

Wednesday Afternoon, October 21, 2015

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 211B - Session IS+SS+NS+BI+VT+MN+AS-WeA

In situ Imaging of Liquids using Microfluidics

Moderator: Xiao-Ying Yu, Pacific Northwest National Laboratory, Stephen Nonnenmann, University of Massachusetts - Amherst

2:20pm **IS+SS+NS+BI+VT+MN+AS-WeA1 In Situ Multimodal Biological Imaging using Micro- and Nanofluidic Chambers, James Evans, C. Smallwood**, Pacific Northwest National Laboratory **INVITED**
Biological organisms have evolved a number of spatially localized and highly orchestrated mechanisms for interacting with their environment. Since no single instrument is capable of probing the entire multidimensional landscape, it is not surprising that one of the grand challenges in biology remains the determination of how dynamics across these scales lead to observed phenotypes.

Therefore, there is a need for in-situ correlative multimodal and multiscale imaging to fully understand biological phenomena and how chemical or structural changes at the molecular level impact the whole organism. We have been advancing new methods for both cryogenic and in-situ correlative analysis of biological samples using electron, ion, optical and x-ray modalities. Central to this work is the development of new micro- and nanofluidic chambers that enable in-situ observations within precisely controlled liquid-flow environments. In this talk I will review the design of these new chambers, highlight current science applications and outline our future goals for adding additional functionality and expanding the versatility of the devices to other disciplines.

3:00pm **IS+SS+NS+BI+VT+MN+AS-WeA3 Glyoxal Aqueous Surface Chemistry by SALVI and Liquid ToF-SIMS, Xiao Sui, Y. Zhou, Z. Zhu**, Pacific Northwest National Laboratory, J. Chen, Shandong University, China, X.-Y. Yu, Pacific Northwest National Laboratory

Glyoxal, a ubiquitous water-soluble gas-phase oxidation product in the atmosphere, is an important source of oxalic acid, a precursor to aqueous secondary organic aerosol (SOA) formation. Many recent laboratory experiments and field observations suggest that more complex chemical reactions can occur in the aqueous aerosol surface; however, direct probing of aqueous surface changes is a challenging task using surface sensitive techniques. The ability to map the molecular distribution of reactants, reaction intermediates, and products at the aqueous surface are highly important to investigate surface chemistry driven by photochemical aging. In this study, photochemical reactions of glyoxal and hydrogen peroxide (H_2O_2) were studied by a microfluidic reactor, System for Analysis at the Liquid Vacuum Interface (SALVI), coupled with Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Aqueous surfaces containing glyoxal and hydrogen peroxide were exposed to UV light at variable lengths of time and were immediately analyzed in the SALVI microchannel by in situ liquid ToF-SIMS. In addition, various control samples were conducted to ensure that our findings were reliable. Compared with previous results of bulk solutions using ESI-MS, our unique liquid surface molecular imaging approach provided observations of glyoxal hydrolysis (i.e., first and secondary products, dimers, trimers, and other oligomers) and oxidation products (i.e., glyoxylic acid, oxalic acid and formic acid) with sub-micrometer spatial resolution. We potentially provide a new perspective and solution to study aqueous surface chemistry as an important source of aqueous SOA formation of relevance to atmospheric chemistry known to the community.

3:20pm **IS+SS+NS+BI+VT+MN+AS-WeA4 Investigating Shewanella Oneidensis Biofilm Matrix in a Microchannel by In Situ Liquid ToF-SIMS, Yuanzhao Ding**, Nanyang Technological University, Singapore, X. Hua, Y. Zhou, J. Yu, X. Sui, J. Zhang, Z. Zhu, Pacific Northwest National Laboratory, B. Cao, Nanyang Technological University, Singapore, X.-Y. Yu, Pacific Northwest National Laboratory

Biofilms consist of a group of micro-organisms attached onto surfaces or interfaces and embedded with a self-produced extracellular polymeric substance (EPS) in natural environments. The EPS matrix, like the "house of the cells", provides bacteria cells with a more stable environment and makes them physiologically different from planktonic cells. *Shewanella oneidensis* MR-1 is a metal-reducing bacterium, forming biofilms that can reduce toxic heavy metals. This capability makes *S. oneidensis* biofilms very attractive in environmental applications. To better understand the biofilm EPS matrix composition at the interface, in situ chemical imaging

with higher spatial resolution and more molecular level chemical information is strongly needed. Traditionally, electron microscopy and fluorescence microscopy are common imaging tools in biofilm research. However, the bottlenecks in these imaging technologies face the limitations that it is difficult for them to provide chemical information of small molecules (e.g., molecule weight <200). In this study, we use an emerging technology liquid Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to observe *S. oneidensis* biofilm cultured in a vacuum compatible microchannel of the System for Analysis at the Liquid Vacuum Interface (SALVI) device. Chemical spatial distributions of small organic molecules that are considered to be the main building components of EPS in live biofilms are obtained. Principal component analysis is used to determine differences among biofilms sampled along the microchannel. This new approach overcomes previous limitations in live biofilm analysis and provides more chemical information of the EPS relevant to biofilm formation. Better understanding of the biofilm matrix will potentially fill in the knowledge gap in biofilm surface attachment and detachment processes and improve the engineering and design of *S. oneidensis* biofilms with high efficiencies in heavy metal reduction.

4:20pm **IS+SS+NS+BI+VT+MN+AS-WeA7 Ultrafast Proton and Electron Dynamics in Core-Level Ionized Aqueous Solution, Bernd Winter**, Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherring BESSY II, Germany **INVITED**

Photo- and Auger electron spectroscopy from liquid water reveals a novel electronic de-excitation process of core-level ionized water in which a pair of two cations forms, either $\text{H}_2\text{O}^+\cdot\text{H}_2\text{O}^+$ or $\text{OH}^+\cdot\text{H}_3\text{O}^+$. These reactive species are the delocalized analogue to H_2O^{2+} , formed in a localized on-site Auger decay, and are expected to play a considerable role in water radiation chemistry. Both cationic pairs form upon autoionization of the initial ionized water molecule, and we are particularly interested in the situation where autoionization occurs from a structure that evolves from proton transfer, from the ionized water molecule to a neighbor molecule, within a few femtoseconds. The actual autoionization is either through intermolecular Coulombic decay (ICD) or Auger decay. Experimental identification of the proton dynamics is through isotope effects. A question that arises is whether such so-called proton-transfer mediated charge separation (PTM-CS) processes occur in other and similarly hydrogen-bonded solute molecules as well. This is indeed the case, and is illustrated here for ammonia and glycine in water, as well as for hydrogen peroxide in water, where characteristic differences are detected in the Auger-electron spectra from the light versus heavy species, i.e., NH_3 in H_2O versus ND_3 in D_2O , glycine(H) in H_2O versus glycine(D) in D_2O , and H_2O_2 in H_2O versus D_2O_2 in D_2O . The important spectral feature here is the high-kinetic energy tail of the Auger spectrum, which has no gas-phase analogue, and hence reflects the participation of solvent water in the relaxation process. The probability of the proton dynamics, judged from the intensities of the electron signal and inferred from methods of quantum chemistry and molecular dynamics, is found to depend on hydrogen-bond strength and hence on the specific hydration configuration. Favorable configurations for hydrogen peroxide(aq) occur due to the molecule's flexible structure. In ammonia(aq) the PTM processes are found to be less probable than for water(aq), which is attributed to the planarization of the ammonia molecule upon core-level ionization. The effect is smaller for the neutral $-\text{NH}_2$ (aq) group of glycine at basic pH, where intramolecular dynamics is less likely. Nature and chemical reactivity of the initial transient species and their role for radiation chemistry and for local reactions relevant for biological molecules in an aqueous environment are discussed for the different molecular hydrogen-bonded systems.

5:00pm **IS+SS+NS+BI+VT+MN+AS-WeA9 Water Dissociation in Metal Organic Frameworks with Coordinatively Unsaturated Metal Ions: MOF-74, Kui Tan**, The University of Texas at Dallas, S. Zuluaga, Wake Forest University, E. Fuentesf, The University of Texas at Dallas, H. Wang, Rutgers University, P. Canepa, Wake Forest University, J. Li, Rutgers University, T. Thonhauser, Wake Forest University, Y.J. Chabal, The University of Texas at Dallas

Water dissociation represents one of the most important reactions in catalysis, essential to the surface and nano sciences. However, the dissociation mechanism on most oxide surfaces is not well understood due to the experimental challenges of preparing surface structures and characterizing reaction pathways. To remedy this problem, we propose the metal organic framework MOF-74 as an ideal model system to study water reactions. Its crystalline structure is well characterized; the metal oxide node mimics surfaces with exposed cations; and it degrades in water. Combining *in situ* IR spectroscopy and first-principles calculations, we explored the MOF-74/water interaction as a function of vapor pressure and

temperature. Here, we show that, while adsorption is reversible below the water condensation pressure (~19.7 Torr) at room temperature, a reaction takes place at ~150 °C even at low water vapor pressures. This important finding is unambiguously demonstrated by a clear spectroscopic signature for the direct reaction using D₂O, which is not present using H₂O due to strong phonon coupling. Specifically, a sharp absorption band appears at 970 cm⁻¹ when D₂O is introduced at above 150 °C, which we attribute to an O-D bending vibration on the phenolate linker. Although H₂O undergoes a similar dissociation reaction, the corresponding O-H mode is too strongly coupled to MOF vibrations to detect. In contrast, the O-D mode falls in the phonon gap of the MOF and remains localized. First-principles calculations not only positively identify the O-D mode at 970 cm⁻¹ but derive a pathway and kinetic barrier for the reaction and the final configuration: the D (H) atom is transferred to the oxygen of the linker phenolate group, producing the notable O-D absorption band at 970 cm⁻¹, while the OD (or OH) binds to the open metal sites. Experimental data and theoretical modeling further shows that the reaction is facilitated by a cooperative effect of several H₂O molecules. This finding explains water dissociation in this case and provides insight into the long-lasting question of MOF-74 degradation. Overall, it adds to the understanding of molecular water interaction with cation-exposed surfaces to enable development of more efficient catalysts for water dissociation.

Ref: K. Tan, S. Zuluaga, Q. Gong, P. Canepa, H. Wang, J. Li, Y. J. Chabal and T. Thonhauser, *Chem. Mater.*, 2014, **26**, 6886-6895.

5:20pm **IS+SS+NS+BI+VT+MN+AS-WeA10 Competitive Co-Adsorption of CO₂ with H₂O, NH₃, SO₂, NO, NO₂, N₂, O₂, and CH₄ in M-MOF-74 (M= Mg, Co, Ni): The Role of Hydrogen Bonding.** K. Tan, The University of Texas at Dallas, **Sebastian Zuluaga**, Wake Forest University, **H. Wang**, Rutgers University, **Y. Gao**, The University of Texas at Dallas, **J. Li**, Rutgers University, **T. Thonhauser**, Wake Forest University, **Y.J. Chabal**, The University of Texas at Dallas

The importance of co-adsorption for applications of porous materials in gas separation has motivated fundamental studies, which have initially focused on the comparison of the binding energies of different gas molecules in the pores (i.e. energetics) and their overall transport. By examining the competitive co-adsorption of several small molecules in M-MOF-74 (M= Mg, Co, Ni) with *in-situ* infrared spectroscopy and *ab initio* simulations, we find that the binding energy at the most favorable (metal) site is not a sufficient indicator for prediction of molecular adsorption and stability in MOFs. Instead, the occupation of the open metal sites is governed by kinetics, whereby the interaction of the guest molecules with the MOF organic linkers controls the reaction barrier for molecular exchange. Specifically, the displacement of CO₂ adsorbed at the metal center by other molecules such as H₂O, NH₃, SO₂, NO, NO₂, N₂, O₂, and CH₄ is mainly observed for H₂O and NH₃, even though SO₂, NO, and NO₂ have higher binding energies (~70-90 kJ/mol) to metal sites than that of CO₂ (38 to 48 kJ/mol) and slightly higher than water (~60-80 kJ/mol). DFT simulations evaluate the barriers for H₂O↔CO₂ and SO₂↔CO₂ exchange to be ~ 13 and 20 kJ/mol, respectively, explaining the slow exchange of CO₂ by SO₂, compared to water. Furthermore, the calculations reveal that the kinetic barrier for this exchange is determined by the specifics of the interaction of the second guest molecule (e.g., H₂O or SO₂) with the MOF ligands. Hydrogen bonding of H₂O molecules with the nearby oxygen of the organic linker is found to facilitate the positioning of the H₂O oxygen atom towards the metal center, thus reducing the exchange barrier. In contrast, SO₂ molecules interact with the distant benzene site, away from the metal center, hindering the exchange process. Similar considerations apply to the other molecules, accounting for much easier CO₂ exchange for NH₃ than for NO, NO₂, CH₄, O₂, and N₂ molecules. In this work, critical parameters such as kinetic barrier and exchange pathway are first unveiled and provide insight into the mechanism of competitive co-adsorption, underscoring the need of combined studies, using spectroscopic methods and *ab initio* simulations to uncover the atomistic interactions of small molecules in MOFs that directly influence co-adsorption.

Ref: K. Tan, S. Zuluaga, Q. Gong, Y. Gao, N. Nijem, J. Li, T. Thonhauser and Y. J. Chabal, *Chem. Mater.*, 2015, **27**, 2203-2217.

6:00pm **IS+SS+NS+BI+VT+MN+AS-WeA12 In Situ STM Observation of Pd(110) Under the Hydrogen Pressure Between 10⁻⁶ Pa and 10⁻³ Pa.** Jun Yoshinobu, H. Kikuchi, T. Koitaya, K. Mukai, S. Yoshiomoto, University of Tokyo, Japan

Hydrogen adsorption and absorption on/in Pd and Pd alloys are vital processes for the hydrogen storage and hydrogen permeation materials. We investigated the Pd(110) surface under the hydrogen pressures between 10⁻⁶ Pa and 10⁻³ Pa at room temperature using in-situ atom-resolved scanning tunneling microscopy (STM). We observed missing-atom, missing-row and added-row structures and the number of atoms in these structures were quantitatively analyzed as a function of exposure time. Note that adatoms were not detected probably because they were mobile in the present

experimental conditions. At 10⁻⁶ Pa, the numbers of missing-row and added-row atoms increased up to ~20 L (langmuir) and after that they were gradually reaching the saturation (steady-state). On the other hand, the number of missing-atoms decreased gradually from the initial stage. With increasing the hydrogen pressures the number of missing-row atoms and added-row atoms increased, and the whole surface was covered with these reconstructed structures after large exposures (>1000 L). It has been known that not only hydrogen adsorption but also hydrogen absorption occur in such conditions. Thus, the missing-row and added-row reconstructed structures are inevitable for hydrogen absorption on Pd(110).

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