Substrate Preparation for Ultrafast Vibrational Spectroscopy Experiments

CNF Project Number: 1936-10

Principal Investigator: Poul B. Petersen

User: Stephanie Sanders

Affiliation: Department of Chemistry and Chemical Biology, Cornell University

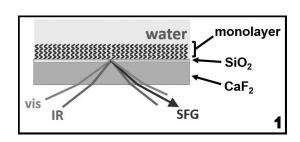
Primary Source of Research Funding: National Science Foundation

Contact: pbp33@cornell.edu, ses422@cornell.edu

Website: http://petersen.chem.cornell.edu/ Primary CNF Tools Used: Oxford ALD FlexAL

Abstract:

Water is ubiquitous and an active component in many natural and technological processes. Vibrational spectroscopy can be used to probe the structure and dynamics of water in a variety of environments. We use sum-frequency generation, a surface specific vibrational spectroscopy, to probe the structure and dynamics of interfacial water at chemically tunable surfaces. Interfaces with tunable surface character are created with self-assembled monolayers. In order to create substrates compatible for both silane self-assembly and sum-



frequency generation, infrared and visible transparent CaF₂ windows are coated with SiO₂. Then after surface functionalization with silane monolayers, the water structure and dynamics at the interfaces can be explored with sum-frequency generation.

Summary of Research:

Water is an active component in many natural and technological processes [1]. Interfaces terminates the H-bonded network of water. We aim to study the structure and dynamics of water at self-assembled monolayers (SAMs) with varying surface character using sum-frequency generation (SFG) spectroscopy. In SFG, an infrared photon interacts with a dipole transition of the molecule and a visible photon excites the molecule to a virtual electronic state where it can undergo an anti-Stokes Raman transition resulting in a photon at the sum of the two incident frequencies being emitted [2,3]. In order to collect SFG spectra of solid-aqueous interfaces, we must probe through the window so the infrared photons are not absorbed by water. However, silica, a common SAMs substrate, also absorbs in the infrared.

To create an infrared and visible transparent substrate compatible with SAMs syntheses, we start with a CaF₂ window, which is transparent through the visible and infrared. Then approximately 10 nm of SiO₂ is deposited on the CaF₂ window via atomic layer deposition (ALD) with the Oxford ALD FlexAL. The SiO₂ layer is thin enough to not absorb all the IR photons and prevent SFG spectra of the sample from being collected, but thick enough to form a surface compatible with the self-assembly of silanes.

Once the SiO₂ is deposited, hydrophobic, hydrophilic, or mixed monolayer are synthesized with self-assembly of silanes on the surface. Figure 1 shows a schematic of the surface in contact with water. Then, the surfaces and water at the surfaces are analyzed with SFG [2-5].

References:

- [1] Ball, P. Life's Matrix: A Biography of Water; University of California Press: Berkeley, 2001.
- [2] Barrett, A. R.; Petersen, P. B. Order of Dry and Wet Mixed-Length Self-Assembled Monolayers. J. Phys. Chem. C 2015, 119 (42), 23943-23950.
- [3] Vanselous, H.; Petersen, P. B. Extending the Capabilities of Heterodyne-Detected Sum-Frequency Generation Spectroscopy: Probing Any Interface in Any Polarization Combination. J. Phys. Chem. C 2016, 120 (15), 8175-8184.175-8184.
- [4] Sanders, S.E.; Vanselous, H.; Petersen, P. B. Water at Surfaces with Tunable Surface Chemistries. J. Phys. Condens. Matter 2018, 30(11), 113001.
- [5] Kocsis, I.; Sorci, M.; Vanselous, H.; Murail, S.; Sanders, S.; Licsandru, E.; Legrand, Y-M.; van der Lee, A.; Baaden, M.; Petersen, P. B.; Belfort, G.; Barboiu, M. Oriented chiral water wires in artificial transmembrane channels. Sci. Adv. 2018 4(3), eaao5603.