

Substrate Preparation for Ultrafast Vibrational Spectroscopy Experiments

CNF Project Number: 1936-10

Principal Investigator(s): Poul B. Petersen

User(s): Stephanie Sanders

Affiliation(s): Chemistry and Chemical Biology, Cornell University; Physical Chemistry II, Ruhr-University Bochum, Germany

Primary Source(s) of Research Funding: National Science Foundation

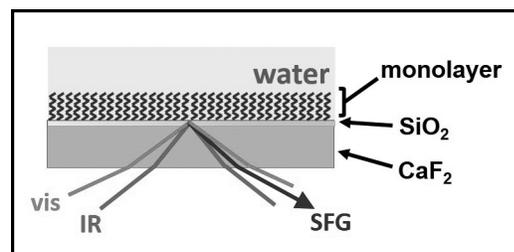
Contact: poul.petersen@rub.de, ses422@cornell.edu

Website: <https://www.ruhr-uni-bochum.de/pc2/petersen/>

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 CaF_2 windows are coated with SiO_2 . 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 terminate 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 calcium fluoride (CaF_2) window, which is transparent through the visible and infrared. Then approximately 10 nm of SiO_2 is deposited on the CaF_2 window via atomic layer deposition (ALD) with the Oxford ALD FlexAL. The SiO_2 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 SiO_2 is deposited, hydrophobic, hydrophilic, or mixed monolayers 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 [2-6].

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] Vanselow, 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.
- [4] Sanders, S.; Vanselow, H.; Petersen, P. *Water at Surfaces with Tunable Surface Chemistries*. *J. Phys. Condens. Matter* 2018.
- [5] Kocsis, I.; Sorci, M.; Vanselow, 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.
- [6] Sanders, S.E.; Petersen, P.B. Heterodyne-Detected Sum Frequency Generation of Water at Surfaces with Varying Hydrophobicity. *J. Chem. Phys.*, 2019, 150 (20), 204708.

