.

### 8.3 References


7. King, J. T.; Kubarych, K. J. Site-Specific Coupling of Hydration Water and Protein Flexibility Studied in Solution with Ultrafast 2D-IR Spectroscopy Site-


