Wednesday Morning, November 12, 2014

Biomaterial Interfaces
Room: 317 - Session BI+AS-WeM

Nonlinear Optical & Vibrational Spectroscopy
Moderator: Luke Hanley, University of Illinois at Chicago

8:40am **BI+AS-WeM3 Characterizing Adsorbate Structure at the Solid-Liquid Interface through Nonlinear Vibrational Spectroscopy and Modelling Approaches**, *S. Roy, P.A. Covert, K.-K. Hung, U. Stege,* ***Dennis Hore***, University of Victoria, Canada **INVITED**

Even-order nonlinear spectroscopies such as second harmonic (SHG) and sum frequency generation (SFG) are valued for their sensitivity to interfacial structure as they are capable of discriminating from adjacent bulk phases based on symmetry. Visible-infrared SFG spectroscopy additionally harnesses the sub-molecular structural probe of a vibrational spectroscopy by tuning the infrared laser over molecular resonances. As a result, over the past two decades, SFG spectroscopy has been successfully applied to a wide variety of solid, liquid, and vapor interfaces, revealing signatures of the molecular organization that provide clues to the surface structure. Our group has been working on techniques to assist in the molecular interpretation of the SFG response. For small molecules, this includes grid computing-based searches to validate candidate orientation distributions based on the experimental data. For larger molecules with additional conformational flexibility, we employ molecular dynamics simulations to further refine our efforts to interpret the SFG data. Our most recent efforts explore the use of phase-resolved SFG spectra in order to develop more sensitive functions for scoring trial molecular orientation distributions. Our goal is to develop tools that are scalable to molecules of arbitrary complexity. This talk will provide some examples to illustrate our path towards this direction.

9:20am **BI+AS-WeM5 Vibrational Spectroscopy Investigation of the Giant Surface Potential of Organic Semiconductors**, ***Laura Kraya***, Princeton University, *C. Krekeler, C. Weigel,* Technical University Braunschweig, Germany, *P. Zhao,* Princeton University, *W. Kowalsky,* Technical University Braunschweig, Germany, *C. Lennartz,* BASF, *A.L. Kahn, B. Koel*, Princeton University

A phenomenon known as the giant surface potential (GSP), where the surface potential of organic films display linear growth with increasing film thicknesses in the absence of light was first reported by Ito et al. on (8 hydroxyquinoline)aluminum(Alq_3), a prototypical fluorescent material used in OLEDs. It has been shown that the surface potential of Alq_3 has reached 28 V for a 560 nm thick film by Kelvin probe measurements in vacuum in the absence of light. Since then this phenomenon has been observed for a broad range of molecules thermally evaporated on varying substrates under similar conditions. The effect is independent of the substrate, dependent on film thickness and decays quickly with illumination at the normal mode of the respective molecule. The spontaneous buildup of the GSP cannot be explained by any classical interfacial phenomena. Investigations into the cause of GSP, including the analysis of light and heat on the surface potential, are not yet understood.

In this study we use vibrational spectroscopy to understand the nature of the GSP buildup, where we have found a significant change in the vibrational structure of the organic material in thick films where the GSP is present as compared to thin films. The vibrational spectra of the most commonly studied light-emitting material, Alq_3, on indium tin oxide (ITO) is investigated as a function of thickness using high resolution energy electron loss spectroscopy (HREELS), Raman spectroscopy, high resolution x-ray photoelectron spectroscopy (HR-XPS), attenuated total reflectance infrared spectroscopy (ATR-IR), and density functional theory (DFT) calculations. In order to provide a holistic understanding of the GSP, the results are compared to the vibrational spectra of 1,3,5-tris(N-phenylbenzimiazole-2-yl)benzene (TPBi) on ITO, an electron transporter host material with a measured GSP of 0.07 V/nm, and bis(triphenylsilyl)-dibenzofuran (BTDF) on ITO, a typical electron-conducting host used in combination with hole-conducting deep-blue emitter with a measured GSP of 0.08V/nm. The observed spectra show significant changes with the presence of the GSP in the organic material on ITO, which can be explained in terms of different symmetries of the isomers as well as between complexes and isolated anions. Additionally, it has been found that the surface phase differs from the bulk phase, where a structured layer is evident at the interface of the organic semiconductor, and this layer shifts with increasing thickness and in the presence of the GSP. The present work has provided direct evidence that a different molecular orientation exists at the interface than in the bulk, where the GSP exists.

9:40am **BI+AS-WeM6 Diatom Biomineralization at the Molecular Level Probed by SFG Spectroscopy**, *H. Lutz,* Max-Planck-Institute for Polymer Research, Germany, *J.E. Baio,* Oregon State University, *V. Jaeger, A. Roehrig, G. Drobny, J. Pfaendtner,* University of Washington, ***Tobias Weidner***, Max-Planck-Institute for Polymer Research, Germany

Specialized mineral proteins control the growth of biogenic hard tissue. Using specific recognition motifs, proteins bind and release mineral facets and grow the intricate mineral morphologies found in Nature. Particularly fascinating examples of biomineralization are the high fidelity silica nanostructures in the shells of diatoms. Within the unicellular algae Cylindrotheca fusiformis, proteins called silaffin play a crucial role in the molecular biomineralization machinery. In order to harness the concepts used by Nature to efficiently fabricate mineral nanostructures we aim to understand the underlying protein–silica interactions. We found that artificial peptides consisting of lysine and leucine (LK peptides) can mimic silaffin's capability of forming various biosilica nanostructures. These peptides were designed to adopt helical or beta-sheet structures due to their hydrophobic periodicities and represent simple model systems to study the effect of protein folding on mineralization. Using surface sensitive sum frequency generation (SFG) vibrational spectroscopy we have studied the interactions of LK peptides with biosilica surfaces and within biosilica composites. We monitored how different LK peptides fold at the silica-water interface and we found that interfacial folding is crucial for the silica morphology: spheres, rods and flakes were produced by LKs – depending on their surface folding. Side chains also actively participate in the mineralization process. We probed the side chain structure of LKs in contact with silicic acid solution and observed increased ordering of charged lysine side chains during the formation of biosilica, indicating their involvement in silica nucleation. Combined with cryo-TEM measurements and MD simulations of different stages of nanoparticle nucleation the SFG studies provide important details of peptide-driven silica formation.

11:00am **BI+AS-WeM10 Water, Charge and Membrane Interface Stability**, ***Sylvie Roke***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

Life occurs in three dimensional turbid aqueous systems. A cell consists for ~60 % of water and contains many organelles and interfaces. The average distance between two molecules, or a molecule and a membrane interface is approximately 1 nm. The molecular, structural, dynamic, and biological properties of water, aqueous systems and aqueous interfaces are essential in understanding the complexity of life, and our ability to harness its features for novel (nano)technologies.

Here, I will introduce nonlinear light scattering methods that can be used to gain label-free molecular level information about model membrane interfaces in liquid aqueous nanoscopic systems. The use of these methods will be illustrated around the following questions:

· Does water behave charge asymmetrically?

· What is the role of water in determining the stability of amphiphilic interfaces?

· Is the molecular structure of model membranes influenced by the above considerations?

11:40am **BI+AS-WeM12 Second Harmonic Scattering: Characterizing the Interaction between Lipid Membranes and Water**, ***Cornelis Lütgebaucks***, *C. Macias-Romero, S. Roke,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Lipid membranes are essential for all organisms by separating functional compartments and mediating cellular signaling. Dioleoylphosphatidylcholine (DOPC) and Dioleoylphosphatidylserine (DOPS) are the main constituents of mammalian cell membranes. Molecular level understanding of cell membrane architecture often involves supported lipid membranes and invasive methods. We designed a second harmonic scattering (SHS) instrument that allows for investigating the molecular properties of interfaces from lipid vesicles in aqueous solution, label-free, and substrate independent. Characterizing DOPC:DOPS composed liposomes, we find that the water-lipid interaction is mainly responsible for the SHS signal. Moreover, the SHS signal increases up to a lipid mixing ratio of 9:1 and remains unchanged at lower ratios. This value coincides with the saturation value of DOPS in the outer leaflet of the mammalian membrane, when spontaneous apoptosis occurs.

12:00pm **BI+AS-WeM13 Analyzing the Structure of Amyloid Fibrils in Bacterial Biofilms *In Vitro* and in Real Time Using Sum-Frequency-Generation Spectroscopy**, *P. Johansson, R. Francisco, J. Bryers,* ***Patrick Koelsch***, University of Washington

Curli fimbriae are thin, needle-like structures formed by proteins. These so-called amyloid fibrils are typically associated with neurodegenerative conditions such as Alzheimer and Parkinson's disease; however, they can also play a beneficial role in various other processes in nature. *Curli fimbriae* have been shown to be involved in e.g. the colonization of abiotic surfaces, biofilm formation, and internalization of bacteria into eukaryotic cells. The structure of amyloid fibrils has been studied by IR spectroscopy, far UV CD spectroscopy, NMR, scanning probe techniques, and fluorescent probes that bind to fibrils. What is common to those approaches is the need for labelling or an *ex vitro* character, typically involving purification steps. Here we show how to use sum-frequency-generation (SFG) spectroscopy to study early stages of amyloid fibrillar formation within biofilms formed by a *Pseudomonas* strain of the *P. fluorescens* group. Studies have been performed *in vitro*, over several days of biofilm formation, under defined environmental conditions, and in real time - without the need for labels or any other disruptive sample preparation. In addition to the wild-type strain, genetically modified *P. fluorescence* were studied that are either overexpressing fibrils, or for which the fibrillar formation was suppressed. Furthermore, SFG spectra from purified amyloids were used to correlate *in vitro* and *ex vitro* results.

Authors Index

Bold page numbers indicate the presenter