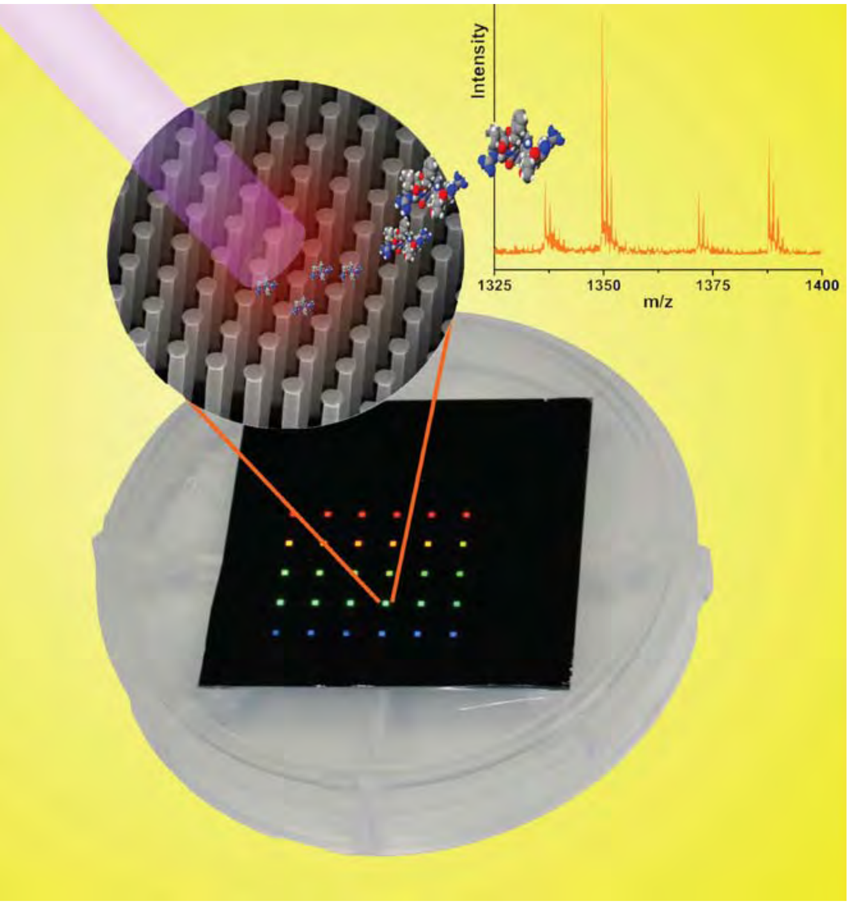
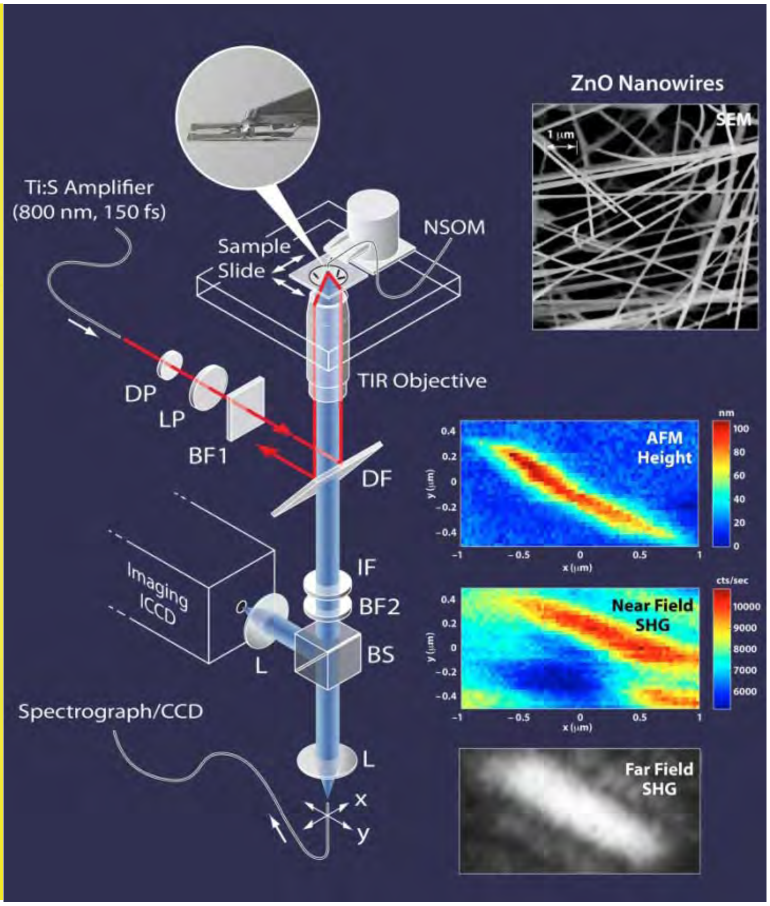
2010 DOE Separations and Analysis Research Meeting





Hyatt Regency
Baltimore, MD
April 25 - 28, 2010

U.S. DEPARTMENT OF ENERGY | Office of Science

Office of Basic Energy Sciences
Chemical Sciences, Geosciences &
Biosciences Division

Program and Abstracts

Separations and Analysis Program

Contractors' Meeting

Hyatt Regency
Baltimore, MD
April 25 - 28, 2010

Chemical Sciences, Geosciences, and Biosciences Division
Office of Basic Energy Sciences
Office of Science
U.S. Department of Energy

Cover Graphics:
The cover artwork on the left is a representation of nanophotonic ion sources discovered by Akos Vertes, et al. (see page 15 of this book) from the cover of *J. Phys. Chem. C* ***114****/11 (March 25, 2010)*. Used by permission of ACS Publications. The image on the right represents a Near-Field SHG Imaging apparatus and results (see Shaw et al. on page 1 of this book) from the cover of *Applied Spectrosccopy* ***64****/1 (January 2010)*. Used by permission of the Society for Applied Spectroscopy.

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Foreword

This abstract booklet provides a record of the U.S. Department of Energy biennial contractors' meeting in separations and analysis science. This year the meeting is co-chaired by Dr. Julia Laskin (Pacific Northwest National Laboratory) and Professor Nick Winograd (Penn State University). This meeting is sponsored by the Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences and includes invited presentations from two Energy Frontier Research Centers. Also featured in this meeting are five poster presentations invited from early career researchers by the meeting co-chairs.

The objective of this meeting is to provide a fruitful environment in which researchers with common interests will present and exchange information about their activities, will build collaborations among research groups with mutually reinforcing strengths, will identify needs of the research community, and will focus on opportunities for future research directions. The agenda has invited talks, oral presentations, as well as invited and regular posters, organized so that papers in related disciplines are loosely clustered together. With ample time for discussion and interactions, we emphasize that this is an informal meeting for exchange of information and building of collaborations; it is not a review of researchers' achievements or a forum to choose future directions for the program.

We are pleased to collaborate with Julia Laskin and Nick Winograd in organizing this joint meeting and appreciate their service to this community. We also appreciate the privilege of serving as the managers of our respective research programs. In carrying out these tasks, we learn from the achievements and share the excitement of the research of the many sponsored scientists and students whose names appear on the papers in the following pages. We also hope that this meeting will enhance your research efforts and will nurture future collaborations and initiatives.

We thank all of the researchers whose dedication and innovation have advanced our research and made this meeting possible and, we hope, productive. We also hope that all of you will build on your successes and that we will assemble in two years for our next joint meeting.

We thank Diane Marceau of the Chemical Sciences, Geosciences and Biosciences Division, and Loretta Friend and Connie Lansdon of the Oak Ridge Institute for Science and Education for their important contributions to the technical and logistical features of this meeting.

William S. Millman
Mark Pederson
Larry A. Rahn

Agenda

2010 Separations and Analysis Research Meeting

Hyatt Regency, Baltimore, MD   April 25 - 28, 2010

Sunday, April 25 2010

3:00 –	6:00	p.m.	**Registration**
6:00 –	6:30		**Reception** (no host bar)
6:30 –	7:30		**Dinner**

Monday, April 26

7:30 –	8:00	a.m.	**Continental Breakfast**
8:00 –	8:10		Welcome – Bill Millman, Julia Laskin, Nick Winograd
8:10 –	8:35		Eric Rohlfing – DOE Update

Session 1 – Imaging Analysis I – Dr. Emily Smith, Chair

8:35 –	9:00	a.m.	Dr. Robert W. Shaw – Nanoparticle Imaging using Linear and Nonlinear Spectroscopy
9:00 –	9:25		Professor Joel Harris – Analytical Spectroscopy Methods for Liquid/Solid Interfaces
9:25 –	9:50		Professor Daniel K. Schwartz – Mapping Non-covalent Surface Functionality using Single Molecule Probes
9:50 –	10:20		**Break**

Session 2 – Ionization Processes/MS – Dr. Vilmos Kertesz, Chair

10:20 –	10:45	a.m.	Dr. Julia Laskin – Ion-Surface Interactions in Mass Spectrometry
10:45 –	11:10		Professor Paul B. Farnsworth – Ion Production and Transport in Atmospheric Pressure Ion Source Mass Spectrometers
11:10 –	11:35		Dr. Scott A. McLuckey – Electron Transfer, Charge Inversion, and Selective Covalent Bond Formation in Gas-Phase Ion/Ion Reactions

Session 3 – Invited Early Investigators – Dr. Julia Laskin, Prof. Nick Winograd, Chairs

11:40 –	11:45	a.m.	Professor Sarah Trimpin – Laserspray Ionization – A Process for Producing Multiply Charged Gas-Phase Ions from Solid Solutions
11:45 –	11:50		Professor Daniel Austin – Microfabricated Ion Trap Mass Analyzers using Two Opposing Plates
11:50 –	11:55		Professor Lane Baker – Ionic and Electronic Properties of Nanopores and Nanostructures
11:55 –	12:00	p.m.	Professor Hao Chen – Polysaccharide Degradation and Collection via Ambient Ion Dissociation and Soft-Landing
12:00 –	12:05		Dr. Yingzhong Ma – Femtosecond Electronic Spectroscopy of Nanostructures and Their Functional Assemblies
12:10 –	1:10		**Working Lunch**
1:10 –	4:00		**Interaction Time** – Put up posters for Poster Sessions

Monday, April 26 (Cont'd)

Session 4 – Imaging Analysis II – Professor Steven K. Buratto, Chair

4:00 – 4:25 p.m. Professor Paul S. Weiss – From DC to Daylight: Local Spectroscopies with the Scanning Tunneling Microscope
4:25 – 4:50 Professor Akos Vertes – Nanostructured Substrates and Imaging Applications of Soft Laser Desorption Ionization
4:50 – 5:15 Professor David H. Russell – Chemically Tailored Gold Nanorods as Biosensors for Mass Spectrometry Applications
5:15 – 5:40 Dr. Young-Jin Lee – Mass Spectrometric Imaging of Plant Metabolites

5:40 – 6:00 Break – Put up posters for Poster Sessions

6:00 – 7:30 **Working Dinner**

Poster Session 1

7:30 – 9:00 Poster Session 1 – with no-host bar at Bistro 300
P1-1 Professor Joseph T. Hupp – Coordination-Chemistry–Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities
P1-3 Professor Steven K. Buratto – Chemical Imaging with 100nm Spatial Resolution: Combining High Resolution Fluorescence Microscopy and Ion Mobility Mass Spectrometry
P1-5 Professor Benny D. Freeman – Novel Membranes for Carbon Dioxide Removal from Natural Gas Based on Thermally Rearranged Polymers
P1-7 **Invited Poster –** Professor Sarah Trimpin – Laserspray Ionization – A Process for Producing Multiply Charged Gas-Phase Ions from Solid Solutions
P1-9 Professor Nicholas Winograd – Chemical Imaging with Cluster Ion Beams and Lasers
P1-11 Professor Gary M. Hieftje – Fundamental Studies of the Inductively Coupled Plasma and Glow Discharge
P1-13 Professor Osman A. Basaran – Electrohydrodynamic Tip Streaming
P1-15 Dr. Douglas Goeringer – Tip Enhanced Laser Desorption/Ionization and Thermal Desorption with Secondary Ionization
P1-17 **Invited Poster –** Professor Daniel Austin – Microfabricated Ion Trap Mass Analyzers using Two Opposing Plates
P1-19 Professor Jan D. Miller – Surface Chemistry Issues in the Development of Flotation Technology for the Processing of Low Grade Bauxite Resources
P1-21 Dr. Emily Smith – Chemical Analysis of Nanodomains
P1-23 Professor Georges Belfort – Combinatorial and High Throughput Membrane Synthesis and Testing: Tailoring Membrane Surfaces to Applications

Tuesday, April 27

7:30 – 8:10 a.m. **Continental Breakfast**

Session 5 – Separations I – Professor Benny D. Freeman, Chair

8:10 – 8:55 **Invited Speaker** – Professor Berend Smit – Carbon Capture
9:00 – 9:25 Professor Jordan R. Schmidt – Modeling CO_2 Capture and Separation in Zeolitic Imidazolate Frameworks
9:25 – 9:50 Professor Gerald J. Diebold – Ultrasonic Distillation and the Photoacoustic Effect in Phononic Structures

9:50 – 10:20 **Break**

Tuesday, April 27 (Cont'd)

Session 6 – Separations II – Professor William Koros, Chair

10:20 – 11:05 a.m. **Invited Speaker** – Professor Brian B. Laird – Energy Frontier Research Center – Molecularly Assembled Material Architectures for Solar Energy Production, Storage and Carbon Capture

11:10 – 11:35 Professor Paul W. Bohn – Molecular Aspects of Transport in Thin Films of Controlled Architecture

11:35 – 12:00 Professor Takashi Ito – Molecular-Level Investigation of Diffusion Behaviors within Cylindrical Nanoscale Pores

12:00 – 1:00 p.m. **Working Lunch**

1:00 – 4:00 **Interaction Time**

Poster Session 2

4:00 – 6:00 p.m. Poster Session 2 – with no-host bar at Bistro 300

P2-2 Professor Omar M. Yaghi – Metal-Organic and Zeolite Imidazolate Frameworks (MOFs and ZIFs) for Highly Selective Separations

P2-4 Dr. Mike Simonson – Local Solvation Structure and Ion Association in Aqueous Sulfate Solutions: Toward Understanding of Weak Interactions in Selective Separations

P2-6 **Invited Poster –** Professor Lane Baker – Ionic and Electronic Properties of Nanopores and Nanostructures

P2-8 Professor Merlin Bruening – Exploring New Methods and Materials in the Formation of Selective, High-Flux Membranes for CO_2 Removal

P2-10 Professor Frank V. Bright – Interfacial Solvation under Aggressive Conditions

P2-12 Professor William Koros – Synthesis and Analysis of Polymers with High Gas Permeabilities and Permselectivities

P2-14 **Invited Poster –** Professor Hao Chen – Polysaccharide Degradation and Collection via Ambient Ion Dissociation and Soft-Landing

P2-16 Dr. Vilmos Kertesz – Sampling, Ionization, and Energy Transfer Phenomena in Mass Spectrometry

P2-18 Professor Maciej Haranczyk – Knowledge-Guided Screening Tools for Identification of Porous Materials for CO_2 Separation

P2-20 Professor Michael D. Barnes – Quantum Dots as a Probe of Charge Transport in Nanostructured Thin Films

P2-22 **Invited Poster** – Dr. Yingzhong Ma – Femtosecond Electronic Spectroscopy of Nanostructures and Their Functional Assemblies

P2-24 Dr. Alla Zelenyuk – Chemistry and Microphysics of Small Particles

P2-26 Professor J. Douglas Way – Investigation of Transport Mechanisms in Surface Modified Inorganic Membranes

P2-28 **Invited Poster** – Professor Yao Houndonougbo – Functionalization of Zeolitic Imidazolate Frameworks (ZIFs) for Gas Capture and Separation

6:00 p.m. **Dinner** on your own and interaction time

Wednesday, April 28

7:30 – 8:10 a.m. **Continental Breakfast**

Session 7 – Analysis and Material Properties – Professor Gary M. Hieftje, Chair

8:10 – 8:35 a.m. Professor Georges Guiochon – Analysis of the Metabolites of Lipids in Microalgae by Two-Dimensional HPLC
8:35 – 9:00 Professor Richard M. Crooks – Bipolar Electrode Focusing for Concentration Enrichment and Analyte Separations
9:00 – 9:25 Professor Nancy L. Ross – Inelastic Neutron Scattering (INS) Studies of Oxide Nanoparticles
9:25 – 9:50 Dr. Richard E. Russo – Laser-Material Interactions (Ablation) for Chemical Analysis
9:50 – 10:15 Professor J. Thomas Dickinson – Laser-Material Interactions Relevant to Analytic Spectroscopy of Wide Band Gap Materials

10:15 – 10:30 **Break**

Session 8 – Close Out Session – Prof. Nick Winograd, Dr. Julia Laskin, Chairs

10:30 – 12:00 Presentation of program summaries and discussion

12:00 – 1:00 p.m. **Working Lunch** – box lunch for those who have to leave early

1:00 – 3:00 Open Discussion and take down posters

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Session 2 – Ionization Processes/MS

Session 3 – Invited Early Investigators – See Poster Sessions 1 and 2

Session 4 – Imaging Analysis II

Poster Session 1

Session 5 – Separations I

Session 6 – Separations II

Poster Session 2

Session 7 – Analysis and Material Properties

Abstracts Not Presented

Session 1 – Imaging Analysis I

Nanoparticle Imaging using Linear and Nonlinear Spectroscopy

Robert W. Shaw, Principal Investigator
William B. Whitten, Co-Principal Investigator
Kent A. Meyer and Katherine Cimatu, Postdoctoral Research Associates
P.O. Box 2008, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37931
Email: shawrw@ornl.gov; Web: http://www.ornl.gov/sci/csd/Research_areas/lscm_group.html

Collaborators: Prof. Charles Feigerle, University of Tennessee, Knoxville, TN
Prof. Kin Ng, Cal State University-Fresno, Fresno, CA
Prof. Zhengwei Pan, University of Georgia, Athens, GA
Prof. Kevin Shuford, Drexel University, Philadelphia, PA

Overall research goals: To understand chemical changes at metal and metal oxide nanoparticle surfaces, we have developed new optical and tip-enhanced spectroscopic techniques, including both linear and nonlinear spectroscopy, to produce nanoscale images with chemical contrast derived from spatially varying local chemical composition. The ability to probe surface layers on individual metal, metal oxide, and semiconductor particles one-at-a-time can relate surface reactivity to key physical characteristics such as size and morphology.

Significant achievements in 2008-2010: We have sought to exploit optical effects near metal and oxide nanoparticles (and assemblies of particles) so that chemical changes of the particle surface due to reactions with its environment can be monitored. To address this challenge, a new apparatus was built to provide chemical information at the nanometer scale by using metal tip enhanced second harmonic generation (SHG) to image nanoparticles (Figure 1). This apparatus permits imaging beyond the optical diffraction limit. It was used to image zinc oxide nanowires, and similar technology was used to study the size-correlated linear spectroscopy of gold nano-octahedra, and to assemble and image gold nanoparticle dimers.

Chemical imaging requires the ability to discriminate between different surface chemical species in a spatially resolved fashion. SHG allows us to discriminate between different compositions and structures in the image by their symmetry. For example, ZnO produces a strong SHG signal, while zinc carbonate has a bulk center of inversion symmetry rendering $\chi^{(2)} = 0$ and does not produce a SHG signal. Thus, this difference was used to image the reaction of ZnO with CO_2. Such reactions ultimately degrade the electro-optic properties of ZnO. Atomic force microscope, near-field SHG, and far-field SHG images of a ZnO nanowire are shown in Figure 1. Features smaller than 100 nm, below the diffraction limit, are resolved in the near-field SHG image.

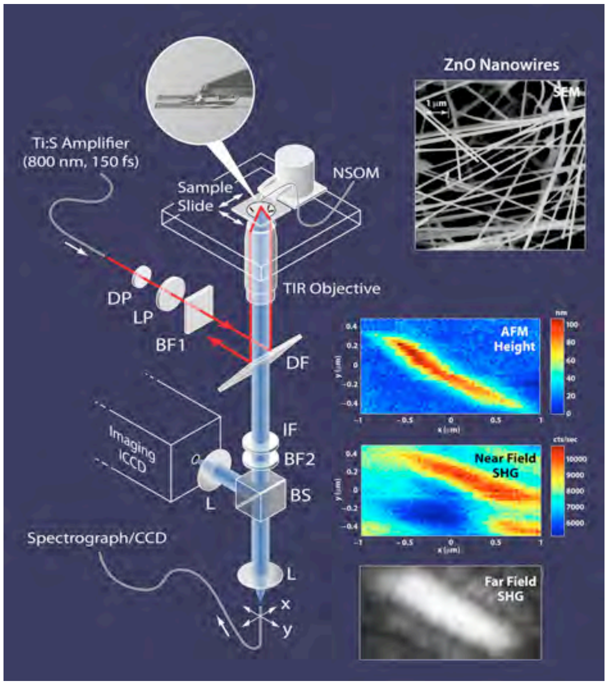

Figure 1. Apparatus for simultaneous AFM and tip-enhanced SHG imaging and a collage of ZnO nanowire images.

Closely spaced nanoparticles are of great interest presently for surface enhanced Raman scattering (SERS) techniques due to the very high electric fields generated in the region between the individual particles (or "nanogaps"). We have developed a method to assemble selected particles into pairs by using the AFM tip and then record the emission spectrum of the dimer. This allows us to test our ability to model the electronic coupling of the particles and exploit the resulting fields for SERS.

Science objectives for 2010-2012: We will continue to improve the sensitivity and spatial resolution of the tools we have created, and we will attempt to answer the following scientific questions.

- Can we monitor the surface chemistry of individual nanoparticles through chemical imaging based upon nonlinear optical spectroscopy to gain insight and control of reactivity?
- What are the effects of metal nanoparticle size and morphology on catalytic processes?
- Can we prepare unique nanoparticle structures by assembly of individual particles where the cluster creates extraordinarily large optical fields for surface enhanced techniques, such as Raman scattering, and for photocatalysis, and can we model, understand, and control these local fields?

References to work supported by this project 2008-2010:

1. C. Li, K. L. Shuford, M. Chen, E. J. Lee, and S. O. Cho, "A Facile Polyol Route to Uniform Gold Octahedra with Tailorable Size and Their Optical Properties," ACS Nano **2,** 1760-1769 (2008).
2. H.-M. Bok, K. L. Shuford, S. Kim, and S. Park, "Multipole Surface Plasmon Modes for a Colloidal Solution of Nanoporous Gold Nanorods and their Comparison to Smooth Gold Nanorods," Nano Lett. **8,** 2265-2270 (2008).
3. K. L. Shuford, K. A. Meyer, C. Li, S. O. Cho, W. B. Whitten, and R. W. Shaw, "Nanoscale Coupling Effects on Single Particle Microscopy," Proc. SPIE 7033, 7033I (2008). (Invited Paper)
4. K. L. Shuford, J. Lee, T. W. Odom, and G. C. Schatz, "Optical Properties of Gold Pyramidal Shells," J. Phys. Chem. C **112**, 6662-6666 (2008).
5. S. Kim, K. L. Shuford, H.-M. Bok, S. K. Kim, and S. Park, "Intraparticle Surface Plasmon Coupling in One-Dimensional Nanostructures," Nano Lett. **8,** 800-804 (2008).
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9. J. A. Bradshaw, O. S. Ovchinnikova, K. A. Meyer, and D. E. Goeringer, "Combined Chemical and Topographic Imaging at Atmospheric Pressure via Microprobe Laser Desorption/ionization Mass Spectrometry-Atomic Force Microscopy," Rapid. Commun. Mass Spectrom. **23**, 3781-3786 (2009).
10. K. L. Shuford, K. A. Meyer, C. Li, S. O. Cho, W. B. Whitten, and R. W. Shaw, "Computational and Experimental Evaluation of Nanoparticle Coupling," J. Phys. Chem. A **113**, 4009-4014 (2009). (Invited Paper)
11. H.-M. Bok, K. L. Shuford, E. Jeong, and S. Park, "Intra-Surface Plasmon Coupling Between Smooth and Nanoporous Blocks in a Gold Nanorod," Chem. Commun. **46**, 982-984 (2010).
12. K. A. Meyer, K. C. Ng, Z. Gu, Z. Pan, W. B. Whitten, and R. W. Shaw, "Combined Apertureless Near-Field Optical Second-Harmonic Generation/Atomic Force Microscopy Imaging and Nanoscale Limit of Detection," Appl. Spectrosc. **64**, 1 (2010). (Cover Article)

Analytical Spectroscopy Methods for Liquid/Solid Interfaces

Joel M. Harris, Principal Investigator
Moussa Barhoum, Eric Peterson, Justin Cooper, and Jennifer Gasser-Ramirez, Graduate Students
University of Utah, Department of Chemistry, 315 South 1400 East, Salt Lake City, UT 84112-0850
Email: harrisj@chem.utah.edu ; Web: http://www.chem.utah.edu/directory/faculty/harris.html
Collaborators: Dr. Paul W. Bohn, University of Notre Dame
Dr. Karl-Heinz (Charly) Gericke, Braunschweig University.

Overall research goals: Many steps in chemical analysis (preconcentration, separation, selective detection) involve adsorption or binding of target species to chemically-modified surfaces in contact with liquids. The transport of molecules at liquid/solid interfaces influences rates of surface reactions, catalysis, and the efficiency of chemical separation processes. The objectives this research are development of surface-sensitive spectroscopy and imaging methods for investigating molecular structure, transport, and reactions at liquid/solid interfaces that govern these applications. We are developing Raman and fluorescence microscopy methods capable of *in situ* characterization of sub-monolayer populations, down to the single-molecule imaging limit.

Significant achievements in 2008-2010: Confocal Raman microscopy has been developed for examining the *interior composition* of individual porous particles, applicable to catalytic and separation materials. This method was applied to investigate the interfacial chemistry of reversed-phase liquid chromatographic support particles, where the composition and interface environment was characterized. The interactions of acetonitrile with C18-functionalized surfaces were observed in small (~1fL) sampling volumes within individual 10-µm particles, where the nitrile stretching (C≡N) frequency of acetonitrile responds to the polarity of its local microenvironment, allowing solution-phase and interfacial populations of acetonitrile to be distinguished and characterized. This method has been extended to studying pore-wetting transitions and interfacial ion-pair interactions.

A second area of spectroscopic microscopy development has been the fluorescence imaging of single molecules used to quantify surface populations and to study transport and binding at the interface. Image analysis tools have been developed to locate molecules, correlate their location across multiple images, and quantify their diffusion and binding behavior. A novel least-squares searching algorithm locates sites rapidly by finding connected pixel intensities as a model for the instrument point-spread function. This method lowers false positive events by factors of 1/600, which allows thresholds to be set closer to the background noise level, significantly improving detection confidence. This result was validated against a statistical model that accurately predicts the observed false-positive and false-negative event probabilities. Fluorescence imaging is also being applied to measuring interfacial dynamics of single-molecules, which allows the contributions of surface diffusion to chemical separations and interfacial reaction kinetics to be characterized.

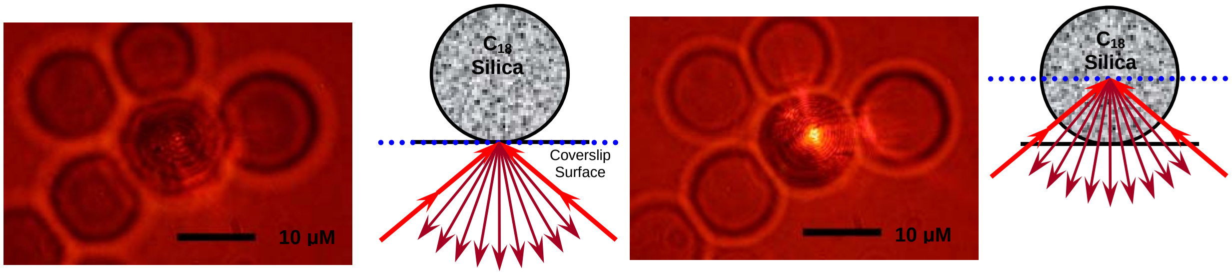

Figure 1 (Left) Image of silica chromatographic stationary phase particles, with the laser focus focused at the cover slip surface. (Right) Image after the focus has been raised 5 µm, to the particle center. The perimeter of the particle is now in focus, where the focal plane (blue dotted line) bisects the particle. The integrity of the laser focus is maintained within the particle, assuring that the Raman scattering is excited and collected from a small (~fL) volume at the particle center.

Science objectives for 2010-2012:

- Raman and fluorescence microscopy are used to study interfacial chemistry in small volumes and under potential control. Potential-dependent kinetics of monolayer self-assembly will be measured by surface-enhanced Raman spectroscopy at electrode surfaces.
- Two approaches to imaging single-molecules at conductive surfaces will be explored. Surface-plasmon-enhanced fluorescence at thin gold films is being developed for imaging molecules at metal surfaces under potential control, where plasmon excited fluorescence is imaged on the *opposite side of the metal film* from where the molecules reside.
- Indium-tin-oxide (ITO) thin films on glass substrates will be used electrodes for fluorescence imaging of single molecules versus applied potential. The double-layer structure at the ITO surface will be determined by quantifying populations of charged molecules in the evanescent-wave region.
- The influence of electric field on axial and lateral transport rates of molecules in the double-layer will be also explored.
- Confocal-Raman microscopy will be applied to single-particle, solid-phase extraction, where the Raman spectra of a few million molecules concentrated into a femtoliter volume particle can be readily detected.

References to work supported by this project 2008-2010:

1. Vanessa Oklejas, Rory H. Uibel, Robert Horton, and Joel M. Harris, “Electric-Field Control of the Tautomerization and Metal-ion Binding Reactivity of 8-Hydroxyquinoline Immobilized to an Electrode Surface,” *Analytical Chemistry*, **80**, 1891 (2008).
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3. Jennifer L. Gasser-Ramirez, Brian C. Dunn, Daniel W. Ramirez, Eric P. Fillerup, Gregory C. Turpin, Yifan Shi, Richard D. Ernst, Ronald J. Pugmire, Edward M. Eyring, Katherine A. Pettigrew, Debra R. Rolison, and Joel M. Harris, “A Simple Synthesis of Catalytically Active, High Surface Area Ceria Aerogels,” *Journal of Non-Crystalline Solids*, **354**, 5509 (2008).
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7. Daniel P. Cherney and Joel M. Harris, “Confocal Raman Microscopy of Optical-Trapped Particles in Liquids,” *Annual Review of Analytical Chemistry*, **3**, in press (2010).
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Mapping Non-covalent Surface Functionality using Single Molecule Probes

Daniel K. Schwartz
Dept. of Chemical & Biological Engineering, 424 UCB, University of Colorado, Boulder, CO 80309
Email: daniel.schwartz@colorado.edu; Web: http://www.colorado.edu/che/faculty/schwartz.html

Overall research goals: Real-time imaging methods are being developed that use individual reactant/adsorbate molecules as probes of surface chemical functionality and reactivity. Our approach is based on observations of individual molecules using total internal reflection fluorescence microscopy (TIRFM), including high-resolution methods involving resonant energy transfer and quenching. Specific aims include the development of multicolor TIRFM methods that permit simultaneous identification and spatial mapping of multiple surface functional groups, methods that provide quantitative information about the kinetics and energetics of reactants at catalytic interfaces, and, single-molecule TIRFM methods that employ resonance energy transfer (FRET) to probe the local molecular environment, and to identify and measure reaction rates at individual immobilized catalytic sites.

Significant achievements in 2009-2010: We have used TIRFM to observe the dynamic behavior of individual fluorescently-labeled fatty acid molecules at the interface between water and a hydrophobically-modified fused silica surface. Patterned surfaces were prepared by photodegradation of trimethylsilane-modified surfaces using a contact photomask; the degree of hydrophobic contrast was varied by controlling the dose of ultraviolent radiation. Cumulative images of single-molecule fluorescence, integrated over various exposure times, exhibited structural features consistent with the photopattern, and the fluorescence contrast was systematically related to the hydrophobic contrast (see Figure 1). Lateral force microscopy was also used to characterize the patterned surfaces, and provided qualitative images when the hydrophobic contrast was relatively high. However, the fluorescent probes provided more sensitive, reproducible, and reliable images of the lateral hydrophobic variations.

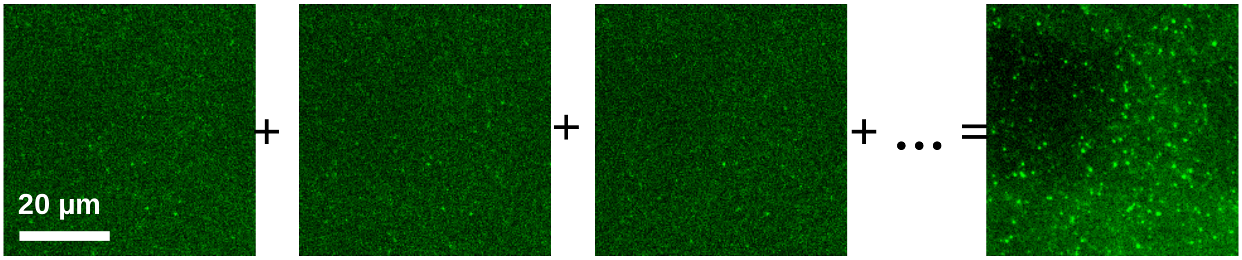

Figure 1: Images representative of individual frames from videos showing single-molecule adsorption, diffusion, and desorption on a patterned surface, along with a composite HIM image where 60 consecutive frames were averaged. The patterned surface had been exposed to UV radiation for 200s through a photomask.

Expanding on these results, we observed the directed motion of 20 nm probe particles on specific regions of surfaces that exhibited strong gradients of hydrophobicity (see Figure 2). Patterned surfaces were again prepared by selective photodegradation (using a contact photomask) of a hydrophobically-modifed fused silica surface. The lateral distribution of hydrophobicity was characterized *in situ* using the selective affinity of amphiphilic probes (i.e. hydrophobic interaction microscopy). Probe particles were observed to move unidirectionally from regions of lower to higher to hydrophobicity over distances of ~1 μm when the hydrophobicity gradient was greater than $d(\cos\theta)/dx=0.05\pm0.02\ \mu m^{-1}$, where θ is the water contact angle on the bare surface. Only adsorption events were observed on energetically homogeneous surface regions.

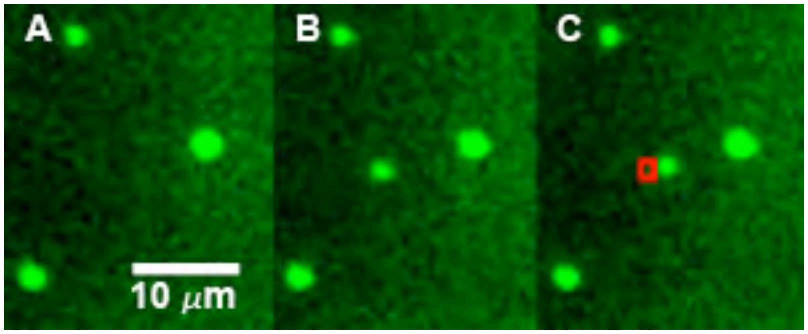

Figure 2. TIRF images showing nanobead adsorption and motion. (a) Three beads are initially present in this region. (b)A new bead adsorbs on the surface. (c) Eight seconds after adsorption, the bead has moved in the direction of increasing hydrophobicity; the red circle indicates the position at which the bead originally adsorbed.

Science objectives for 2010-2012(style=Stand alone text heading):

- Multicolor TIRF methods that permit simultaneous identification and spatial mapping of multiple surface functional groups, e.g. hydrophobic, hydrogen-bonding, acid/base moieties will be developed.
- Methods will be developed to provide quantitative information about the kinetics and energetics of adsorbate/reactant adsorption, desorption, and interfacial mobility.
- Single-molecule TIRFM methods will be developed that employ resonance energy transfer (FRET) to probe the local molecular environment, and to identify and measure reaction rates at individual immobilized catalytic sites.

References to work supported by this project 2009-2010:

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Session 2 – Ionization Processes/MS

Ion-Surface Interactions in Mass Spectrometry

Julia Laskin, Principal Investigator
Qichi Hu and Patrick Roach, Postdoctoral Research Associates
Pacific Northwest National Laboratory, P.O. Box 999, K8-88, Richland, WA 99352
Email: Julia.Laskin@pnl.gov; Web: http://emslbios.pnl.gov/id/laskin_j

Collaborators: Graham Cooks, Purdue; Sergey Nizkorodov, UC Irvin; Ivan Chu, U Hong Kong, Hong Kong, China; Prof. K. W. Michael Siu, York University, Toronto, Canada; Alex Laskin, PNNL

Overall research goals: The objectives of our research is to achieve a fundamental understanding of activation and dissociation of complex molecular ions in mass spectrometry, develop molecular level understanding of interactions of complex ions and molecules with surfaces, and develop new approaches for selective modification of substrates using beams of mass-selected hyperthermal ions. This research addresses analytical challenges relevant to a broad range of applications within the Department of Energy (DOE) mission areas.

Significant achievements in 2008-2010:. Continued studies of soft- and reactive landing of mass-selected ions on surfaces demonstrated that preparatory mass spectrometry can be utilized for controlled preparation of conformationally selected films of complex molecules that cannot be prepared using conventional approaches. In addition, reactive deposition can be used for selective covalent immobilization of complex molecules on substrates. In situ FTIR that has been recently coupled with the ion deposition instrument allowed us to quantify the efficiency of bond formation between the precursor ion and the surface. The initial experiments utilizing this system demonstrated that almost every collision results in bond formation between the primary amino group and the reactive monolayer surface.

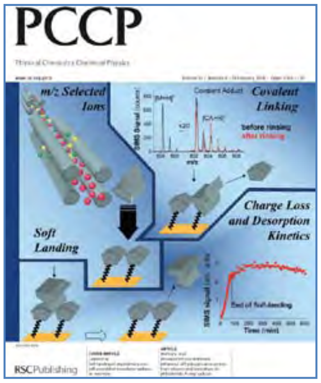

Figure 1 Physical processes occurring during ion soft-landing

First studies of surface-induced dissociation (SID) of non-covalent complexes demonstrated that entropy plays a major role in determining the dissociation rate. Non-covalent complexes between peptides and metal-salen complexes were utilized as model systems for understanding the competition between proton transfer, electron transfer and loss of the neutral ligand. SID of peptide radical cations demonstrated the presence of two distinct families of conformations separated by a high free energy barrier that has never been observed for even-electron peptide ions.

Science objectives for 2010-2012:

- Ion deposition studies will focus on the kinetics of reactive and non-reactive deposition of catalytically active complexes, dendrimers and proteins.
- Examine the effect of the position of charge and the radical site on the fragmentation energetics, dynamics and mechanisms of dissociation of odd-electron peptide ions;
- Explore the energetics of cation-phospate interactions and phosphate transfer relevant to the analysis of complex molecules with labile modifications;

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Ion Production and Transport in Atmospheric Pressure Ion Source Mass Spectrometers

Paul Farnsworth, Principal Investigator[†]
Ross Spencer, Co-Principal Investigator[‡]
[†]Department of Chemistry and Biochemistry and [‡]Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602
Email: Paul_Farnsworth@byu.edu; Web: http://people.chem.byu.edu/pbfarnsw

Overall Research Goals: We are studying the production of ions at atmospheric pressure and their transport into mass analyzers in two contexts: plasma source mass spectrometers and mass spectrometers that rely on so called “ambient ionization” techniques. Two well-known examples of the latter are Desorption Electrospray Ionization (DESI) and Direct Analysis in Real Time (DART). In both contexts we seek to gain a fundamental understanding of the processes that control the production of ions and that control and limit their transport from the atmospheric-pressure sources into high-vacuum mass analyzers. Fundamental understanding of the ICP-MS is further enhanced by our development of a Monte Carlo simulation the gas flow through this instrument.

Significant achievements in 2008-2010: **Plasma source mass spectrometry.** We are conducting parallel computational and experimental efforts to characterize ion production and transport in inductively coupled plasma mass spectrometers (ICP-MS). We continue to model the flow of plasma through the vacuum interface of the ICP-MS by means of the Direct Simulation Monte Carlo Algorithm (DSMC). Recent work has focused on flow through the skimmer and on modifying the code so that it can take advantage of the power of parallel computing.

On the experimental front, we have built a system that allows us to simultaneously measure atom and ion densities at positions immediately upstream and immediately downstream from the skimmer cone of the ICP-MS vacuum interface. The measurements provide a comparison of skimming performance in a functioning interface to what would be predicted based on ideal skimming within the zone of silence of a supersonic expansion. With the same hardware, we can measure velocity distributions of atoms in the beam. The velocity distributions give a direct measure the degree of shock formation at the skimmer tip and in the skimmer throat. We have compared several different commercial skimmer cones and have noted significant differences in their performance.

To complement the experimental measurements, we have studied skimmer designs computationally with our DSMC code and can clearly see that some designs have strong shocks at the skimmer and others have weaker shocks. We can also clearly see that a weaker shock gives improved ion transmission through the skimmer. Temperature contour maps for argon flow through two skimmer designs are shown in figure 1.

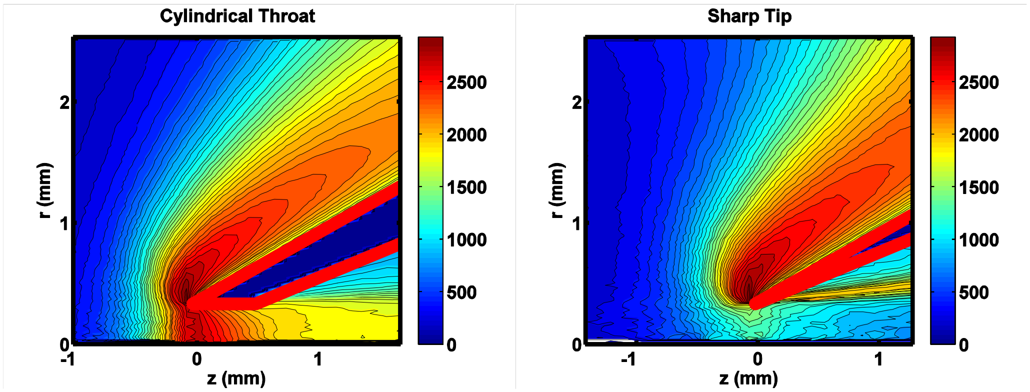

Fig. 1. Temperature contour plots of argon flow through two skimmer types.

Ambient ionization techniques. We have recorded static and video images of a DESI spray directed at a dye-coated glass surface, and have correlated the removal of dye from the surface with the appearance of signals on a mass spectrometer. The images, combined with experiments in which a barrier was placed between the spray impact zone and the inlet to the mass spectrometer, indicate that gas phase ions are produced at the ends of rivulets that form on the glass surface. The layout of the experiment is shown in figure 2.

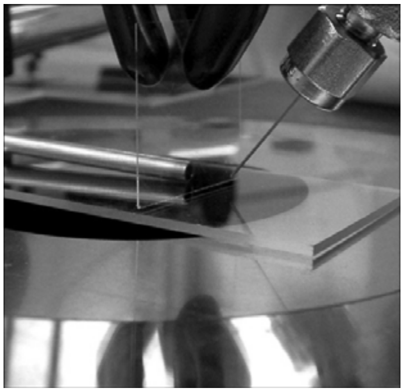

Fig. 2. Photograph of DESI source, barrier, and mass spectrometer inlet.

Science objectives for 2010-2012

- Image the ion beam at the entrance to the quadrupole in a working ICP-MS and characterize the effect of sample matrix on beam formation and focusing.
- Use time-resolved emission spectroscopy from a pulsed ICP to test hypotheses about the formation and importance of doubly-charged ions in ICP-MS
- Combine experimental measurements with monodisperse particle introduction into the ICP-MS with recently-developed models of flow through the vacuum interface to test the practical limits of ICP-MS for single particle measurements.
- Continue development of the computer simulation of flow through the ICP-MS interface.
- Use comparisons of DESI on a variety of surface types to refine understanding of ion formation.
- Develop models for analyte removal from surfaces by ambient ionization sources based on helium plasmas.

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Electron Transfer, Charge Inversion, and Selective Covalent Bond Formation in Gas-Phase Ion/Ion Reactions

Scott A. McLuckey
560 Oval Drive, Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084
Email: mcluckey@purdue.edu ; Web: www.chem.purdue.edu/mcluckey/

Collaborators: Dr. Richard O'Hair, University of Melbourne, Melbourne, Australia
Dr. Jack Simons, University of Utah, Salt Lake City, Utah
Dr. Gary L. Glish, University of North Carolina, Chapel Hill

Overall research goals: The overall goals of this project are to study the structures, stabilities, and reactivities of gaseous ions derived from macromolecules, such as linear synthetic polymers, dendrimers, and biopolymers. Of primary interest is the chemistry of the ions, including unimolecular, ion/molecule, and ion/ion chemistries. Insights derived from this work lead to new or improved means for the mass and structural analysis of macromolecules and their complexes. Furthermore, ion/ion chemistry also appears to provide a novel means for the synthesis of macro-molecular complexes, ion charge state manipulation, and structural interrogation. In this reporting period, we have strongly emphasized ion/ion reactions, according to our plan of research. In particular, we have made significant progress in understanding electron transfer, charge inversion, and ion/ion reactions.

Significant achievements in 2008-2010:

Ion/ion Electron Transfer. We continue to advance our understanding of the factors that underlie electron transfer dissociation (ETD). In the current reporting period, we have shown that hydrogen bonding to the amide nitrogen plays little role in the overall ETD process, which stands in contrast to a recent proposal for the mechanism for ETD. In a larger study, conducted in collaboration with researchers at the University of North Carolina, we have examined the role of electrostatic repulsion in ETD and electron capture dissociation (ECD). We have discovered that the magnitude of the electrostatic repulsion present in the cation that captures an electron can have a dramatic effect on product ion partitioning. We plan to submit the results of this work for publication in the coming months.

Charge Inversion. We have discovered that some species will undergo charge inversion most efficiently if an anion, such as a chloride ion, can be transferred in the process, rather than the usual removal of a proton. Protonated steroids, for example, undergo charge inversion much more efficiently via chloride or acetate attachment, than via the transfer of multiple protons. We are now examining this phenomenon within the context of the overall thermochemistry associated with the competing mechanisms to determine if they correlate. We have also examined charge inversion efficiency as a function of reagent ion charge and find that there is an optimum size/charge ratio for optimum efficiency. This is consistent with our current hypotheses regarding the competition between charge transfer at crossing points versus the formation of a long-lived complex.

Specific covalent bond formation via ion/ion chemistry. We have recently shown the first examples of specific covalent bond formation within the context of a gas-phase ion/ion reaction. We demonstrated that an aldehyde functionality in a reagent ion can react with primary amines in peptide ions to generate a Schiff base product. We have shown this to occur both is charge reduction experiments an in charge inversion experiments. We have also very recently noted that acyl chloride containing species also generate Schiff base products. This chemistry allows use to covalently modify polypeptide ions in the gas-phase and within the context of an MS^n experiment. This will add new capabilities for the structural characterization of species that contain primary amine groups (such as peptides and proteins).

Science objectives for 2010-2012:

- We will complete our systematic studies aimed at determining the roles of charge bearing sites, electrostatic repulsion, and total charge on the partitioning of products in the ETD experiment. This work will establish a firm experimental data set to guide theory and to facilitate efforts to predict the outcomes of ETD and ECD experiments.
- We will devote increasing attention to the ion/ion reactions of solvated species. This work will underlie our goal of expanding the range of gas-phase ion/ion reactions to those ordinarily deemed to be possible only in solution.
- We will continue to explore the use of multi-functional reagents for charge inversion experiments that promise to provide new means for the selective screening of mixtures with particular attention being paid to important compound classes, such as steroids, or functional groups, such as phosphates in phosphorylated peptides.
- We will study a newly discovered means for the collisional activation of ions in a linear ion trap. The approach is non-selective, which makes it complementary to conventional single-resonance ion trap collisional activation.

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Session 4 – Imaging Analysis II

From DC to Daylight: Local Spectroscopies with the Scanning Tunneling Microscope

Paul S. Weiss, Principal Investigator
California NanoSystems Institute and Department of Chemistry & Biochemistry, UCLA, Los Angeles, CA 90095
Email: psw@cnsi.ucla.edu; Web: www.nano.ucla.edu

Collaborators: Dr. Mark Ratner, Northwestern University, Evanston, IL
Dr. Alex Jen, University of Washington, Seattle, WA

Overall research goals: The research objectives are to develop broadly applicable local, imaging spectroscopies based on the scanning tunneling microscope (STM) for the infrared and visible ranges. To this, we have also added the goal of measuring polarizability of species in the tunnel junction. All of these measurements give insight into the buried interfaces that are usually difficult to study using scanning probe microscopies.

Significant achievements in 2008-2010: We have measured the photoisomerization of single, isolated, tethered molecules. We have shown how steric hindrance and electronic coupling reduce or prevent photoisomerization. We have shown that one-dimensional lines of molecules can be photoisomerized or can be isomerized using sufficiently energetic electrons, but that intermolecular coupling reduces this efficiency. We have measured the polarizability of individual and assembled molecules, thereby determining their connection to the substrates on which they are adsorbed. We have developed STMs for coupling visible and infrared light into the tunneling junction. With evanescently coupled visible light, we have shown that we can induce photoreactions between adjacent molecules (Fig. 1).

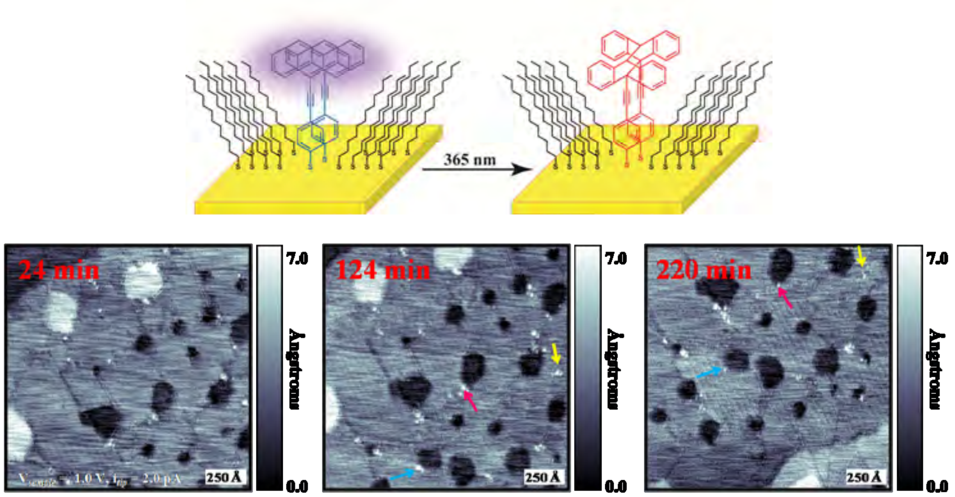

Figure 1. A stabilized STM is used to image the photodimerization of inserted molecules as a test of both the stability of the microscope and the evanescent coupling of light into the tunnel junction. (Top) Molecules used in this study. (Bottom) Three from a series of SM images in which photodimerization can be detected with the STM both through images and from the cessation of switching of the molecules measured.

We couple electromagnetic radiation into the tunneling junctions of scanning tunneling microscopes such that we can record local spectra with submolecular resolution. We associate these spectra with their macroscopic, ensemble-averaging equivalents in order to understand nanoscale phenomena and environments. The ability to measure molecular polarizability gives us a means to explore the buried bonds/contacts between adsorbed molecules and their substrates. In one system, we employ multiple microwave signals in order to heterodyne to convenient low frequencies and to avoid the effects of stray capacitance. Close coupling to theory enables significant insight into the meaning of the measurements and the character of the buried interface bonds. Visible excitation of well-defined isolated molecules will enable measurements of intrinsic photoconductance, so as to yield a useful figure of merit for optimizing the designs, connections, and environments of molecules and materials for photovoltaics and photo-induced capacitance. Local infrared excitation should ultimately yield chemical identification and bonding changes. In each of these microscopes, general approaches are employed in order to yield the widest applicability.

Science objectives for 2010-2012:

- Continue to develop a scanning tunneling microscope that can measure local/molecular photoconductivity and optical spectra, and apply this to molecules and materials for photovoltaics.
- Develop a scanning tunneling microscope that employs molecular polarizability as a means of chemical differentiation and to measure the electronic connection of molecules and their contacts.
- Continue to develop a scanning tunneling microscope that can measure molecular vibrations at room temperature; work out the noise and stability issues with our current design, based on the

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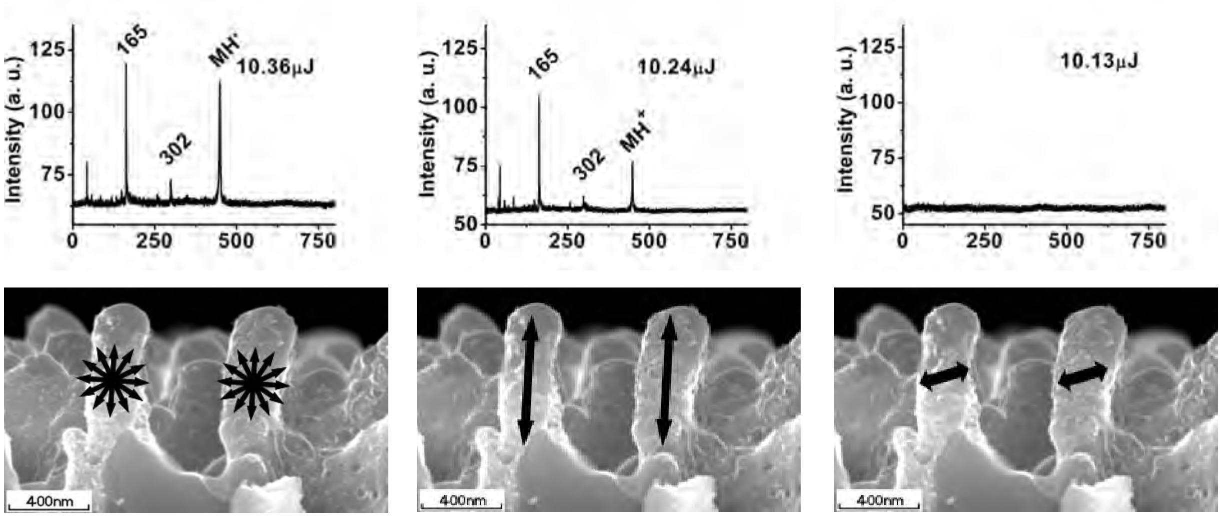
Nanostructured substrates and imaging applications of soft laser desorption ionization

Akos Vertes, Principal Investigator
Zhaoyang Chen, Yue Li and Prabhakar Sripadi, Postdoctoral Research Associates
Department of Chemistry, George Washington University, Washington, DC 20052
Email: vertes@gwu.edu; Web: http://www.gwu.edu/~vertes

Overall research goals: Laser desorption ionization and laser ablation are essential ionization methods for the mass spectrometry (MS) of biomolecules cells and tissues. Our research goals for the current grant period are to explore ion production from nano- and mesoscopic structures and to develop new molecular imaging methods at atmospheric pressure.

Significant achievements in 2008-2010: During the reporting period we discovered a dramatic disparity in the efficiency of ion production from silicon microcolumns depending on the polarization of the incident laser. When the electric field of the radiation has a component that is parallel to the column axes (p-polarized beam) the desorption and ionization processes are efficient, whereas in case they are perpendicular (s-polarized waves) minimal ion production is observed (see Figure 1). This strong directionality in ion production is a unique feature of these nanostructures.



(A) unpolarized ray **(B) p-polarized ray** **(C) s-polarized ray**

Figure 1. Ion yields from LISMA were compared for laser desorption ionization experiments with (A) unpolarized, (B) p-polarized and (C) s-polarized rays at ~10 μJ from a nitrogen laser. The p-polarized ray had similar ionization efficiency to the unpolarized ray, whereas no signal was detected with the s-polarized ray.

Three-dimensional (3D) imaging of molecular distributions offers insight into the correlation between biochemical processes and the spatial organization of a biological tissue. Simultaneous identification of diverse molecules is a virtue of MS that in combination with ambient ion sources enables the atmospheric pressure investigation of biomolecular distributions and processes. We developed an MS-based technique that allows 3D chemical imaging of tissues under ambient conditions without sample preparation. The method utilizes laser ablation electrospray ionization (LAESI) for direct molecular imaging with lateral and depth resolutions of ~300 μm and 30 to 40 μm, respectively. We demonstrate the feasibility of LAESI 3D imaging MS of metabolites in the leaf tissues of Peace lily (*Spathiphyllum lynise*) and the variegated Zebra plant (*Aphelandra squarrosa*). The 3D distributions are found to exhibit tissue-specific metabolite accumulation patterns that correlate with the biochemical roles of these chemical species in plant defense and photosynthesis.

Science objectives for 2010-2012(style=Stand alone text heading):

- **Nanophotonic ion production:** We plan to enhance ion production from LISMA and NAPA structures by exploring the effect of the semiconductor doping level, optical, geometry and morphology factors on the ion yield and fragmentation patterns. In a related new project we will start to explore direct ion production from microorganisms on these structures.
- **Direct metabolic imaging of biological systems with mass spectrometry:** By analyzing a variety of tissues from *Arabidopsis thaliana* and corn (*Zea mays*), we will examine the role of tissue tensile strength, shape and feature size on imaging performance. Tissue phantoms will also be used to study the effect of water content and tensile strength on depth resolution, a key parameter in 3D imaging.
- ***In situ* analysis of single cells and cell populations:** We plan to study metabolic changes in small cell populations and in single cells of *A. thaliana* and *Z. mays* using sampling based on ablation via a sharpened optical fiber. Metabolic response to environmental stress will be studied at the single cell level. We will build metabolic images of plant tissue by analyzing the surface cell by cell.

References to work supported by this project 2008-2010:

1. P. Nemes, A. S. Woods and A. Vertes, “Simultaneous Imaging of Small Metabolites and Lipids in Rat Brain Tissues at Atmospheric Pressure by Laser Ablation Electrospray Ionization Mass Spectrometry,” *Anal. Chem.*, **2010**, **82**, 982-988.
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4. P. Nemes, A. A. Barton and A. Vertes, “Three-Dimensional Imaging of Metabolites in Tissues under Ambient Conditions by Laser Ablation Electrospray Ionization Mass Spectrometry,” *Anal. Chem.*, **2009**, *81*, 6668-6675.
5. B. N. Walker, T. Razunguzwa, M. Powell, R. Knochenmuss and A. Vertes, “Nanophotonic Ion Production from Silicon Microcolumn Arrays,” *Angew. Chem. Int. Ed.*, **2009**, *48*, 1669-1672.
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7. B. Shrestha, Y. Li and A. Vertes, “Rapid analysis of pharmaceuticals and excreted xenobiotic and endogenous metabolites with atmospheric pressure infrared MALDI mass spectrometry,” *Metabolomics*, **2008**, *4*, 297-311.
8. A. Vertes, P. Nemes, B. Shrestha, A. A. Barton, Z. Chen and Y. Li, ”Molecular Imaging by Mid-IR Laser Ablation Mass Spectrometry,” *Appl. Phys. A*, **2008**, *93*, 885-891.

9. G. Luo, I. Marginean, L. Ye and A. Vertes, "Competing Ion Decomposition Channels in Matrix-Assisted Laser Desorption Ionization," *J. Phys. Chem. B*, **2008**, *112*, 6952-6956.
10. P. Nemes, A. A. Barton, Y. Li and A. Vertes, “Ambient Molecular Imaging and Depth Profiling of Live Tissue by Infrared Laser Ablation Electrospray Ionization Mass Spectrometry,” *Anal. Chem.*, **2008**, *80*, 4575-4582. (Accelerated Article)
11. Z. Chen and A. Vertes, “Early plume expansion in atmospheric pressure mid-infrared laser ablation of water-rich targets,” *Phys. Rev. E*, **2008**, *77*, 036316.
12. Y. Li, B. Shrestha and A. Vertes, “Atmospheric Pressure Infrared MALDI Imaging Mass Spectrometry for Plant Metabolomics,” *Anal. Chem.*, **2008**, *80*, 407-420. (Cover Page Article)

Chemically Tailored Gold Nanorods as Biosensors for Mass Spectrometry Applications

David H. Russell, Principal Investigator
Edward T. Castellana, Postdoctoral Research Associate
Roberto Gomez, Graduate Research Associate
Department of Chemistry, Texas A&M University
PO Box 30012, College Station, TX 77842-3012
russell@mail.chem.tamu.edu; Web: http://www.chem.tamu.edu/rgroup/russell/new_site_content/

Overall research goals: Our research objectives are focused at developing nanomaterial based biosensor platforms for mass spectrometry applications. The work presented here is focused on two main themes: i) to exploit the optical properties of gold nanorods to facilitate the laser desorption ionization (LDI) of analytes under near IR laser irradiation and ii) to tailor the surface chemistry of gold nanorods to capture specific and/or low abundance analytes from complex solutions.

Significant achievements in 2008-2010: A 'strategy' for analyte capture/ionization based on chemical derivatization of gold nanorods and infrared laser desorption ionization (IR-LDI) is described. Here, LDI is performed at wavelengths (1064 nm) that overlap with the longitudinal surface plasmon resonance (LSPR) mode of gold nanorods. By controlling the aspect ratio of the rods and functionalizing their surface with a self-assembled monolayer of 4-aminothiophenol, we have tuned the wavelength of the longitudinal SPR absorption to overlap with the output of a Nd:YAG laser. The absorbed energy from the laser facilitates desorption and ionization of the analyte. We show that a variety of biomolecules can be efficiently desorbed and ionized by 1064 nm irradiation of nanorods.

The LSPR-LDI mass spectra of the peptide angiotensin II acquired using AuNR and 1064 nm laser irradiation is shown in **figure 1a**. Note that peptide ions are only observed when the hexadecyltrimethylammonium bromide (CTAB), a capping agent that is essential for the synthesis of AuNRs, is replaced with a self-assembled monolayer (SAM) of 4-aminothiophenol (4-ATP). Analyte ions are not observed from sample spots containing mixtures of 4-ATP capped AuNP (no LSPR absorption) and peptide or from mixtures of 4-ATP and peptide (data not shown). Additionally, we have established that a variety of biomolecules can be efficiently desorbed and ionized by 1064 nm irradiation of nanorods.

The surface chemistry of metallic NR can be exploited to capture analytes from complex solutions. To demonstrate analyte capture and MS based detection CTAB capped AuNR were incubated in a dilute solution containing benzyldimethylammonium chloride (BDAC) and then removed from solution by centrifugation. In **figure 1b** we display the successful capture and detection of the analyte BDAC using our AuNR biosensor. Our platform has potential for applications in biomarker screening to capture and identify unknown analytes present in low abundances from complex biological fluids. The results of these studies are important for designing nanomaterial based capture assays for mass spectrometry assays and interfacing nanomaterials with imaging/spatial profiling mass spectrometry experiments.

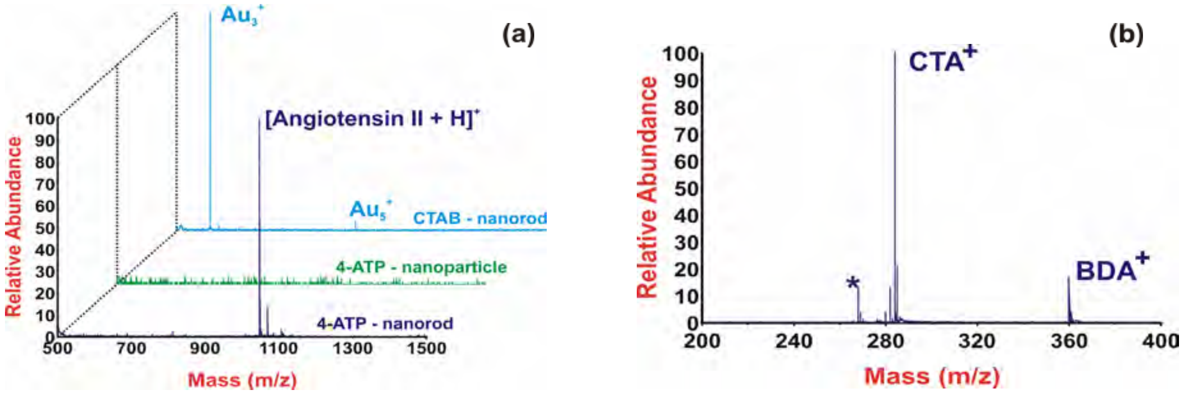

Figure 1. (a) LSPR-LDI mass spectra of angiotensin II, m/z = 1046.5 Da using 4-ATP capped AuNR (dark blue), 4-ATP capped AuNP (green), and CTAB capped AuNR (light blue). (b) LSPR-LDI mass spectrum of benzyldimethylhexadecylammonium ion (BDA$^+$), m/z = 360.36 Da, captured in the CTAB bilayer capping of AuNR. The peak labeled with a * designates a CTA$^+$ fragment ion.

Science objectives for 2010-2012:

- **Selective Analyte Capture.** By functionalizing nanomaterials with mass spectrometry transparent capture ligands we aim to develop a platform capable of selectively capturing and concentrate low abundance analytes prior to MS analysis.
- **Optical Multiplexing.** Utilizing the wavelength dependent ionization properties of nanomaterials, we are working to include optical multiplexing into our selective capture experiments. By functionalizing different aspect ratio nanorods with different capture lignads we aim to combine selective capture with selective ionization.
- **Mechanistic Studies.** Ongoing efforts in our laboratory are directed toward understanding the mechanism of LDI from nanomaterials. We plan to expand these studies to include wavelength dependent studies for gold nanorods and other nanomaterials with interesting optical properties.

References to work supported by this project 2008-2010:

- **Castellana, E. T.**; Gamez, R. C.; Russell, D. H., "Gold Nanorod supported Lipid Bilayers as a Mass Spectrometry Biosensing Platform", In preparation *J. Am Chem. Soc.*
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Mass Spectrometric Imaging of Plant Metabolites

Basil Nikolau, Principal Investigator
Young-Jin Lee, Co-Principal Investigator
Edward S. Yeung, Co-Principal Investigator
Robert S Houk, Co-Principal Investigator
142 Spedding Hall, Ames Laboratory, Ames, IA 50011
Email: yjlee@iastate.edu; Web: http://yjlee.public.iastate.edu/

Overall research goals: We develop mass spectrometric imaging techniques to map metabolite distributions within plant tissues, and eventually among individual plant cells. Such information will provide unprecedented details on the distribution of metabolites from cell to cell, cooperative and antagonistic effects among the metabolites, and environmental influences on metabolism. Such details will ultimately lead to a predictive understanding of the mechanisms that multicellular organisms use to regulate metabolic processes.

Significant achievements in 2008-2010:
Colloidal-silver laser desorption ionization (LDI) mass spectrometry (MS) was employed to directly profile and image epicuticular wax metabolites on a variety of different surfaces of *Arabidopsis thaliana* leaves and flowers. Major cuticular wax compounds, such as very long chain fatty acids, alcohols, alkanes, and ketones were successfully detected as silver adduct ions. Variations of wax products between different spatial locations for wild-type and for a mutant strain, cer2, were investigated. The spatially-resolved surface metabolite profiling data of this mutant has provided new insights into the complexity of epicuticular wax deposition at the cellular-resolution scale.

Mass profiles and images of *Arabidopsis thaliana* were recorded directly from various plant surfaces, subsurfaces and cross-sections using graphite-assisted laser desorption ionization (GALDI). Mass spectral profiles revealed tissue-specific accumulation of flavonoids in flowers and petals. The location and the degree of light-induced flavonoid accumulation in stem sections were successfully probed. In addition, by controlled pretreatment with chloroform to remove the waxes, metabolites underneath the cuticle of plant tissues could be imaged with little loss of spatial resolution. Colloidal graphite was also successfully applied to APMALDI of various compounds, including direct profiling of flavonoids on *Arabidopsis* flower.

Single cell level high spatial resolution of 12-µm size was achieved using optical fibers with narrow inner core diameter and a matrix application method, and applied to *Arabidopsis thaliana* flowers and roots, and revealed molecular details of metabolites localization. High resolution mass spectrometry capability was obtained by upgrading the previous MALDI LTQ instrument to MALDI LTQ-Orbitrap. The capacity of HRMS was successfully demonstrated in identifying unknown metabolites on *Arabidopsis* roots and differentiating isobaric wax metabolites of C29 alkane and C28 aldehyde.

Mass spectrometric imaging has been utilized to localize individual astrocytes and to obtain cholesterol populations at the single-cell level. The silver ion adduct of membrane-bound cholesterol was monitored to detect individual cells. Good correlation between mass spectrometric and optical images at different cell densities indicates the ability to perform single-cell studies of cholesterol abundance. Feasibility of quantification is confirmed by the agreement between LDI MS ion signals and a traditional enzymatic fluorometric assay.

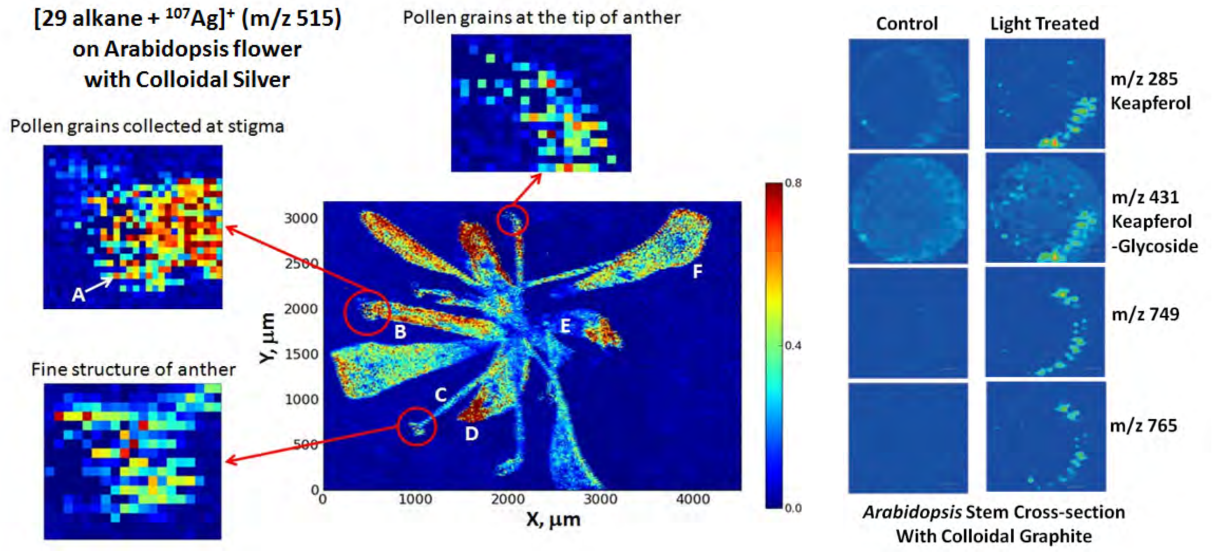

Figure 1. (Left) Single cell level high spatial resolution MS image of C29 alkane on the surface of *Arbidopsis* flower. LDI MS imaging was acquired with laser beam size of 12µm and raster size of 12µm and colloidal silver as additive. **(Right) Chemically selective images of *Arabidopsis* stems grown under a normal light regime as control** (left column) **and under a high-light regime** (right column).

Science objectives for 2010-2012(style=Stand alone text heading):

- We will strive to achieve high spatial resolution down to 5-µm or smaller by replacing current N_2 laser with Nd-YAG laser and using new laser optics.
- Methodology for the quantification of metabolites in cellular and subcellular level will be developed using synthetic liposomes as standard compounds.
- Various *Arabidopsis* mutants, such as tt7, cer1, and cer5, will be studied using the developed MS imaging technique.
- APMALDI imaging will be attempted with LTQ-Orbitrap mass spectrometer.

References to work supported by this project 2008-2010(style=Stand alone text heading):

1. H. Zhang, S. M. Brokman, N. Fang, N. L. Pohl and E. S. Yeung, “Linkage Position and Residue Identification of Disaccharides by Tandem MS and Linear Discriminant Analy-sis”, Rapid Comm. Mass Spectr., 22, 1579 (2008).
2. S. Cha, H. Zhang, H. I. Ilarslan, E. S. Wurtele, L. Brachova, B. J. Nikolau and E. S. Yeung, “Direct Profiling and Imaging of Plant Metabolites in Intact Tissues by using Col-loidal Graphite-Assisted Laser Desorption Ionization (GALDI) Mass Spectrometry”, Plant J., 55, 348 (2008).
3. S. Cha., Z. Song, B. J. Nikolau and E. S. Yeung, “Direct Profiling and Imaging of Epicuticular Waxes on Arabidopsis thaliana by Laser Desorption/Ionization Mass Spectrometry Using Silver Colloid as a Matrix”, Anal. Chem., 81, 2991 (2009).
4. D. C. Perdian, G. M. Schieffer, and R. S. Houk, "Atmospheric Pressure Laser Desorption/Ionization of Plant Metabolites and Plant Tissue using Colloidal Graphite," Rapid Commun. Mass Spectrom., 24, 397-402 (2010).
5. D. C. Perdian, S. Cha, J. Oh, D. Sakaguchi, E. S. Yeung, and Y. J. Lee, “In Situ Probing of Cholesterol in Astrocytes at the Single Cell Level using Laser Desorption Ionization Mass Spectrometric Imaging with Colloidal Silver”, Rapid Commun. Mass Spectrom., in press.
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Poster Session 1

Coordination-Chemistry-Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities

Joseph T. Hupp, SonBinh. T. Nguyen, Randall Q. Snurr
Omar K. Farha, Youn-Sang Bae
Departments Of Chemistry and Chemical & Biological Engineering, Northwestern University
2145 Sheridan Road, Evanston, IL 60208
Email: j-hupp@northwestern.edu, stn@northwestern.edu, snurr@northwestern.edu;
Web: chemgroups.northwestern.edu/hupp, chemgroups.northwestern.edu/nguyengroup,
zeolites.cqe.northwestern.edu

Overall research goals: Develop, computationally model, structurally characterize, and experimentally and computationally evaluate metal-organic framework (MOF) and related materials for important small-molecule separations. Discover general design rules for MOFs that can function as materials for efficient chemical separations.

Significant achievements in 2008-2010: A variety of new MOFs have been synthesized, characterized, and tested for small-molecule separations. Significant examples are described in the following paragraphs.

We studied separations of CO_2 / CH_4, CO_2 / N_2, and O_2 / N_2 mixtures in three porous coordination polymers made from the same carborane ligand and Co(II) nodes [1]. This work showed that the adsorption selectivities can be changed dramatically in coordination polymers made of the same ligand and metal, depending upon the activation conditions and resulting pore structure. High selectivities for CO_2 over CH_4 (~47) and CO_2 over N_2 (~95) were obtained. Selective adsorption for O_2 over N_2 was demonstrated in a material with open Co(II) sites. Such oxygen selective behavior is highly unusual for zeolite and MOF materials; these materials are usually selective for nitrogen. Several recent papers by other groups reported selective adsorption of O_2 over N_2 in coordination polymers due to molecular sieving, but we are aware of only one other example in the absence of molecular sieving. Li and Yang reported a very mild O_2 / N_2 selectivity of 1.8 in MOF-177, but the origin of this selectivity is not well understood. The coordinatively unsaturated Co(II) sites in our materials provide a possible explanation for the higher O_2 selectivity observed here.

In addition to MOFs and other coordination polymers, we have begun designing and synthesizing porous organic polymer (POP) materials. An example is shown in Figure 1, where amine and anhydride species are condensed to generate a robust diimide polymer. The material is microporous and possesses an internal surface area of ca. 700 m^2/g. We observed good selectivities (ca. 10 to 30, depending on pressure and composition) for uptake of CO_2 versus methane [2]. By reducing the polymer and doping with lithium ions, we observed substantial enhancement of selectivities [3].

Coordinatively unsaturated metal ions can function as specific sites for analyte binding. We reasoned that framework-anchored alkoxides could be introduced into MOFs and used as such sites. To test the concept, a new non-catenated MOF containing pendant alcohol functionalities was synthesized [4]. The alcohols were then post-synthetically converted to either lithium or magnesium alkoxides, with the incorporated metals anchored far from nodes or carboxylate functionalities. The metal alkoxide sites can be obtained stoichiometrically while maintaining the permanent porosity and large surface area of the parent hydroxylated material.

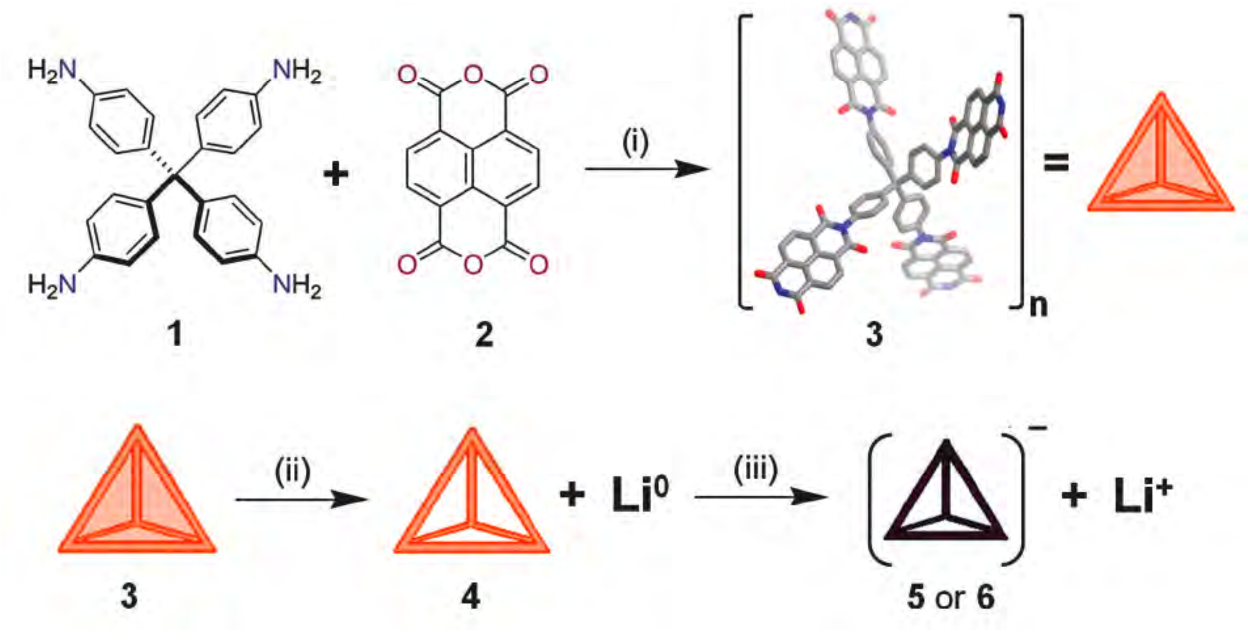


Figure 1. Synthesis of diimide-based porous polymer **3** and its modification by reduction with lithium. Experimental conditions: (i) DMF, propionic acid, 150 °C; (ii) 10^{-2} mm. Hg vacuum, 120 °C; (iii) DMF. Structure of **3** is shown as MM2 minimized geometry of repeat unit (carbons are grey, oxygens are red, nitrogens are blue and hydrogens are omitted for clarity) [3].

Science objectives for 2010-2012:

- Understand physical basis for highly selective carbon dioxide sorption as an example for starting to develop design rules for adsorption separation materials
- Target separation of alkane/alkene mixtures
- Computationally identify and experimentally obtain materials that kinetically separate small molecules.

Selected references from work supported by this project 2008-2010:

1. “Separation of Gas Mixtures Using Co(II)-Carborane-Based Porous Coordination Polymers,” Y.-S. Bae, A. M. Spokoyny, O. K. Farha, R. Q. Snurr, J. T. Hupp, C. A. Mirkin, submitted.
2. “Synthesis, Properties and Gas Separation Studies of a Robust Diimide-based Microporous Organic Polymer,” O. K. Farha, A. Spokoyny, B. Hauser, Y. S. Bae, S. Brown, R. Q. Snurr, C. A. Mirkin, J. T. Hupp, *Chem. Mater.*, **21**, 3033-3035 (2009).
3. “Chemical reduction of a diimide based porous polymer for selective uptake of carbon dioxide versus methane,” O. K. Farha, Y-S. Bae, B. G. Hauser, A. M. Spokoyny, R. Q. Snurr, C. A. Mirkin and J. T. Hupp, *Chem. Commun.*, accepted.
4. “Post-Synthesis Alkoxide Formation Within Metal-Organic Framework Materials: A Strategy for Incorporating Highly Coordinatively Unsaturated Metal Ions,” K. L. Mulfort, O. K. Farha, A. Sarjeant, J. T. Hupp, *J. Am. Chem. Soc.*, **131**, 3866-3868 (2009).
5. “Enhancement of CO_2 / N_2 selectivity in a metal-organic framework by cavity modification,” Y.-S. Bae, O. K. Farha, J. T. Hupp, R. Q. Snurr, *J. Mater. Chem.*, **19**, 2131-2134 (2009).
6. “Strategies for characterization of large-pore metal-organic frameworks by combined experimental and computational methods,” Y.-S. Bae, D. Dubbeldam, A. Nelson, K. S. Walton, J. T. Hupp, R. Q. Snurr, *Chem. Mater.*, **21**, 4768–4777 (2009).

Chemical Imaging with 100nm Spatial Resolution: Combining High Resolution Flurosecence Microscopy and Ion Mobility Mass Spectrometry

Don Dunn III, Nick Dupuis, Paul Kemper, Michael T. Bowers, and Steven K. Buratto
Department of Chemistry and Biochemistry
University of California, Santa Barbara

Overall research goals: Our research goals are to combine, in a single instrument, high spatial resolution optical microscopy with the chemical specificity and conformational selectivity of ion mobility mass spectrometry. We apply this technique to thin films of molecular semiconductor materials in order to probe the conformer distribution within the film and relate this distribution to the luminescence properties.

Significant achievements in 2008-2010: We have successfully designed and constructed a combination laser scanning confocal microscope (LSCM) and near-field scanning optical microscope (NSOM) that replaces the source chamber of an ion mobility mass spectrometer. The microscope source chamber is capable of operating in vacuum with an ultimate spatial resolution of better than 100nm. A schematic of the new source chamber is shown below in Figure 1.

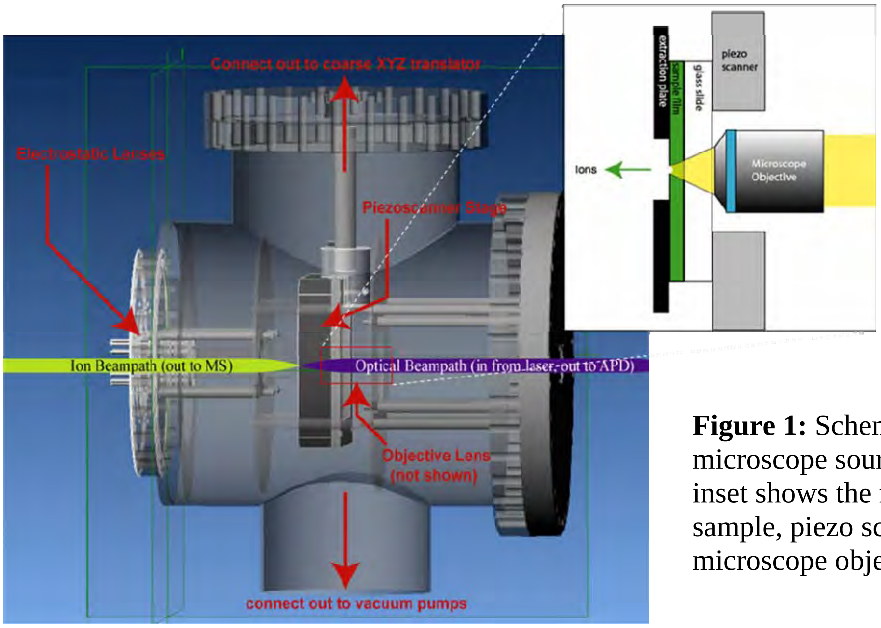


Figure 1: Schematic of the microscope source chamber. The inset shows the relative position of the sample, piezo scanner, and microscope objective.

The chamber of Fig. 1 is designed such that the microscope can be inserted and removed without disrupting the alignment of the microscope or ion optics. The modular design of this chamber allows us to use the optical microscope in air to image samples prior placing the microscope in vacuum. Ions are formed by focusing the desorption laser (frequency-tripled YAG laser 355 nm, 100 nJ/pulse 7 ns pulse width) using the same microscope objective as used in optical microscopy. The gas phase part of the imaging apparatus uses an existing ion mobility mass spectrometer. This spectrometer is a high sensitivity and high resolution instrument used previously in the study of

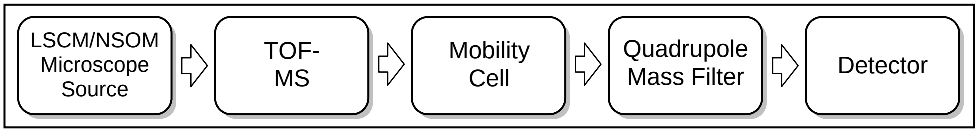


Figure 2. Block diagram of instrument.

small metal ion clusters. The capabilities of this instrument are described in detail elsewhere. [1] A block diagram of the overall instrument is given in Figure 2.

We have demonstrated the capability of the microscope and the ion mobility mass spectrometer on a thin films of oligo-p-phenylene vinylene (OPV) molecules, a molecular semiconductor used as the active layer in organic light-emitting diodes. A high resolution fluorescence image of an OPV film is presented in Figure 3 along with the arrival time distribution of the conformers in the film taken using ion mobility mass spectrometry.

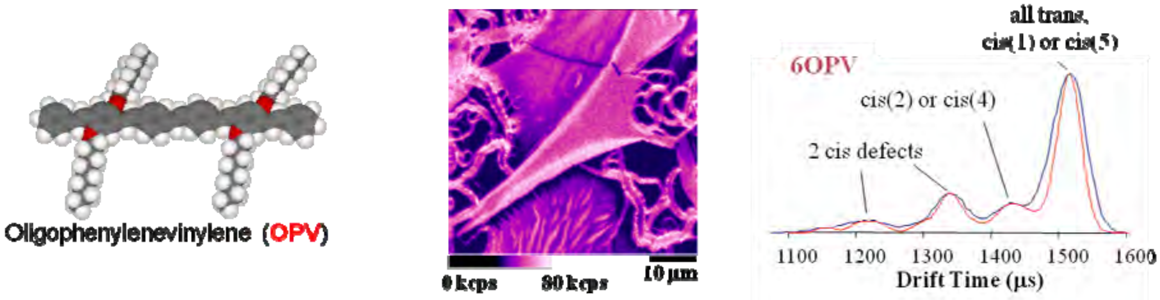


Figure 3: Model of an oligo-p-phenylene vinylene (OPV) molecule (left), a luminescence image of a thin flim of OPV (center) and the arrival time distribution of the OPV film (right).

Science objectives for 2010-2012:

- Couple the microscope and mass spectrometer and record an arrival time distribution *in situ*.
- Study of a variety of OPV thin films in order to map the conformer phase separation within the film and correlate with the luminescence properties.
- Apply our imaging technique to blended films of molecular semiconductors to map the chemical identity of the luminescence contrast. These materials will include films used in organic solar cells and light-emitting electrochemical cells.

References:

1. P.R. Kemper, P. Weis, and M.T. Bowers, *Int. J. Mass. Spectrom.* **160**, 17 (1997).
2. M.A. Summers, S.K. Buratto and L. Edman, “Morphology and environment-dependent fluorescence in blends containing a phenylenevinylene-conjugated polymer” *Thin Solid Films* **515**, 8412 (2007).
3. D. Dunn, N. Dupuis, M.T. Bowers and S.K. Buratto, "A Combined Confocal Microscope and Ion Mobility Mass Spectrometer for Chemical Imaging at 100nm Spatial Resolution," Review of Scientific Instruments submitted.

Novel Membranes for Carbon Dioxide Removal from Natural Gas Based on Thermally Rearranged Polymers

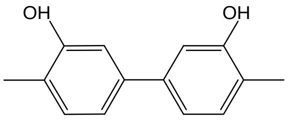
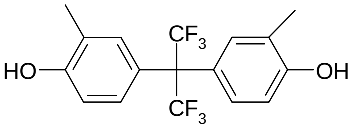
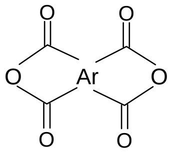
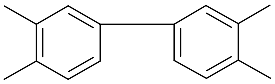
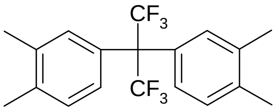
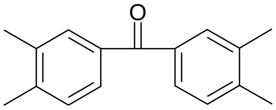
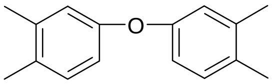
Dr. Benny D. Freeman, Principal Investigator
David Sanders, Zachary Smith, Dr. Claudio Ribeiro
10100 Burnet Rd., Bldg 133, Room 1.308B, Austin, TX, 78758
Email: freeman@che.utexas.edu; Web: http://membrane.ces.utexas.edu

Collaborators: Dr. Jim McGrath, Virginia Tech University, Virginia

Overall research goals: The research objectives in this project are to investigate the effect of chemical structure on the fundamental transport properties of polybenzoxazoles prepared through thermal rearrangement of ortho-functional aromatic polyimides; determine what fraction of permeability changes in these polymers is due to solubility and what fraction is due to diffusivity; and to characterize the physical aging process of these thermally rearranged polymers.

Significant achievements in 2008-2010: Synthesis work focused on homopolyimides with varying diamine and dianhydride precursors. Soluble polyimides were synthesized using a two step method. First, a poly(amic acid) precursor was formed from the polycondensation of a diamine and a dianhydride. The poly(amic acid) was then converted into an aromatic polyimide using a mixture of acetic anhydride and pyridine. Polyimides with varying diamine and dianhydrides have been successfully synthesized including HAB-6FDA, APAF-6FDA, APAF-BTDA, APAF-ODPA, APAF-BPDA. Structures of diamines and dianhydrides are shown in Table 1. All soluble polymer structures were confirmed using H-NMR and FTIR.

Table 1: Diamines and dianhydrides used to synthesize of aromatic polyimides, precursors to thermally rearranged polymers

$H_2N-Ar^*-NH_2$ $Ar^*=$	 HAB  APAF
 Ar=	 BPDA  6FDA  BTDA  ODPA

Polyimides were rearranged in a programmable Carbolite Split-Tube furnace. All samples underwent thermal rearrangement in the range of 350-450ºC, as reported in the literature. Thermogravimetric Analysis (TGA) was used to observe mass loss in the sample during thermal rearrangement. Results showed that mass loss depended on temperature and proved that some thermal decomposition occurs at higher temperatures.

Pure gas permeability and sorption measurements were made for the HAB-6FDA polyimide before and after thermal conversion at 350 and 400ºC. Results showed that both permeability and sorption are a function of rearrangement temperature. Large increases in permeability were seen after rearrangement as reported in the literature. Sorption data was fit using the dual-mode sorption model with good correlation. Using the solution diffusion model, the diffusion coefficient was calculated from permeability and solubility results. This work showed that the large increase in permeability seen after thermal rearrangement was primarily associated with a large increase in the diffusion coefficient. Permeability and solubility results for the HAB-6FDA sample treated at 400ºC for one hour are shown below in Figure 1.

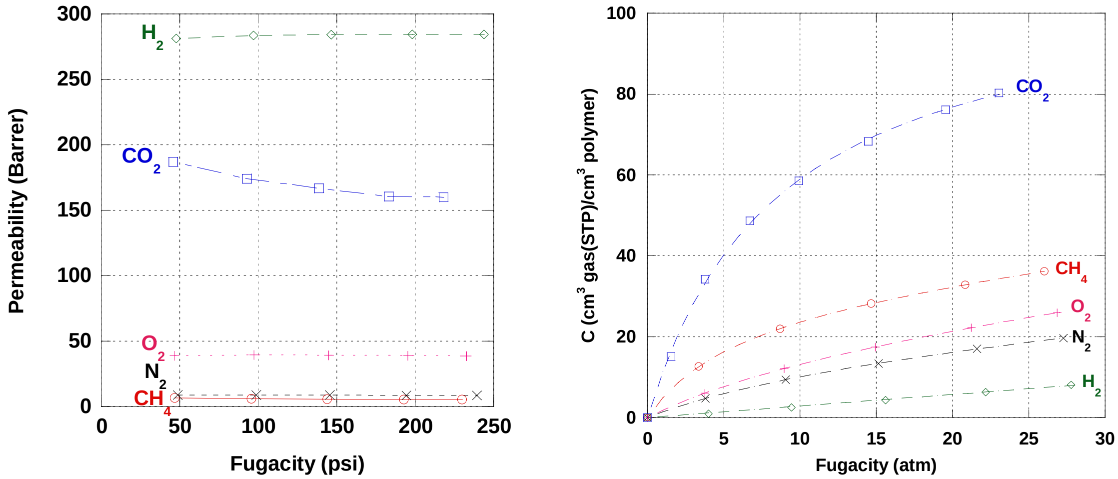


Figure 1: Permeability (left) and Sorption (right) plots for H_2, CO_2, O_2, N_2, and CH_4.

Science objectives for 2010-2012:

- Permeability and sorption measurements will continue on the HAB-6FDA polyimide for different rearrangement conditions to characterize transport properties as a function of conversion.
- A systematic structure/property study will be conducted for thermally rearranged polyimides with different chemical structures.
- Polyimide copolymers will be synthesized using high free volume diamines to exploit the large increase in permeability due to an increase in the diffusion coefficient.
- The effects of thermal rearrangement on free volume will be studied in detail using Positron Annihilation Lifetime Spectroscopy.
- Thin films will be cast using a spin coating technique and physical aging will be monitored through permeability tests.

References to work supported by this project 2008-2010):

No work has been published at this time.

Laserspray Ionization - A Process for Producing Multiply Charged Gas-Phase Ions from Solid Solutions

Sarah Trimpin, Department of Chemistry, Wayne State University, Detroit, MI

Two primary differences between electrospray ionization (ESI) and matrix-assisted laser desorption/ionization (MALDI) are the sample environment (solution *vs.* solid) and the observable charge state(s) (multiply *vs.* singly charged). The multiply charged ions observed in ESI-MS enhance the yields of fragment ions, a key benefit in structure characterization, and allow analysis of high molecular weight compounds on mass spectrometers with a limited mass-to-charge (*m*/*z*) range. In contrast, MALDI MS is ideal for the analysis of heterogeneous samples, because it often requires less sample and mass spectra of singly charged ions are easier to interpret. ESI is easily interfaced with liquid separation methods whereas MALDI is most often used as a direct ionization method and, for complex samples, benefits from post-ionization separation methods such as high resolution MS or ion mobility spectrometry.

We report here the astonishing observation of highly charged molecular ions (e.g. lysozyme charge state +13) by laser ablation of a solid matrix/analyte mixture typically used in MALDI-MS analyses. The *distribution* and *abundances* of multiply charged ions by this laserspray ionization (LSI) method are similar to those obtained by ESI. Importantly, the traditional singly charged ionization mechanism can be "turned on" at operator's will, by changing either the matrix/matrix preparation conditions or the voltage applied to the MALDI target plate to produce exclusively singly charged ions; this capability is not available with any other ionization method. These findings show, for the first time, that singly charged ions as well as multiply charged ions are available in MALDI processes. Besides having important mechanistic implications relating to MALDI and ESI our findings have enormous practical analytical utility especially for mass range limited high resolution mass spectrometers.

Because one motivation of our research is to make inroads in the daunting task of chemical analysis related to both complexity and insolubility, we are developing total solvent-free methods that avoid the use of solvents to the greatest extent possible. LSI is an excellent fit with this goal and has now been interfaced with an IMS-MS (Synapt G2) instrument and the solvent-free gas phase separation of LSI generated protein ions demonstrated. LSI-IMS-MS separates isomeric amyloid (1-42) vs. (42-1) mixtures. We are currently pursuing solvent-free MALDI sample preparation approaches, especially related to total solvent-free tissue imaging. Total solvent-free analysis and separation also require aids to structural characterization such as accurate mass measurement and mass selected fragmentation. In this regard, electron transfer dissociation (ETD) using LSI on an LTQ-ETD-MS has been shown to give nearly complete sequence coverage of ubiquitin (MW 8500), similar to previous results using ESI.

Chemical Imaging with Cluster Ion Beams and Lasers

Nicholas Winograd
209 Chemistry Bldg, Penn State University, University Park, PA 16875
Email: nxw@psu.edu; Web: http//nxw.chem.psu.edu

Overall research goals: Our work is aimed toward exploiting developments in two and three dimensional imaging mass spectrometry. This unique technique allows the chemistry of small molecules in the near surface region of a solid to be mapped with a lateral resolution of a few hundred nanometers, and a depth resolution of about 10 nm. The basic idea is to utilize an energetic cluster ion beam, consisting of C_{60} molecules, that is focused to a well-defined point on the target. During the energy deposition process, both neutral and ionized molecules are desorbed from the surface. This research is aimed toward finding novel ways to ionize the neutral molecules using a suitable light source to enhance the sensitivity to allow improved imaging and to produce as little photo-induced fragmentation as possible. The photoionized molecular ions are detected by time-of-flight mass spectrometry and an image is created by scanning the ion beam over an appropriate area. This instrumentation will be utilized in a number of fundamental studies aimed at determining the chemical composition of aerosol particles associated with the environment, and will emphasize the study of biological particles at the single cell level to provide insight into the mechanism of how algae produce organic molecules that could be used as biofuels.

Significant achievements in 2008-2010: Molecular photoionization is potentially an intriguing method to increase the number of molecular ions available for detection. Although our group has been pursuing different strategies using various types of lasers, the results have not been very successful since laser irradiation most often produces extensive fragmentation and the desired molecular specificity is lost. During the last two years, however, we have focused our efforts on the use of mid-IR wavelengths generated from high field fs pulsed lasers with peak powers of greater than 10^{12} watts/cm^2. This work was inspired by earlier work (1) which showed somewhat counter intuitively that longer wavelengths might be better suited for this type of experiments. From a theoretical perspective, this regime increases the probability of tunnel ionization and reduces the probability of multiphoton ionization, presumably since the slower rate of field oscillation allows more time for the electron to escape. Our results, as noted below, quite spectacularly support this notion (2). For guanine, for example, no molecular ion is observed using 800 nm radiation, but at 1.6 um wavelength, the molecular ion dominates the spectrum. At the present time, all of our data points to the fact that even better results can be achieved at higher laser fields. Our laser system is rather dated, and the newer ones have the capability of producing at least a factor of 20 more peak power in the mid-IR region. We have begun some experiments with Professor Nick Lockyer at the University of Manchester at their Photon Sciences Institute where such new lasers are in place. So far, their equipment has not been operation above 800 nm, but we are hopeful that experiments in the mid-IR can proceed during the next year.

Our experiments have proceeded along two tracks. First, we are looking for the best experimental conditions for maximizing the molecular ion yield of sputtered molecules and for minimizing photofragmentation. Secondly, we are exploring applications of detecting the neutral species desorbed from surfaces for molecular depth profiling experiments (3) and for 2

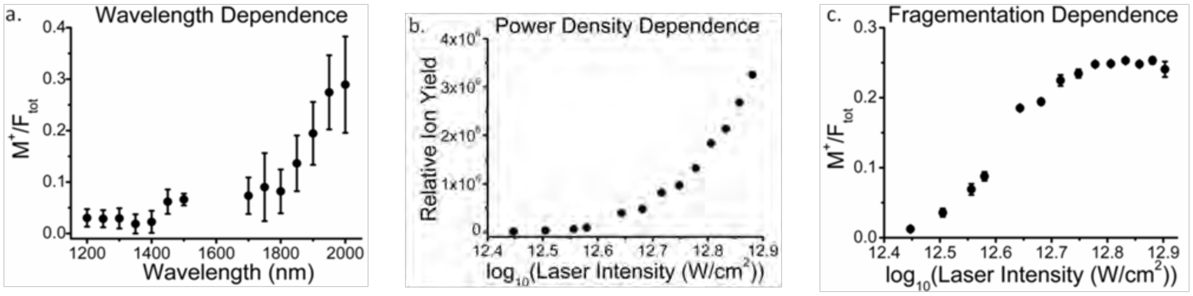


Figure 1. Wavelength and power dependence of photoionization spectra for thermally evaporated histamine molecules. The wavelength dependence of the M^+/F_{tot} ratio is shown in (a) using 4 x 10^{12} W/cm^2 of laser power density at each wavelength. The power dependence of the M^+/F_{tot} ratio is shown in (b) using a fixed wavelength of 1450 nm. The change in molecular ion signal with laser power density at m/z 111.13 is shown in (c).

and 3 dimensional imaging of biological cells. An example of the first track is shown in Figure 1, where the ratio of molecular ions to fragments is shown as the wavelength is increased. Along the second track, we have utilized this laser scheme to monitor the concentration of neutral molecules during depth profiling experiments using a 150 nm thin film of guanine as a model. These studies are important for setting up protocols for determining the depth scale during erosion by the C_{60} ion beam. In connection with these experiments, we will present preliminary 2-dimensional images of a variety of molecules desorbed from tissue sections.

Science objectives for 2010-2012:

- Photoionization experiments will be continued at Penn State and at Manchester to determine how much laser power and what wavelength yields the best results.
- Efforts will be continued to upgrade the fs system currently in operation at Penn State.
- 3-dimensional imaging protocols will be established for a variety of cell lines including energy producing algae specimen. In addition, we will be looking to determine the internal structure of aerosol particles in collaboration with faculty at Penn State.

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Fundamental Studies of the Inductively Coupled Plasma and Glow Discharge

Gary M. Hieftje, Principal Investigator
George Chan, Assistant Scientist; Jacob T. Shelley, Graduate Student
Department of Chemistry, Indiana University, 800 E. Kirkwood Ave., Bloomington, IN 47405
Email: hieftje@indiana.edu; Web: http://www.indiana.edu/~gmhlab/

Overall research goals: Develop novel plasma sources and improve the performance of plasma-based analytical spectrochemistry by understanding the plasma fundamental mechanisms and through characterizing the behavior of key plasma species.

Significant achievements in 2008-2010: *Developed a robust algorithm to determine matrix-effect-free crossover points for overcoming interferences in Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES):* The presence of matrix interferences, without the awareness and subsequent correction by an analyst, will lead to an analytical error. In the last reporting period, we described a novel and universal method to flag the presence of interferences in ICP–AES, in a real-time fashion during an analysis. The method is based on the fact that plasma behavior and excitation conditions, and hence the magnitude and even direction of matrix interferences, are heterogeneous along the ICP vertical axis. The method now automatically identifies a spatial location in the plasma at which such interferences are eliminated (i.e., the so-called matrix-effect crossover point). Analyte concentrations reported by the algorithm are accurate within 7% even at concentrations approaching the detection limit. The dependence of crossover-point locations on plasma operating conditions, excitation potentials of emission lines, and matrix properties were clarified. The most significant findings are: (1) The first ionization potential is the prime parameter that defines the magnitude of emission enhancement low in the plasma. (2) The second ionization potential of the matrix dictates the signal suppression high in the plasma. (3) This matrix-induced depression is operative at all vertical heights in the plasma. (4) The crossover point correlates with excitation behavior of "soft" and "hard" emission lines; as a result, peak emission maxima of soft and hard lines can be used as a tuning parameter for plasma conditions that result in a readily measurable crossover point, if a plasma-related matrix interference is present.

Developed and characterized the flowing atmospheric-pressure afterglow as a novel source for ambient mass spectrometry): Recently a number of atmospheric-pressure ionization sources have emerged in the field of mass spectrometry, creating a field collectively termed ambient mass spectrometry (AMS). These AMS sources offer several advantages, including little or no sample pre-treatment, direct analysis of solid and liquid samples, and simple mass spectra. One such source, our flowing atmospheric-pressure afterglow (FAPA), utilizes a helium glow discharge, operated at atmospheric pressure, in the flowing afterglow mode for the generation of excited species, ions, and electrons. Analyte molecules are directly desorbed, through predominantly thermal mechanisms, when the afterglow impinges on a solid or liquid sample. Further, the afterglow species interact with ambient air to generate reagent ions, such as solvated protons $[(H_2O)_nH^+]$, O_2^+, and NO^+, which subsequently ionize gas-phase, polar and non-polar analytes. Charge transfer and proton transfer have been identified as the major ionization pathways of the FAPA source; resulting mass spectra are very simple, consisting of mainly the molecular ion (M^+) or protonated molecular ion (MH^+). The FAPA yielded detection limits in the single to tens of femtomole range for many organic compounds. Our FAPA source was further characterized and compared with other plasma-based AMS sources — direct analysis in real time (DART) and the low-temperature plasma (LTP) probe. Despite their apparent similarity, the discharges utilized by DART and FAPA were found to be fundamentally different; the DART discharge operates closer to a corona mode (in the corona-to-glow transition regime) whereas the FAPA operates closer to a true glow discharge (in the glow-to-arc transition regime). In addition, reagent-ion production, response to a model gas-phase analyte (ferrocene), infrared thermography of the discharge effluent, and spatial emission characteristics were compared between the DART and FAPA discharges. Ion-suppression matrix effects were found to be a crucial factor for quantitative analysis with all three studied AMS sources (FAPA, DART and LTP). All three exhibited analyte ion suppression when a matrix of higher proton affinity than the analyte was present. Interestingly, FAPA was the least susceptible to the competitive ion suppression process. The FAPA source can be used also to perform molecular, mass spectral imaging when coupled to laser ablation; spatial resolution of 20 μm and a detection limit of 5 fmol for caffeine have been achieved. We also demonstrated that problems from matrix effects and analyte identification with the FAPA can be overcome through fast transient sample introduction (such as from a gas chromatograph) and modulated first-stage collision-induced dissociation in the first vacuum stage of a TOFMS.

Diagnostics of a solution-cathode glow discharge (SCGD): We previously reported the development, analytical figures of merits and plasma fundamental characteristics of SCGD. The SCGD is an atmospheric pressure glow discharge that is sustained in the open atmosphere between an anode pin and a sample solution, which acts as the discharge cathode. The plasma lies directly atop the liquid surface of the analyte solution; analyte is then desolvated, atomized, and excited, and the constituent atoms observed by atomic emission spectrometry. Development and diagnostics of the SCGD continue. With the aid of high-speed imaging, we found that introduction of the analyte solution into the plasma occurs by a unique sputtering mechanism, which promises high efficiency and rapid response. Experimental conditions for stable discharges with different electrolytes were obtained, and spectroscopic properties and analytical figures of merits were determined.

Science objectives for 2010-2012:

- Continue characterizing excitation and ionization processes and interference effects in the ICP. Thomson scattering will be used to evaluate the change in electron number density for matrices with low second ionization potentials. The hypothesis that Penning ionization causes matrix effects will be studied by various techniques (e.g., radial mapping of the excited-argon population and analyte excited states).
- Devise indicators and correction methodologies for interferences in ICPs in axial viewing mode.
- Continue characterization of the FAPA source. Areas of interest include understanding desorption processes, characterizing desorption and ionization matrix effects, developing methodologies to overcome ion suppression, and improving analyte detection and identification.

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Electrohydrodynamic Tip Streaming

Osman A. Basaran, Principal Investigator
School of Chemical Engineering, Purdue University, W. Lafayette, IN 47907
Email: obasaran@purdue.edu
Web: https://engineering.purdue.edu/ChE/People/ptProfile?id=4239

Collaborators: Prof. Michael T. Harris, Purdue University

Overall research goals: When subjected to strong electric fields, liquid drops and films form conical tips and emit thin jets from their tips. Such electrohydrodynamic (EHD) tip streaming or cone-jetting phenomena, which are sometimes referred to as electrospraying, occur widely in nature and technology. Well known examples of cone-jetting include ejection of streams of small charged drops from pointed tips of raindrops in thunderclouds and the popular technique of electrospray mass spectrometry. More recently, EHD cone-jetting has emerged as a powerful technique for direct printing of solar cells. Currently, electrosprays either find use or are being considered for utilization in a growing number of areas including electric field-driven extraction, micro- and nano-particle production, and encapsulation for controlled release. Motivated by applications in separations (electric field-driven extraction), analysis (electrospray mass spectrometry), and energy (drop-wise printing of solar cells), the main goal of this research program is to develop a fundamental understanding of the temporal development of EHD tip streaming phenomena.

Significant achievements in 2008-2010: The reason why a fundamental understanding of EHD tip streaming had heretofore been elusive is the existence of the large disparity in length scales between the macroscopic drops/films and the microscopic or nanoscopic jets that emanate from the conical tip structures [1]. In this research, computation and experiment are being used in concert to investigate EHD tip streaming from liquid drops and films of finite conductivity.

By using a combination of high accuracy simulation and high speed visualization (Fig. 1), a comprehensive physical picture is being developed of the mechanisms of cone formation, jet emission and break-up that occur during EHD tip streaming. Key to achieving this understanding is based in part on accounting for the finite conductivity of the liquid. In this work, the full Taylor-Melcher leaky-dielectric model, which accounts for charge relaxation, is solved along with the other equations governing the dynamics [2]. Indeed, simulations show that EHD tip streaming does not occur if the liquid is perfectly conducting or perfectly insulating, as had been assumed in all previous studies.

The new simulation results are also allowing answering one of the oldest and most celebrated questions in science, viz. the size and charge of the small drops that are produced in EHD tip streaming. Currently, conflicting theoretical expressions exist in the literature (cf. [2]) for predicting the sizes of the micro-(nano-)scale drops produced from the breakup of the thin jets [3]. The new results show that there exist multiple scaling regimes for drop size. Moreover, the simulations also show that the amount of charge that these droplets carry is 43% of that at the Rayleigh limit, which is the maximum amount of charge that a drop can carry before it becomes Coulombically unstable and explodes [4].

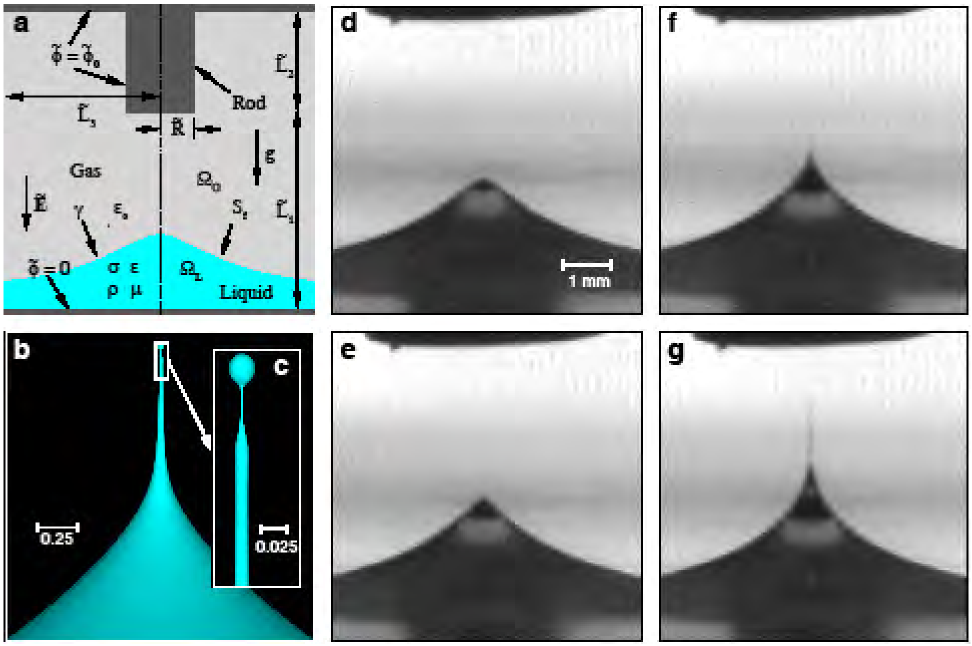

Figure 1. EHD tip streaming from a planar film. (a) Definition sketch. (b) Computational prediction of tip streaming from a film of a Taylor-Melcher leaky-dielectric. The inset (c) shows a magnified view of the jet's tip and the about-to-form drop. (d-g) Experimental images depicting tip streaming from a film of canola oil.

Science objectives for 2010-2012:

- Computations will be continued to probe whether EHD tip streaming from films, free drops, and pendant drops are dynamically similar. In other words, is EHD tip streaming a universal phenomenon independent of the type of experiment or simulation?

- New computations will be carried out to investigate differences in the dynamical response of a free drop bearing zero net charge that is subjected to an electric field and that of a free drop bearing a finite amount of net charge at or above the Rayleigh limit.

- Uncharged drops subjected to an external electric field and charged drops in the absence of an externally applied electric field comprise two important limits in the study of EHD tip streaming. We will next investigate the fate of charged drops that are subjected to an external electric field.

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Sampling, Ionization, and Energy Transfer Phenomena in Mass Spectrometry

Gary J. Van Berkel, Principal Investigator
Douglas E. Goeringer and Vilmos Kertesz, Co-Principal Investigators
James A. Bradshaw, Sofie P. Pasilis, Postdoctoral Research Associates
One Bethel Valley Road, P.O. Box 2008, Oak Ridge National Laboratory, Oak Ridge, TN 37831
Email: vanberkelgj@ornl.gov; Web: www.ornl.gov/sci/csd/Research_areas/obms_group.html

Collaborators: Dr. Kent A. Meyer, Oak Ridge National Laboratory, Oak Ridge, TN
Dr. Kin C. Ng, California State University, Fresno, CA
Dr. Stephen Jesse, Oak Ridge National Laboratory, Oak Ridge, TN
Olga S. Ovchinnikova, University of Tennessee, Knoxville, TN

Overall research goals: With emphasis on atmospheric pressure (AP) ionization sources, fundamental processes in mass spectrometry (MS), and electrochemistry (EC), and now with an additional focus on ambient surface sampling/ionization and chemical imaging, our studies seek to understand, advance, and create means to transfer chemical species at atmospheric pressure (AP) from complex matrices in the condensed-phase (solid or liquid) to the gas-phase without loss of information, particularly in the context of electrochemistry/mass spectrometry (EC/MS), nanoscale surface sampling/ionization, and mass spectrometry imaging (MSI).

Significant achievements in 2008-2010: Using an emitter geometry that maximizes mass transport to the electrode, we demonstrated that analyte electrolysis could be switched on/off simply by using pulsed high voltage with variable duration and frequency. Thus, the advance produces maximum analyte ionization/sensitivity on the time-scale of chromatographic elution into a (nano)electrospray ionization (ESI) source. Another achievement was to develop a solution for analyte electrolysis prevention that could be applied under any flow rate and electrode geometry conditions. Using a poly(pyrrole) (PPy) modified electrode emitter in an ESI source in place of the typical metal emitter electrode, we showed that the PPy film acted as a surface-tethered redox buffer resulting in suppressed oxidation of model analytes. Online reduction of the PPy polymer layer using negative ion mode ESI was shown to successfully restore the redox buffering capacity of the polymer film.

In desorption electrospray ionization (DESI)-MS studies, we found that the size of the plume-surface impact region, nebulizing gas jet velocity, sample spot size, sample-surface characteristics, analyte-surface interaction, and surface scan direction and speed were critical parameters for maximizing analyte signal levels and signal reproducibility on a planar surface. For analyses of sample spots on planar surfaces, DESI-MS signal intensities as much as five times greater could be routinely observed when the bottom of the sampling capillary into the mass spectrometer was appropriately positioned beneath the surface plane compared to when the capillary just touched the surface. We also attained spatial imaging resolution approaching 40 µm, a five-fold improvement over the best resolution reported previously, using careful control of operational parameters (particularly spray tip-to-surface distance, solvent flow rate, and spacing of lane scans).

The use of tip-enhanced electrical fields, resulting from laser illumination of a sharp probe tip, were investigated as a means of producing nanoscale desorption/ionization; the process could obviate the inherent spatial resolution limits imposed by diffraction in conventional laser desorption/ionization (LDI)-MSI. A scanning surface probe was developed and used to demonstrate that tip-enhanced laser ablation could produce nanoscale surface features (~50 nm FWHM craters). The setup was adapted to produce a unique instrument for combined atomic force microscopy (AFM) topographic mapping and MSI of surface regions at AP. The AFM operating mode was used to produce topographic surface images having nanometer-scale spatial and height resolution. Spatially resolved mass spectra, produced from the same surface via microprobe-mode AP-LDI, then were used to create a 100 x 100 µm chemical image. The effective spatial resolution of the image (~2 µm) was constrained by the limit of detection (~ 10^9-10^{10} molecules), rather than by the laser spot size.

Science objectives for 2010-2012:

- To improve the sensitivity in DESI-MS, secondary ionization sources will be investigated to ionize the droplets desorbed from the surface, and thus, to maximize the detectable signal from a given surface area/concentration of material. The utility of heating the solvent and nebulizing gas to increase the speed of extraction and maximize solubility of the analyte also will be examined.
- To improve the lateral resolution for nanoscale MSI effected via tip-enhanced LDI, which is currently sample volume limited, research will focus on improving the overall limit of detection via enhancements in ion generation, ion collection efficiency, and mass spectrometer design.
- To mitigate the current compromise in online EC/ESI-MS between an optimum solution/electrolyte composition for EC and that needed for ESI-MS, we will investigate a liquid microjunction-surface sampling probe interface to sample the products generated on the working electrode in a bulk EC cell.
- To advance our current millimeter-to-micrometer scale thermal desorption surface sampling/ionization capabilities, a new approach for MSI will be investigated. Termed AP hybrid proximal probe topography chemical imaging, a heated AFM probe will be used to thermally desorb surface materials that are then drawn into an AP ionization source; the molecular ions created are subsequently detected or further interrogated using MS.

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Microfabricated Ion Trap Mass Analyzers using Two Opposing Plates

Daniel E. Austin, Principal Investigator
Zhiping Zhang, Postdoctoral Research Associate
Brigham Young University, Department of Chemistry & Biochemistry, C-310 BNSN, Provo, UT 84602
Email: austin@chem.byu.edu; Web: people.chem.byu.edu/austin

Collaborators: Dr. Milton L. Lee (Chemistry), Brigham Young University
Dr. Aaron Hawkins (Electrical Engineering), Brigham Young University

Overall research goals: My research focuses on novel devices for analytical chemistry and physics using a two-plate "sandwich" assembly of lithographically-patterned substrates. We are pursuing, among other devices, a miniaturized mass analyzer that can form the basis for portable, high-performance mass spectrometry.

Significant achievements in 2008-2010: With funding from NASA (ending spring 2010) we have developed a series of radiofrequency ion trap mass analyzers made using two-plate assemblies. With them we have demonstrated mass resolution of 1300 (m/Δm), among the highest resolution of any miniaturized mass analyzer to date. Tested designs include a quadrupole ion trap (the "Planar Paul trap"), a toroidal ion trap (the "Halo ion trap"), and a combination of the two, the "Coaxial ion trap", which includes superimposed quadrupolar and toroidal trapping regions. We are also now testing a high-aspect-ratio linear ion trap. Using our novel two-plate approach we are able to compensate for individual higher-order multipoles, carry out precise plate alignment, and create all device features and dimensions with sub-micron precision. Figure 1 shows a photograph and design of the Planar Paul trap, as well as representative mass spectra. Figure 2 shows a diagram of the Coaxial ion trap. These devices are being developed for in situ characterization of planetary atmospheres, but are amenable to other areas requiring portable mass spectrometers, such as environmental monitoring, manufacturing process control, emergency response, national security, law enforcement, and field sciences. Miniaturized mass analyzers have been developed by many groups for many years, but all suffer from lower mass resolution due to imperfections in the analyzing electric fields. The two-plate approach solves this problem by utilizing the high precision in 2 dimensions of microfabrication techniques and eliminating dependence on out-of-plane fabrication. These devices are less expensive to batch-fabricate than machined ion-optics devices.

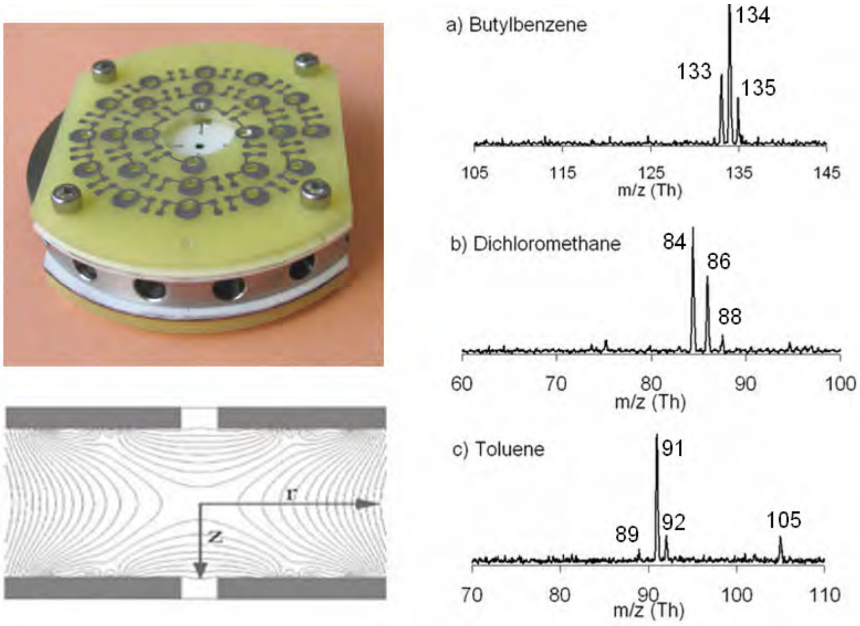


Figure 1. Photo, isopotential contour plot, and mass spectra from the Planar Paul ion trap.

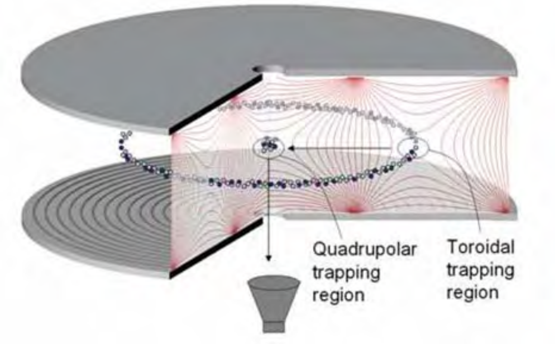


Figure 2. Schematic of the Coaxial Ion Trap showing a superimposed toroidal and quadrupolar trapping region.

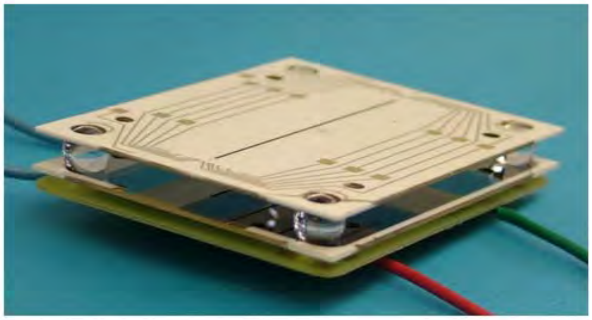


Figure 3. Photograph of prototype linear ion trap mass analyzer.

Science objectives for 2010-2012:

- Depending on future funding, we are developing a high-aspect-ratio linear ion trap, and expect also to develop a parallel array of linear ion traps. High mass resolution in such a device depends on sub-micron alignment of the two plates long the whole length of the mass analyzer. This alignment can be achieved using piezoelectric actuators: with one plate held fixed, alignment involves only 6 degrees of freedom. Aligned plates can be held exactly in place using epoxy.
- We plan to continue studying the capabilities of the coaxial ion trap, including mass-selective transfer between trapping regions, tandem capabilities between trapping regions (possibly a neutral-loss scan), and quantifying the enhanced sensitivity resulting from the larger storage volume of the toroidal region.
- We anticipate work on several new devices that rely on this two-plate approach, including a miniaturized Fourier-transform mass spectrometer and a particle accelerator.

References to work supported by this project 2008-2010:

1. D. E. Austin, B. J. Hansen, Y. Peng, Z. P. Zhang, “Multipole Expansion in Quadrupolar Devices Comprised of Planar Electrode Arrays,” Int. J. Mass Spectrom., submitted (Feb 2010).
2. Z. Zhang, Y. Peng, B. J. Hansen, I. W. Miller, M. Wang, M. L. Lee, A. R. Hawkins, D. E. Austin, “Paul Trap Mass Analyzer Consisting of Opposing Microfabricated Electrode Plates,” Analytical Chemistry, **81,** 5241-5248, (2009).
3. D. E. Austin, Y. Peng, B. J. Hansen, I. W. Miller, A. L. Rockwood, A. R. Hawkins, S. E. Tolley, “Novel Ion Traps Using Planar Resistive Electrodes: Implications for Miniaturized Mass Analyzers,” J. Am. Soc. Mass Spectrom. **19,** 1435-1441, (2008)
4. D. E. Austin, M. Wang, S. E. Tolley, J. D. Maas, A. R. Hawkins, A. L. Rockwood, H. D. Tolley, E. D. Lee, M. L. Lee, “Halo Ion Trap Mass Spectrometer,” Analytical Chemistry **79**, 2927-2932, (2007).
5. D. E. Austin, S. A. Lammert, “Ion Traps with Circular Geometry”, in *Practical Aspects of Trapped Ion Mass Spectrometry*, vol. 4, March, R. and Todd, J. F. J. Eds., CRC Press, in press (Dec 2009).
6. D. E. Austin, S. A. Lammert, “Mass Analyzer Miniaturization,” in *Encyclopedia of Mass Spectrometry*, vol. 7, Watson, T., Sparkman, O. D. Eds., submitted (January 2010).

Surface Chemistry Issues in the Development of Flotation Technology for the Processing of Low Grade Bauxite Resources

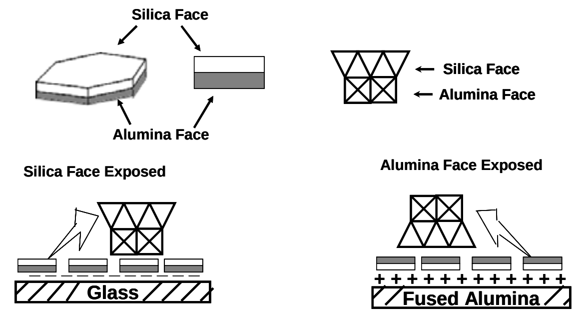
Jan D. Miller, Principal Investigator
Xuming Wang, Research Assistant Professor
Shoeleh Assemi, Postdoctoral Research Associate
Department of Metallurgical Engineering, College of Mines and Earth Sciences, University of Utah,
135 S. 1460 E., Rm. 412, Salt Lake City, UT 84112-0114
Email: Jan.Miller@utah.edu; Web: www.metallurgy.utah.edu

Collaborators: Dr. Hao Du, National Engineering Laboratory, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China
Dr. Anh Nguyen, School of Chemical Engineering, The University of Queensland, Brisbane, QLD, 4072, Australia
Dr. Liem Dang, Chemical Material Sciences Division, Pacific Northwest National Laboratory, Mail Stop K1-83, 902 Battelle Blvd., Richland, WA 99352

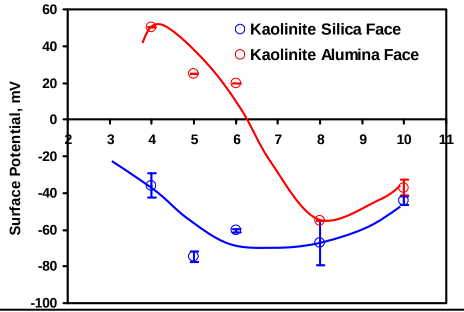
Overall research goals: The primary goal of this research program is to provide a basis for improved flotation separation efficiency in nonsulfide mineral systems by establishing the fundamental features of collector (surfactant) adsorption reactions associated with the hydrophobic surface state and developing appropriate surface chemistry control strategies. Advanced experimental techniques together with more traditional experimental methods are being used to provide crucial information concerning the interfacial surface state and collector adsorption phenomena in various nonsulfide mineral systems. Of current interest is flotation technology for low grade bauxite resources.

Significant achievements in 2008-2010: Advanced surface chemistry research to support the development of flotation technology for low grade bauxite resources has included; atomic force microscopy (AFM) surface force studies, vibrational spectroscopy analysis (FTIR and SFVS), and molecular dynamics simulations (MDS) to describe the hydration and adsorption characteristics of bauxite minerals including quartz, kaolinite, and alumina minerals.

In one part of the research program, dealing with kaolinite, a procedure has been developed to order 500nm kaolinite particles, measure surface forces, and determine the surface potentials of the silica tetrahedral face and the alumina octahedral face as a function of pH. Atomic force microscopy has been used to investigate the two faces of kaolinite. The interaction forces between a silicon nitride tip and the kaolinite faces have been measured at varying solution chemistry conditions (ionic strength and pH). AFM surface force measurements for kaolinite particles reveal for the first time the iso-electric point of the silica tetrahedral face to be at pH < 4 and that of the alumina octahedral face between pH 6 and 8.



The kaolinite particles (500nm) were prepared on glass and alumina substrates in order to selectively expose the two basal plane surfaces (silica tetrahedral face and alumina octahedral face).

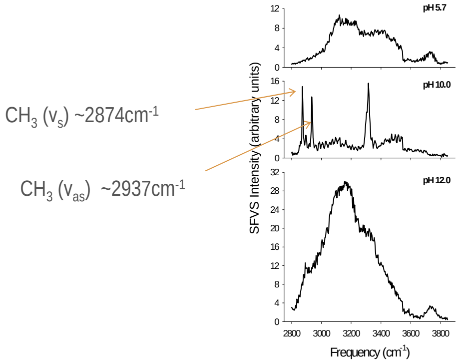


PZC of kaolinite silica face < pH 4

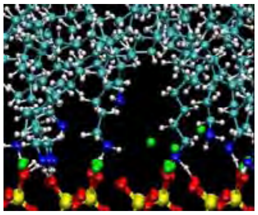
PZC of kaolinite alumina face pH 6 - 8

In the case of collector adsorption, another part of the research program, in-situ vibrational spectroscopy research has revealed new information on dodecyl amine adsorption by quartz and the critical importance of pH for dehydration and creation of a hydrophobic surface state. States of adsorbed dodecylamine (DDA) at a silica surface have been studied as a function of pH by vibrational spectroscopy (SFVS, FTIR), contact angle measurements and MD simulations. The results show that the state of adsorbed DDA at a silica surface varies significantly at different pH values. At pH 6.30, there is no pronounced adsorption of DDA cations and the surface is hydrophilic. At pH 10.0 the vibrational spectroscopy results together with contact angle measurements and MD simulations suggest that amine is adsorbed as a well organized monolayer, the hemimicelle structure. Under these conditions, dehydration occurs based on SFVS analysis and the silica surface becomes hydrophobic. In the case of pH 12.3 it has been confirmed that continued adsorption of DDA neutral molecules occurs with the amine surface state changing from a monolayer to a bilayer, or a micellar surface state. At this high pH extensive surface hydration is evident from SFVS results and the silica surface becomes hydrophilic.

SFVS spectra of $4x10^{-5}$ M DDA solution at silica surface



MD simulation of 40 DDA molecules near a quartz surface at pH 10



Red: Oxygen
Yellow: Silicon
Blue: Nitrogen
Green: Sodium

Of particular significance is the first evidence that interfacial water removal is required to create the hydrophobic surface state necessary for flotation.

Science Objectives for 2010-2011

- Research will continue in the area of kaolinite surface/colloid chemistry in order to model the electrokinetic behavior of kaolinite, to describe particle-particle interactions, and to explain the rheology of suspensions.
- Research will continue on the use of MDS and SFVS to describe the interfacial chemistry of nonsulfide mineral flotation systems.
- Fabrication of a rotational IRE has been completed and the influence of shear on interfacial chemistry will be examined as revealed from FTIR/IRS experiments.

References to work supported by this project (2008-2010): Selected recent publications include,

1. X. Wang, J. Liu, H. Du, and J.D. Miller, “States of Adsorbed Dodecyl Amine and Water at a Silica Surface as Revealed by Vibrational Spectroscopy,” Langmuir, **in press** (2010).
2. V. Gupta and J.D. Miller, “Surface Force Measurements at the Basal Planes of Ordered Kaolinite Particles,” J. Coll. Inter. Sci. **in press** (2010).

In addition to 16 journal/proceedings publications, 17 presentations were made between 2008 and 2010.

Chemical Analysis of Nanodomains

Emily A. Smith, Principal Investigator
Ning Fang, Co-Principal Investigator
Edward S. Yeung, Co-Principal Investigator
Jacob Petrich, Co-Principal Investigator
142 Spedding Hall, Ames Laboratory, Ames, IA 50011
Email: esmith1@iastate.edu; Web: www.external.ameslab.gov/pbchem/MP research

Overall research goals: Instrumentation and methodology for the analysis of phenomena that occur at nanometer length scales and picosecond time scales at ambient laboratory conditions are being developed. The instrumentation and methodology will be applied to diverse separation and catalysis systems of interest to the DOE mission.

Significant achievements in 2008-2010:

Subtask #1: High Axial Resolution Total Internal Reflection (TIR) Raman Measurements. A scanning angle TIR Raman instrument has been developed with 34 nm axial resolution perpendicular to the focal plane. This is a roughly 30-fold improvement relative to confocal Raman microscopy. The developed instrument has an incident angle range of 25.50° to 75.50°, with a 0.05° angle resolution. Raman scatter can be collected from a ZnSe/organic interface over a range of roughly 35 to 180 nm for high axial resolution depth profiling measurements. Models have been developed to correlate the distance over which Raman scatter is collected and spectral peak intensities for homogeneous films.

Subtask #2: Sub-diffraction Microscopy. (1) Plasmonic metal nanoparticles have been used for selective imaging with dual-wavelength differential interference contrast (DIC) microscopy for the unambiguous identification of nanoprobes in complex environments for real-time high-precision 3D tracking. **(2)** The geometry confined plasmon resonance modes of gold nanorods result in anisotropic absorption and scattering of polarized light. We have shown using DIC microscopy that the orientation of gold nanorods in 2D and 3D can be resolved with 2-3° angular resolution on glass surfaces. **(3)** An automatic calibration scanning-angle prism-type total internal reflection fluorescence microscope (TIRFM) has been constructed and tested for 10 nm axial resolution. **(4)** The advanced ultrasensitive imaging tools listed in 1- 3 are being incorporated into microfluidic devices to generate high-fidelity optical images. **(5)** A continuous wave (CW) stimulated emission depletion (STED) fluorescence microscope has been developed. The instrument has a 532 nm excitation diode laser and a 671 nm STED diode laser. A spatial light modulator imparts a donut profile on the STED laser, which stimulates emission at the periphery of the diffraction limited excitation laser to generate a sub-diffraction excitation volume.

Subtask #3: Single Molecule Fluorescence. The interactions between protein and DNA molecules and nanoporous polycarbonate membranes were investigated at the single molecule level. Entrapment of these biomolecules was shown to be size and shape selective, and was dependent on the membrane pore diameter. A pore size that is only slightly larger than the maximum dimension of the molecule was inadequate for intrusion into the pores. For a given molecule, the number found at a given depth decreased as the pore size decreased. In addition, as the depth increased, for a given size pore, the number of molecules decreased rapidly. The depth-dependent histograms fit a one-dimensional diffusion model. However, a highly restricted motion was observed even when the pore diameter was 10 times the size of the molecule, resulting in anomalously small diffusion coefficients. These results give unique insights into the detailed mechanism of size-exclusion chromatography and membrane filtration. In another study, we demonstrated the first detection of a single biomolecule based on its chemiluminescence. This extends the study of single-molecule reactions to non-fluorescent systems.

Science objectives for 2010-2012:

- The methodology and models for depth profiling of thin polymer laminates and biofilms using scanning angle TIR Raman measurements will be developed.

- Novel imaging tools based on gold nanorod probes and DIC microscopy will be developed to decipher rotational motion in chemical and biological systems.
- 3D super-resolution fluorescence microscopy will be developed based on the new TIRFM.
- Microfluidic platforms will be developed for non-invasive high-fidelity *in situ* imaging.
- Nanosecond temporal resolution will be added to the CW STED microscope using phase imparting optics, and the instrument will be used to measure 2D domain formation in polymer supported lipid bilayers using fluorescence correlation STED microscopy.

References to work supported by this project 2009-2010:

1. W. Sun; G. Wang; N. Fang; E.S. Yeung. Wavelength-Dependent Differential Interference Contrast Microscopy: Selectively Imaging Nanoparticle Probes in Live Cells. Analytical Chemistry, 81(22), 9203-9208 (2009) (Cover of the November 15, 2009 issue)
2. G. Wang; A.S. Stender; W. Sun; and N. Fang. Optical Imaging of Non-Fluorescent Nanoparticle Probes in Live Cells. Analyst, 135(2), 215-221 (2010) (Cover of the February 2010 issue)
3. C. Liu; Y. Luo; J. Maxwell; N. Fang; D.D.Y. Chen. Reverse of Mixing Process with a Two-Dimensional Electro-Fluid-Dynamic Device. Analytical Chemistry, in press, DOI: 10.1021/ac902938g (2010)
4. W. Sun; K. Marchuk; G. Wang; N. Fang. Auto-Calibrated Scanning-Angle Prism-Type Total Internal Reflection Fluorescence Microscopy for Nanometer-Precision Axial Position Determination. Analytical Chemistry, in press, DOI: 10.1021/ac902789z (2010)
5. H. Chen, H. Gai and E. S. Yeung. Inhibition of Photobleaching and Blue Shift in Quantum Dots, Chem. Comm., 13, 1676 (2009).
6. L. Xiao, Y. He and E. S. Yeung, "High Throughput Single Molecule Spectral Imaging of Photoactivated Luminescent Silver Clusters on Silver Island Films", J. Phys. Chem. C, 113, 5991 (2009).
7. W. Xie, A. Xu and E. S. Yeung, “Determination of NAD(+) and NADH in a Single Cell under Hydrogen Peroxide Stress by Capillary Electrophoresis”, Anal. Chem., 81, 1280 (2009).
8. J. Li, W. Xie, N. Fang and E. S. Yeung. Single-Molecule Immunosorbent Assay as a Tool for Human Immunodeficiency Virus-1 Antigen Detection, Anal. Bioanal. Chem., 394, 489 (2009).
9. C. Liu, Y. J. Li, M. H. Wang, Y. He and E. S. Yeung. Rapid Fabrication of Large-area Nanoparticle Monolayer Films via Water-induced Interfacial Assembly. Nanotechnology, 20, 65604 (2009).
10. L. H. Xiao, R. Zhou, Y. He and E. S. Yeung. Direct Observation of Nanoparticle Self-Assembly Dynamics at the Water-Air Interface Using Differential Interference Contrast Microscopy. J. Phys. Chem. C. 113, 1209 (2009).
11. N. Li,, H. Tang, H. W. Gai and E. S. Yeung. Determination of Protein Surface Excess on a Liquid/Solid Interface by Single-molecule Counting. Anal. Bioanal. Chem., 394, 1879 (2009).
12. M. H. Wang, Y. J. Li, Z. X. Xie, C. Liu and E. S. Yeung. Fabrication of Large-scale One-dimensional Au Nanochain and Nanowire Networks by Interfacial Self-assembly. Mat. Chem. Phys., 119, 153 (2010).
13. H. W. Gai, X. Bu, H. Chen, R. H. Yang and E. S. Yeung. Scattering Imaging of Single Quantum Dots with Dark-field Microscopy. Anal. Chem., 81, 7507 (2009).
14. S. H. Kang, S. Lee and E. S. Yeung. Detection of Single Enzyme Molecules Inside Nanopores based on Chemiluminescence. Angewandte Chem. Int. Ed., in press (2010).
15. C. Ma and E. S. Yeung. Entrapment of Individual DNA Molecules and Nanoparticles in Porous Alumina Membranes. Anal. Chem., 82, 654 (2010).
16. C. Ma and E. S. Yeung. Single-Molecule Investigation of the Interactions between Protein Molecules and Nanoporous Membranes. Anal. Chem., 82, 478 (2010).
17. K.J. McKee and E.A. Smith. Development of a Scanning Angle Total Internal Reflection Raman Spectrometer for High Axial Resolution Depth Profiling Measurements. Rev. Sci. Inst., in press (2010).
18. Lupoi, J.S. and E.A. Smith. Effects of Cellular Immobilization on Enzyme Efficiency under Sub-Optimal Hydrolysis Conditions. Submitted.
19. M. Meyer and E.A. Smith. Surface Enhanced Raman Spectroscopy of Amino Acids and Peptides: Comparision of Dispersive 1064 and 785 nm Spectrometers. Submitted.

Meeting **2010 DOE-BES Separations and Ana;lysis Contractors' Meeting**
http://www.orau.gov/sepanalysis2010/default1.htm

Hyatt Regency Baltimore, MD
New London, NH
April 25th – 28th, 2010

Combinatorial and High Throughput Membrane Synthesis and Testing: Tailoring Membrane Surfaces to Applications

DOE Grant #: DE-FG02-09ER16005

Minghao Gu, Chip Kilduff and Georges Belfort
Howard P. Isermann Department of Chemical and Biological Engineering

Abstract

We have developed a combinatorial high throughput atmospheric plasma graft-induced polymerization (HT-APGP) method to *synthesize* and *screen* for surfaces with any desired characteristics. Specifically, we are interested in isolating vinyl monomers that resist protein adsorption and that can be grafted onto poly(ether sulfone) (PES) without initiating agents. Using a photo-induced polymerization variant of the high throughput method, we have confirmed previously discovered monomers (poly(ethylene glycol) (PEG) and zwitterionic (Zwit) and discovered new monomers (amine) that exhibit protein-resistance. We have also shown that molecular weight and small chemical variations within a class (i.e. PEG or Zwit) can substantially change the efficacy of such monomers. Grafting conditions, besides power and residence time, such as solvent conditions are also very important to the grafting efficiency.

Here, we graft vinyl PEG and Zwit monomers using the HT-APGP method with PES and search for optimal conditions for repelling bovine serum albumin (BSA) in aqueous solution. We also conduct ATR/FTIR spectroscopy to track the degree of grafting in lab scale (not HT). Filtration performance is assessed using a fouling index (relative to the as received non modified PES membrane), permeation flux and protein sieving. Comparison with earlier extensive photo graft-induced polymerization, shows that the HT-APGP method is very competitive.

Session 5 – Separations I

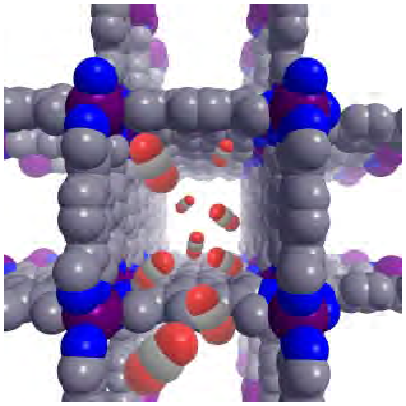
Carbon Capture

Berend Smit

Center for Gas Separations Relevant to Clean Energy Technologies
Department of Chemical Engineering
Department of Chemistry
UC Berkeley
http://www.cchem.berkeley.edu/CO2EFRC/

Many different scenarios have been written on achieving a substantial reduction in carbon emissions.[1] In all these scenarios Carbon Capture and Sequestration (CCS) plays a significant role, as the predicted use of fossil fuels will continue to grow. There are two factors that determine the success of large-scale employment of CCS: (1) the uncertainties associated with the sequestration in geological formations and (2) the costs associated with carbon capture.

In this EFRC we focus on the energy costs associated with the separation of CO_2 from gas mixtures. The current technology has a parasitic energy of 30-40%,[2] which implies a significant decrease in efficiency of power generation. Simple thermodynamic arguments show that the minimal parasitic energy to separate CO_2 from flue gasses is 3.5%. The chemical industry typically operates at 3-5 times the thermodynamic minimum, which suggests that the parasitic energy of carbon capture can be reduced by at least a factor of two.



From a scientific point of view, the separation of CO_2 is very challenging as the differences between the molecules are relatively small. Modern chemistry and nano-science allows us molecular control over the properties of materials. The vision of our EFRC is to develop the science to *create, understand*, and *predict* novel materials that are tailor-made with exactly the right molecular properties to separate gasses relevant for clean energy technologies. The long-term goal of this EFRC is to develop the science and materials that will contribute to the reduction of the parasitic energy costs of CCS.

In gas separations these challenges are significant. The differences between the relevant gas molecules are small and therefore we need use the type of molecular control that is offered by nano science to tailor make materials that have exactly the right adsorption and diffusion selectivity to enable an economic separation process.

We have identified the following four important gas separations:

- Separation of CO_2 from flue gasses

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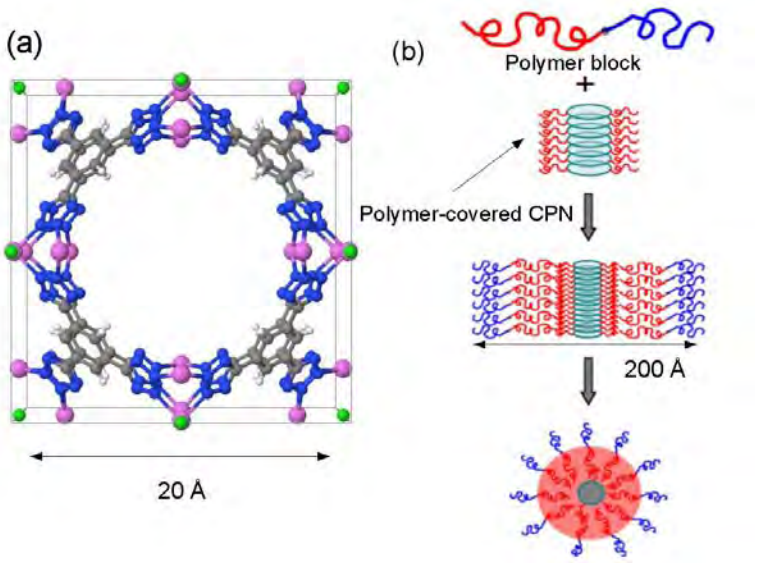
[1] Intergovernmental Panel on Climate Change Special Report on Carbon Dioxide Capture and Storage. (Cambridge University Press, UK. , 2005).

[2] Haszeldine, R. S. Carbon Capture and Storage: How Green Can Black Be? *Science* **325**, 1647-1652 (2009).

- Separation of CO_2 from methane



Candidate materials for efficient CO_2 capture that are currently being studied within this EFRC project. (a) Metal-organic frameworks (MOFs) are porous materials formed by the coordination of metal ions (magenta atoms) with organic linkers (N, H, C: blue, gray and brown atoms); (b) Assembly of polymer-covered cyclic peptide nanotubes and diblock copolymer forming cylindrical microdomanis (the CPNs assemble at the center of the cylinder).

- Separation of O_2 from air
- Separation CO_2 directly from air

Within this EFRC we focus on the first two as our case studies for gas separations
The center will combine personnel with expertise in the following areas of emphasis, with extensive overlap and interaction:

- *Materials Synthesis*: The synthesis of new gas-permeable materials with control over the molecular functionalities that have contact with gas molecules is deemed essential. Our focus here will be on: (i) generating metal-organic frameworks exhibiting high internal surface areas (up to 4,800 m2/g), and surfaces lined with robust and tailorable chemical groups, (ii) self-assembled polymer films with synthetic or biomimetic functional units.
- *Materials Characterization*: Detailed atomic-level structural characterization of the new materials will be necessary both before and after exposure to gas samples in order to probe hypotheses on interaction mechanisms. In addition, accurate means of assessing the selectivity, kinetics, and thermodynamics of gas adsorbate binding will be needed to demonstrate efficacy and test computational models.
- *Computational Separations*: A strong computational component to the research will be essential for understanding the chemical interactions at a molecular level, as well as for guiding the synthetic efforts toward materials exhibiting high specificity and tunable interaction energies.

Modeling CO_2 Capture and Separation in Zeolitic Imidazolate Frameworks

J.R. Schmidt, Principal Investigator
University of Wisconsin, Department of Chemistry, 1101 University Ave, Madison, WI 53706
Email: schmidt@chem.wisc.edu; Web: http://www.chem.wisc.edu/users/schmidt

Overall research goals: The research objectives of the present work are to understand the microscopic origins of the properties of zeolitic imidazolate frameworks (ZIFs), microporous metal-organic compounds consisting of Zn^{2+} cations and organic imidazolate linker groups. We are focusing primarily on those properties of relevance to CO_2 capture and separation, elucidating the microscopic interactions between CO_2 and the ZIF using quantitatively-accurate first-principles techniques, which further allow us to decompose this interaction into it constituent physical components (electrostatic, polarization, Pauli repulsion, dispersion, etc.) These calculations will serve as the basis for the creation of a physically motivated, and thus hopefully robust and transferable, force field for subsequent molecular simulations at finite temperature and pressure.

Significant achievements in 2009-2010: Our initial investigation of CO_2 adsorption on ZIFs have focused on utilizing symmetry adapted perturbation theory (SAPT) calculations to model the interaction of CO_2 with neutral imidazole or anionic imidazolate groups. We choose SAPT rather than standard DFT or *ab initio* calculations because it offers an accurate description of the dispersion (induced dipole-induced dipole) interactions and a natural decomposition of the interaction energy into its constituent components. Initial exploratory calculations involving CO2 and a single imidazolate ligand highlight the importance of dispersion in these systems. In addition, the profound differences in the interaction of CO_2 with neutral and anionic ligands highlight the importance of a realistic and accurate model system. We are currently searching for such a representative small model system that is representative of bulk ZIF. This search is complicated by the stoichiometry of the material, which makes it difficult to arrive at a finite, electrically neutral, chemically representative model. We are working to identify such a small-molecule analogue for use in our SAPT calculations, validating this model by periodic DFT calculations on bulk ZIF.

We are also working to develop the tools necessary for building physically-motivated force fields based off of these SAPT calculations. For example, simple calculations on Ar/water dimers allows us to better understand the functional form of the dipole-induced dipole interaction, and how to fit this contribution to a reasonable functional form for use in molecular simulations. Note that although the correct *asymptotic* form of this interaction is well-known and easily derivable from basic physical principles, we are interested in the form of the interaction at *finite* distances, where overlap between the electron density of the two species introduces complex corrections.

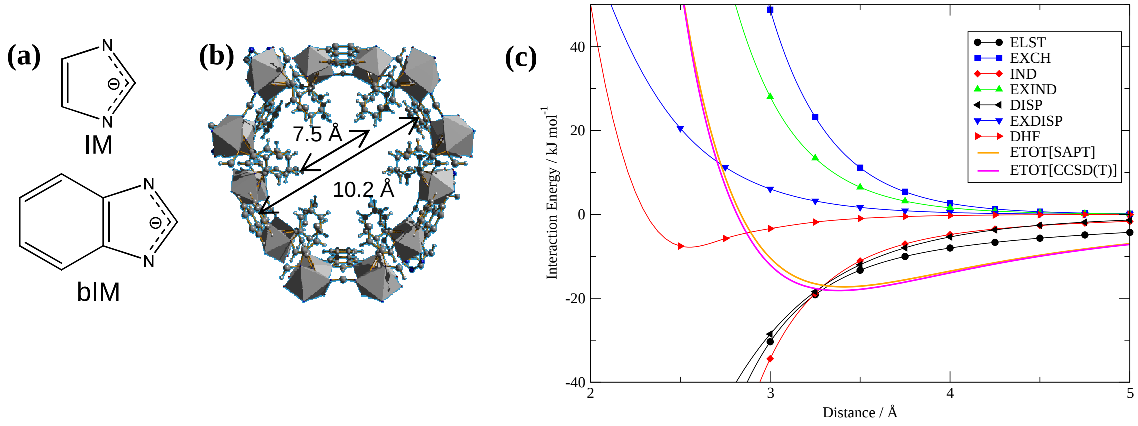


Figure 1. (a) Structures of imidazolate (IM) and benzyl imidazolate (bIM) ligands; (b) ZIF-68, with a large cavity and smaller aperture. Aperture sizes range from 0.7 – 13Å in various ZIFs; (c) Plot SAPT energy-decomposed interaction energy of CO2 with an isolated imidazolate ligand.

Science objectives for 2010-2012:

- Continue symmetry-adapted perturbation theory (SAPT) calculations on the interaction of CO_2 with smaller ZIF model systems; continue search for a validated finite model system which reproduces the relevant chemical and electronic properties of bulk ZIF.
- Construction of a physically-motivated force field based on the SAPT electronic structure calculations; also, incorporation of the perturbative effects of ZIF *functionalization* into this resultant force field in a natural way.
- The merging of the mixed quantum mechanics/molecular mechanics (QM/M) approach with SAPT calculations, to better account for the effects of the extended ZIF environment; this approach is wide-ranging applications outside of gas adsorption.

References to work supported by this project 2009-2010:

(No publications have yet appeared)

Ultrasonic Distillation, Thermal Diffusion, and Photoacoustics

Gerald J. Diebold, Principal Investigator
Department of Chemistry, Brown University, Providence, RI 02912
Email: Gerald_Diebold@Brown.edu
Web:http://www.chem.brown.edu/people/facultypage.php?id=1106970111

Collaborators: Han Jung Park, Hye Yun Jung, Binbin Wu

Overall research goals: This research is directed towards understand the fundamentals of the photoacoustic effect, thermal diffusion, also known as the Ludwig-Soret effect, and a new separation method known as ultrasonic distillation. Specific research goals include experimental investigation of separation of ethanol from water based on ultrasonic distillation, the solution to the problem of the motion of the components of a binary mixture through thermal diffusion, also known as the Ludwig-Soret effect, for the case of a linear temperature field, and the investigation of the generation of a new kind of photoacoustic wave that is predicted to be present at the boundaries of absorbing bodies arising from rapid heat conduction.

Significant achievements in 2008-2010: When high intensity ultrasound is directed upwards towards a liquid-air interface, the radiation pressure in the acoustic wave creates a displacement of the fluid and generates a mist. It has been reported that at 10 C is it possible to achieve a perfect separation of ethanol from water using ultrasonic distillation by removing the vapor with a flow of air. We have investigated this claim using both refractive index determination and nuclear magnetic resonance for quantitation of the composition of the remaining mixture. We have carried out experiments with mixtures of ethanol-water and ethyl acetate-ethanol, an aqueous $CoCl_2$ solution, and with colloidal gold and silica. The results of ultrasonic distillation were compared with sparging of the same mixtures.

When a mixture is placed in a thermal gradient a separation of the components of the mixture takes place with one component moving towards the cold region and the other toward the hot region. We have introduced a new experimental method for studying the time development of the motion of the components of a binary mixture by using a confocal microscope to view the fluorescence from labeled nanoparticles in water. The thermal gradient is produced by using a heated indium tin oxide layer deposited on a glass plate which is separated by spacers from a sapphire plate that is kept cool by a stream of flowing water.

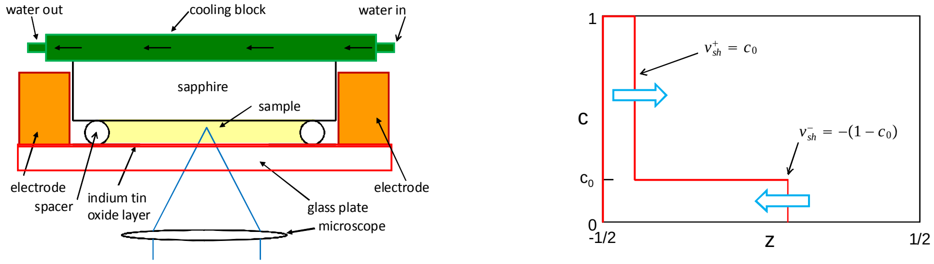


Figure 1. (Left) Schematic of the apparatus used for studying the Ludwig-Soret effect in a linear temperature field. The cell thickness is determined spherical particle spacers with diameters on the order of 100 μ. The confocal microscope is scanned transversely and along its axis to give the spatial profile of fluorescence arising from labelled nanoparticles. (Right) Theoretical motion of concentration profiles following imposition of a linear temperature gradient, neglecting ordinary mass diffusion. The velocities of the fronts v^{+-} are given in terms of the initial density fraction c_0.

We have investigated the generation of the photoacoustic effect when exothermic chemical reactions take place. In particular, we have studied the case of laser irradiation of colloidal carbon in mixtures of water and water-hydrogen peroxide. When carbon particles are heated to a sufficiently high temperature by a pulsed laser, the photoacoustic effect is greatly amplified by the generation bubbles arising from the endothermic carbon steam reaction $C + H_2O \rightarrow H_2 + CO$. It is thus the laser energy that is consumed to drive the reaction forwards. Despite the consumption of laser energy by chemical reaction, the formation of gas phase products from condensed matter causes a "giant" photoacoustic effect to be generated. In the case of H_2O_2 the reactions can be exothermic. We have recorded the photoacoustic amplitude as a function of H_2O_2 concentration in mixtures of H_2O_2 and H_2O, and as a function of laser fluence. Comparison with inert particles and dyes has been made. Other exothermic reactions have been investigated.

We have also investigated the characteristics of the photoacoustic effect in phononic structures, where the generation of sound is governed by an inhomogeneous Mathieu equation. We have studied both infinite structures and those with finite dimensions. Band gaps are found just as in photonic structures; however, in the case of the photoacoustic effect is possible to excite structures in the band gap since the problem is described by an inhomogeneous differential equation.

Science objectives for 2010-2012:

- Investigation of the influence of heat conduction on the time profiles of ultrasonic waves launched at the interfaces between highly absorbing and transparent media is underway. Different materials with varying thermal properties will be studied to determine the presence of large acoustic transients predicted by theory.
- Work will be continued on the generation of photoacoustic waves by exothermic chemical reactions. In particular, the reaction products will be determined by gas chromatography-mass spectral analysis. The time dependence of the photoacoustic and photothermal waves launched by the reactions will be studied using transient grating techniques
- Further theory will be formulated for the response of phononic structures to pulsed and modulated continuous laser radiation.

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Session 6 – Separations II

Energy Frontier Research Center – Molecularly Assembled Material Architectures for Solar Energy Production, Storage and Carbon Capture

High-Throughput Synthesis, Characterization and Modeling of Zeolitic Imidazolate Frameworks for Selective CO_2 Storage and Separation

Vidvuds Ozolins[1], Principal Investigator
Brian Laird[2,*], Mark Asta[3], Yao Houndonougbo[4], and Omar M. Yaghi[5], Co-Principal Investigators
[1]Department of Materials Science and Engineering, University of California, Los Angeles, CA 90095
[2]Department of Chemistry, University of Kansas, Lawrence, KS 66045
[3]Department of Materials Science and Engineering, University of California, Berkeley, CA 94720
[4]Department of Chemistry and Biochemistry, Eastern Washington University, Cheney, WA 99004
[5]Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095
*Email: blaird@ku.edu

Overall research goals: This project features a coordinated effort for the high-throughput synthesis, characterization and modeling of zeolitic imidazolate frameworks (ZIFs). The structures of ZIFs feature high porosity (up to 2000 m^2/g), high thermal stability (500 °C) and unusually high chemical stability. These attributes, coupled to the facility with which the imidazole link can be functionalized, make ZIFs ideal candidates for applications involving highly selective separation and storage of CO_2. We are addressing several outstanding questions in order to elucidate the fundamental molecular mechanisms of CO_2 uptake in ZIFs, and to guide further optimization of these materials for CO_2 separation and storage applications: (1) is their a correlation between the structure of a ZIF and its performance, (2) what is the impact of functionalizing the link on uptake capacity and efficiency of separations, (3) what are the adsorptive sites within the pores of ZIFs, (4) what is the mechanism of uptake and release of gases within ZIFs, and (5) what strategies can be developed for optimizing the performance of ZIFs to affect highly selective separations? To address these questions we are employing an integrated approach combining robust experimental synthesis and characterization efforts with state-of-the-art modeling studies combining electronic-structure calculations, molecular dynamics and grand-canonical Monte Carlo simulations.

Significant achievements: Since the initiation of this project on August 1, 2009, we have demonstrated the synthesis of ZIFs based on the topology of zeolite RHO constructed from a body-centered arrangement in which the largest cage has 48 vertices and 26 faces comprising 6 octahedrons, 8 hexagons, and 12 squares (see Fig. 1). We have shown experimentally that the functionality of the imidazolate can be altered without changing the underlying RHO topology of the ZIF structure to give an isoreticular series whose members have improved carbon dioxide capture properties. Modeling results, based on a combination of electronic density-functional-theory (DFT) calculations and classical grand-canonical Monte-Carlo simulations reproduce the pronounced dependence of CO_2 uptake on the imidazolate functionality measured experimentally in this class of ZIFs. The modeling results further demonstrate that CO_2 absorbs into two primary sites within these framework structures: (i) the large cavities with octahedral symmetry, and (ii) the bridging sites connecting these cavities. Additionally, a primary factor influencing the dependence of

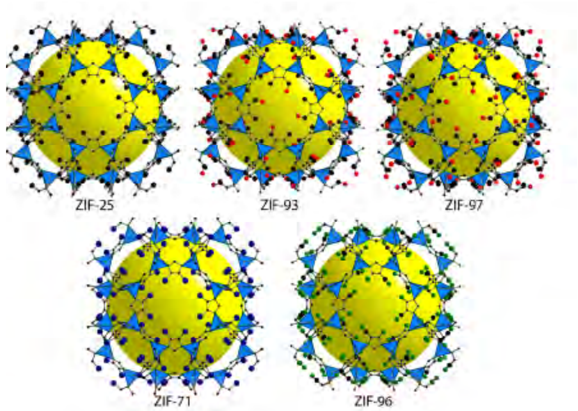

Figure 1. The structures of ZIF-25, -71, -93, -96, and -97 are shown. The yellow ball is situated within the cage to represent the free space. Atom colors: zinc, blue tetrahedra; carbon, black; chlorine, green; oxygen, red; nitrogen, blue. Hydrogen atoms are omitted for clarity.

uptake on functionality, over the relevant range of gas pressures, is the charge-quadrapole electrostatic interaction between the framework and gas molecules. This interaction displays a pronounced sensitivity to the overall symmetry of the framework structures – of the five ZIFs studied the two structures with O_h point-group symmetry show negligible effects of electrostatic interactions on CO_2 uptake, while in those with the lower *O* symmetry display uptakes that increase up to a factor of two when these interactions are included in the simulations.

Science objectives for 2010-2012: Experimental and modeling studies in this project will continue to focus on understanding the effect of imidazolate functionalities on CO_2 uptake and selectivity in a class of ZIFs built from tetrahedrally-coordinated Zn metal ions. This will involve the following measurements and simulations for CO_2, CH_4 and their mixtures:

- Monte-Carlo simulations will be performed to compute equilibrium uptake values as functions of temperature and pressure. These simulations will allow calculations of adsorption enthalpies and entropies as well as equilibrium adsorption isotherms. In addition, CO_2 density maps will be constructed to determine the dependence of the preferred adsorption sites within the ZIF on framework structure and functionalization.
- Modeling techniques will be developed to systematically study the dependence on CO_2 uptake on the details of the framework/CO_2 interaction – especially with regard to the functionalization of the imidazole.
- Molecular-dynamics simulations will be performed in the study of the diffusion coefficients of gas species in ZIF structures with different functionalizations. The results of these simulations will be used to develop a kinetic model for the uptake kinetics of gas mixtures.
- The initial goal of the experimental work will be to collect high-pressure gas adsorption data for the RHO ZIFs described above. This will allow for modeling comparisons above one bar. Furthermore, the synthesis of ZIFs with new topologies and functionalities will be addressed.

References to work supported by this project 2008-2010:

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Molecular Aspects of Transport in Thin Films of Controlled Architecture

Paul W. Bohn, Principal Investigator
Francesca Carpino, Aigars Piruska Postdoctoral Associates
Sean Branagan, Nick Contento, Dane Grismer, Graduate Assistants
Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556 E-mail: pbohn@nd.edu; Web: http://www.nd.edu/~bohngrp/

Collaborators: Jonathan V. Sweedler, University of Illinois
Narayan Aluru, University of Illinois

Overall research goals. The ultimate goal of our program is to establish intelligent control of molecular transport in space and time at small length scales – enabling the construction of materials and structures that can sense molecular characteristics, *e.g.* size, charge, molecular shape, *etc.*, then generate control signals that control transport based on those characteristics. Specifically we seek to manipulate, (separate, isolate, react, detect) low-mass samples with the same precision and level of control currently possible with bench-scale samples by combining microfluidic and nanofluidic structures under the rubric of *integrated microfluidics*.

Significant Achievements 2008-10. *Kinetics of Confined Enzymes*. The behavior of enzymes confined geometrically to the inside surface of a nanometer-scale pore was characterized. Horseradish peroxidase (HRP) was used to catalyze the oxidation of a fluorigenic substrate, Amplex Red (AR), to fluorescent resorufin in the presence of H_2O_2. Surface immobilized HRP was studied bound to the surface of a microfluidic channel and bound to the interior of cylindrical nanopores in NCAMs. HRP immobilized on planar surfaces shows high activity (~10 μM min^{-1}) HRP was also immobilized inside nanopores, and enzymatic reactions inside the nanopores were characterized and compared to finite element simulations of a modified Eley-Rideal mechanism to bracket the value of the initial reaction velocity for the confined enzyme. Reaction velocities were estimated to be ≥ 20-fold higher in the nanopores than for the same enzyme in fluid solution. It is worth noting that the nanopore experiments exhibit a very different enzyme:substrate ratio ([E]/[S] ~ 1000) compared to the same reaction in fluid solution ([E]/[S] ~ 0.001).

Catalytic DNA. DNAzyme-based catalytic molecular beacons have the potential for sensing. A systematic investigation of their performance when immobilized into gold-coated NCAMs was undertaken, which resulted in ~25-fold improvement in performance. These findings form a firm basis on which practical applications of catalytic beacons can be realized, including sensors for both Pb^{2+} and UO_2^{2+} ions. DNAzymes were also immobilized on poly(methyl methacrylate), PMMA, surface using biotin-streptavidin. The immobilized DNAzyme retained its Pb^{2+} detection activity in the microfluidic device and could be regenerated and reused. While prior work had shown that Pb(II)-specific catalytic DNA can be used in its solubilized form and while attached to gold substrates to quantitate Pb^{2+} in solution, this was the first use of the DNAzyme immobilized within a microfluidic platform for real time Pb^{2+} detection.

Specific Objectives for 2010-11. Develop and apply the measurements needed to determine the fundamental chemical and physical factors that determine how transport couples to reactivity under confinement and crowding in nanopores and nanochannels. In the coming year we will execute single molecule studies of translational dynamics in single nanopores under electrokinetic

(EK) flow, where the degree of confinement is systematically varied. In addition, model electrochemical reactions will be studied at embedded annular nanoband electrodes (EANEs) as a function of flow conditions, pore geometry and electrochemical driving force.

Publications Acknowledging DOE BES Support – 2008-10

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Molecular-Level Investigation of Diffusion Behaviors within Cylindrical Nanoscale Pores

Takashi Ito, Principal Investigator
Daniel A. Higgins, Co-Principal Investigator
Thomas Everett, Shaida Ibrahim, Khanh Hoa Tran Ba and Seok Chan Park, Graduate Students
Department of Chemistry, Kansas State University, Manhattan, KS 66506-0401
Email: ito@ksu.edu; Web: http://www.ksu.edu/chem/people/faculty/ito.html)

Overall research goals: The overall goal of this project is to fully understand mass transport within solution-filled nanoscale pores (nanopores) at the molecular level. Single-molecule mass transport behavior and ensemble molecular flux will be systematically measured in identical nanoporous monoliths and the results compared. These measurements will make it possible to quantitatively discuss the molecular-level mechanisms that determine the rate and selectivity of mass transport through nanopores, and thus to design nanoporous materials best suited for separations, catalysis, and power sources. This 3-year project aims to systematically investigate the effects of steric and chemical interactions on ensemble and single-molecule diffusion through cylindrical nanopores (2-35 nm in diameter) fabricated from cylinder-forming block copolymer (CFBCP) and surfactant-templated mesoporous silica (STMS).

Significant achievements in 2009-2010: During the start-up period of this project, we have focused on establishing methods to fabricate and characterize nanoporous monoliths suitable for quantitative ensemble flux and single-molecule fluorescence measurements, in addition to building a new fluorescence microscope for single-molecule tracking.

1. Conductance and flux measurements for characterizing microcapillary-incorporated CFBCP-derived nanoporous monoliths. We demonstrated that conductance and ensemble flux measurements provide a means for assessing mass transport within microcapillary-incorporated, stand-alone nanoporous monoliths prepared from cylinder-forming polystyrene-poly(methylmethacrylate) diblock copolymers (PS-*b*-PMMA). Monoliths containing cylindrical nanopores of 20 nm diameter (**Figure 1a**: AFM image of a PS-*b*-PMMA film surface) have been fabricated by UV-based etching of cylindrical PMMA domains in annealed PS-*b*-PMMA monoliths formed at the apex of silica microcapillaries (**Figure 1b**). Ion mobility in the resulting nanoporous monoliths was assessed by measuring the conductance (**Figure 1c**) and ensemble flux of anionic fluorescent probes (**Figure 1d**) through the monoliths in solutions of different supporting electrolyte (KCl) concentrations at neutral pH. The conductance data (**Figure 1c**) showed the transition from ionic flow within the nanopore cavity to that on the negatively-charged (carboxylate-terminated) nanopore surface with decreasing KCl concentration. In addition, these data clarified that the pore density was much smaller (1/50~1/100) than that estimated from AFM images. The flux data (**Figure 1d**) showed permselective transport of anionic fluorescent probe (sulforhodamine B; SRB) in the absence of KCl due to electrostatic repulsion with the negatively-charged nanopores. The flux of SRB through the monolith in 0.1 M KCl was close to that estimated from its diffusion coefficient in aqueous solution. Importantly, the conductance plateau and permselective transport

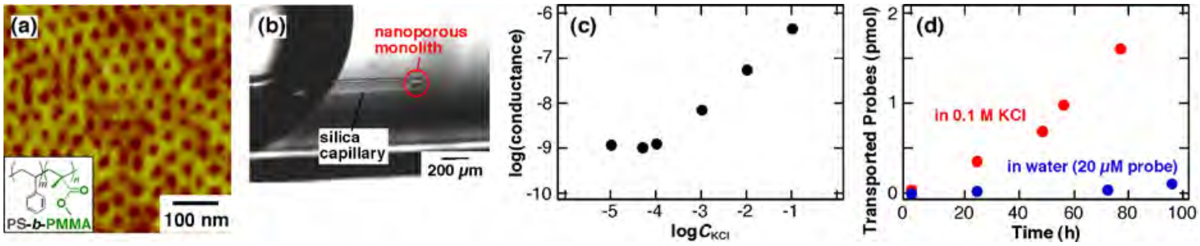

Figure 1. (a) AFM image of a PS-*b*-PMMA-derived nanoporous film. (b) Optical image of a PS-*b*-PMMA-derived nanoporous monolith within a silica microcapillary. (c) Conductance of a microcapillary incorporating a PS-*b*-PMMA-derived nanoporous monolith at different KCl concentrations. (d) Transport plots for anionic sulforhodamine B (SRB) through a capillary-incorporated PS-*b*-PMMA-derived nanoporous monolith in the presence and absence of 0.1 M KCl.

were not observed for nanoporous monoliths in the presence of leakage between the capillary and monolith.

2. Fabrication and characterization of directionally oriented mesoporous silica via vertical spin-coating. We have demonstrated that STMS films incorporating macroscopically-aligned, hexagonally-ordered cylindrical mesopores can be prepared in thin films on glass and silicon substrates. Ordered STMS materials are obtained by "vertical spin coating", in which the substrate is spun about an axis parallel to its surface. Small angle X-ray scattering (SAXS) data obtained from these materials on a powder X-ray diffraction instrument show the presence of ~3.5 nm (d-spacing) hexagonally-ordered cylindrical mesopores. SAXS data obtained as a function of azimuthal angle (**Figure 2a**) shows that the mesopores in the films thus prepared are oriented predominantly perpendicular to the spinning axis. A general user proposal has been submitted to the Advanced Photon Source at Argonne National Lab to perform transmission SAXS anisotropy experiments on both STMS films and microcapillary-supported STMS and CFBCP monoliths. We have also begun recording single molecule diffusion trajectories within oriented STMS films. To date, we have investigated diffusion of a neutral perylene diimide dye under dry and hydrated (i.e., 70% relative humidity) conditions. Condensation of water within the mesopores is required to facilitate dye motion. Fluorescence movies recorded from dye-doped films using polarized light (**Figure 2b,c**) clearly show evidence of domain formation. These data are used to determine single molecule diffusion trajectories (**Figure 2d**), which show that the molecules diffuse in an aligned state, with their long axes oriented parallel to the channel axis. We are now using these data to quantitatively characterize the rate of molecular diffusion and the degree of mesopore alignment as a function of film preparation conditions.

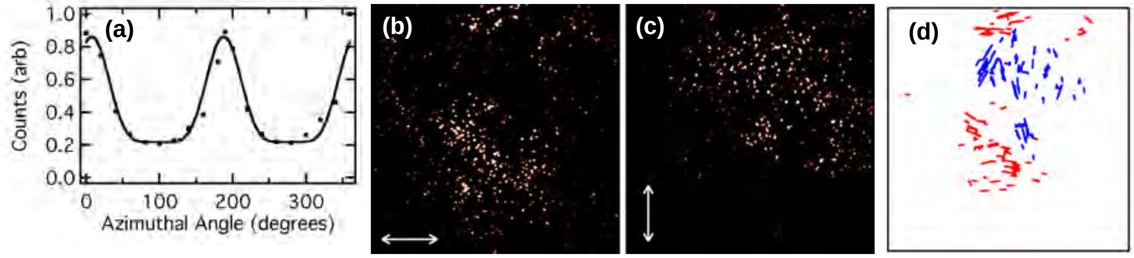

Figure 2. (a) SAXS scattering intensity (first order diffraction peak) as a function of azimuthal angle. These data show the hexagonally-ordered mesopores comprising the film are aligned predominantly perpendicular to the spinning axis (0° and 180° on the data shown). (b),(c) Single frames of fluorescence movies recorded from identical sample regions under orthogonal incident polarizations. (d) Representative diffusion trajectories obtained from the sample region shown in (b) [red] and (c) [blue].

<u>Science objectives for 2010-2012:</u>

- Establish simple methods to improve the alignment of cylindrical nanopores within microcapillary-supported PS-*b*-PMMA-derived monoliths.
- Develop a simple method to prepare microcapillary-incorporated STMS monoliths containing aligned nanopores.
- Characterize ensemble flux and single-molecule mass transport within nanopores under different solution conditions (pH, supporting electrolyte concentrations, types of fluorescent molecules).
- Measure ensemble flux and single-molecule mass transport data for nanopores having different pore diameters and surface functional groups.

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Poster Session 2

Metal-Organic and Zeolite Imidazolate Frameworks (MOFs and ZIFs) for Highly Selective Separations

Omar M. Yaghi
Department of Chemistry and Biochemistry, 607 East Charles E. Young Dr., UCLA, Los Angeles, CA 90095. Email: yaghi@chem.ucla.edu; Web: yaghi.chem.ucla.edu

Overall research goals: The proposed program will be focused on the synthesis of developing metal-organic frameworks (MOFs) and zeolitic imidazolate frameworks (ZIFs) for gas separation technologies. The ZIFs which were recently invented in our laboratory will be studied for their high selectivity in separations and outstanding chemical stability in water and organic media.

Significant achievements in 2008-2010:

1. Control of pore size and functionality in ZIFs: We have reported the synthesis of three new ZIFs, ZIF-68, -69, and -70, which are underlying the same GME topology but their functionalities are different; therefore we extended this concept to design other functionalized GME ZIFs. Specifically, we synthesized and characterized five new ZIFs, ZIF-78, -79, -80, -81, and -82 (Figure 1). In each ZIF, every tetrahedral Zn atom is connected to two 2-nitroimidazolate (nIm) and two other substituted Im (see Figure 1). Interestingly, across the series of Im linkers with -Cl, -CN, -Me, -Br, and $-NO_2$ functionality incorporated into the GME topology, the substituted Im's point into the voids of the *kno* cages (blue cage in Figure 1). Thus, by varying the substituted Im, one can systematically modulate the pore aperture of the *kno* cage from 3.8 to 13.1 Å and the pore diameter from 7.1 to 15.9 Å. Permanent porosity of the ZIFs was demonstrated by measuring the N_2 gas adsorption of the guest-free material. The BET surface areas for the seven ZIFs vary from 620 to 1730 m^2 g^{-1}, where a nearly linear relationship between pore diameter and the specific surface area was observed.

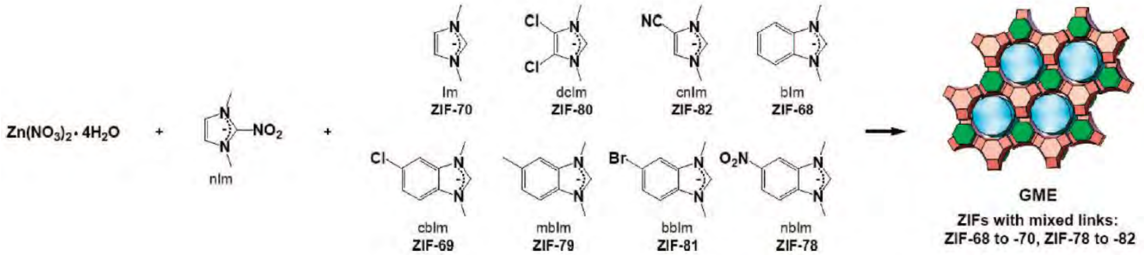

Figure 1. Structures of imidazolate links and their abbreviations. Reaction of nIm plus any other imidazole linker shown results in the **GME** topology, whose tiling is shown at the right. The name of the ZIF resulting from reaction with nIm is given under each linker.

2. Isoreticular Metalation of MOFs: Since we have demonstrated the covalent functionalization of ZIFs by carrying out organic reactions directly on ZIF crystals, we extended this strategy to implement the isoreticular metalation of extended crystalline materials. Specifically, crystals of $(Zn_4O)_3(BDC\text{-}NH_2)_3(BTB)_4$ (**A**, Figure 2) were reacted with 2-pyridinecarboxaldehyde to form the covalently bound iminopyridine chelate derivative $(Zn_4O)_3(BDC\text{-}C_6H_5N_2)_3(BTB)_4$ (**B**), which was reacted with $PdCl_2(CH_3CN)_2$ to give the metal-complexed MOF $(Zn_4O)_3(BDC\text{-}C_6H_5N_2PdCl_2)_3(BTB)_4$ (**C**). The presence of the iminopyridine unit was confirmed by mass spectrometry of digested samples of **B**. The porosities of **B** and **C** were also assessed by performing an 87 K Ar isotherm. To confirm that the Pd is complexed to the iminopyridine unit and to precisely determine the Pd coordination environment within the framework, we performed Pd K-edge extended X-ray absorption fine structure spectroscopy on samples of **C**. The data analysis indicated the presence of two Pd-Cl and two Pd-N ligands. Furthermore, analysis of the X-ray absorption near-edge structure spectrum indicated that the major chemical form of Pd within the framework of **C** was consistent with an iminopyridine-bound moiety.

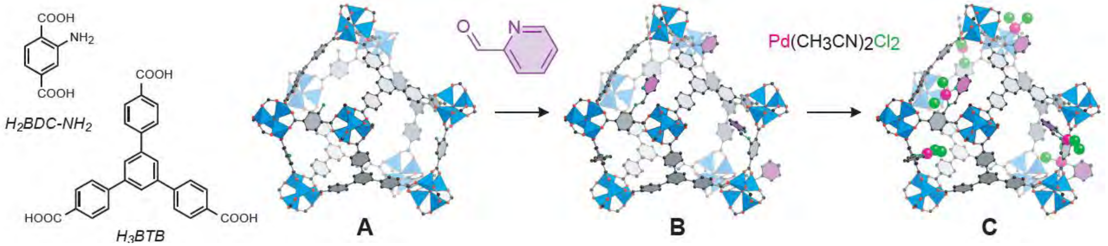

Figure 2. (Left) Molecular structures of organic links. (Right) Isoreticular covalent functionalization followed by metalation.

Science objectives for 2010-2012:

- Future work will focus on optimizing ZIFs and MOFs for gas separation. In particular tuning pore sizes and inclusion of various metals within the pores will be investigated as potential methods for improving gas separation.

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Local Solvation Structure and Ion Association in Aqueous Sulfate Solutions: Toward Understanding of Weak Interactions in Selective Separations

J. Michael Simonson, Principal Investigator
Ariel A Chialvo, Co-Principal Investigator
P.O. Box 6008, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831
Email: simonsonjm@ornl.gov

Overall research goals: The goal of this research is to achieve a predictive understanding of the molecular-level interactions in solution that drive the affinity and selectivity between target ions and receptors in chemical separations. Determining local structure in solution will provide the experimental basis for new understanding of changes in entropy in solvation and binding; molecular-level modeling of solvation and binding interactions will strengthen predictive capabilities for anion extraction; and detailed investigations of the liquid-liquid interface will provide new insights into interfacial effects. Success in this research will enhance the molecular-level predictability of extractive separations, including the important effects of solvent rearrangement.

Significant achievements in 2008-2010: This is a new research project which started in 2009. Molecular-based simulations of the hydration behavior of sulfates in model metal-sulfate aqueous solutions at ambient conditions have been carried out. The main goal is to analyze the balance of energetic and entropic contributions from the aqueous environments that gives rise to the particular sulfate hydration structure, and the potential for anion-cation pair formation. Simulations have been carried out for solutions including three cations: lithium, nickel, and ytterbium. These salts are relatively soluble, and all three cations have isotopic pairs suitable for second-difference neutron diffraction experiments to address experimentally the predicted solvation structures, and hence the calculated relative contributions of energy and enthalpy to the equilibrium structures.

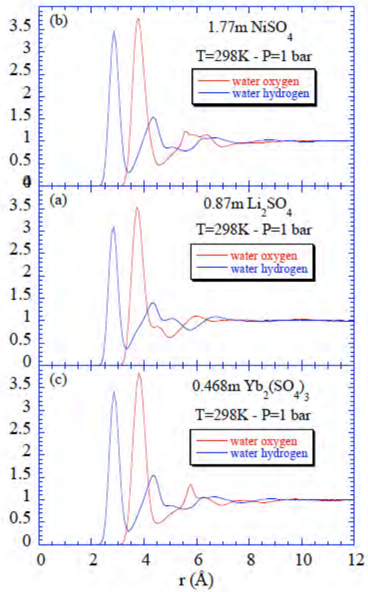

Figure 1. Sulfate ion hydration from molecular dynamics simulation (Chialvo and Simonson, 2010)

To predict the results of scattering experiments, the neutron-weighted radial distribution function of the sulfur site of the sulfate group and its partial contributions in aqueous solutions were calculated. Based on these simulated radial distribution functions we have determined the coordination environment around the sulfate group and the degree of metal-sulfate pair formation according to Poirier-DeLap formalism. Figure 1 shows the calculated radial distribution functions of water around the sulfate ion in $NiSO_4$, Li_2SO_4, and $Yb_2(SO_4)_3$ solutions at the concentrations 1.77, 0.87, and 0.47 $mol \cdot kg^{-1}$ respectively. Hydration numbers as calculated from the number of hydrogen atoms in the first solvation shell (first blue peaks in Figure 1) are 11.2, 9.6, and 9.8, with little ion-water structure seen beyond the second solvation shell. These solvation numbers are relatively large compared with smaller cations in solution, but the absence of longer-range structure indicates relatively weak solvation compared to ions with higher charge density. In addition, ion association has been predicted from these simulations, with effectively one counterion in the first solvation shell for both $NiSO_4$ and Li_2SO_4 solutions. It is expected that the extent of ion pairing, and resulting effective charge on the sulfate anion, will affect the overall separation of sulfate from aqueous solutions using selective extractants. Comparisons of these results with available neutron scattering data are in progress, to establish appropriate conditions for initial experimental measurements in this research.

Science objectives for 2010-2012:

- Neutron diffraction with isotopic substitution will be carried out on sulfate solutions over ranges of pH, total concentration, and the presence of model extractant moieties (e.g., thiourea groups).

- Additional simulations will focus on local structure in the presence of model extractant moieties to determine the effectiveness of extractants in replacing solvation water near sulfate ions.

- Extension of modeling and experimental studies to double-difference techniques will be made to determine specific local effects of cation hydration within an ion paired sulfate on the extent and structural specificity of ligand binding to the overall ion pair.

References to work supported by this project 2008-2010:

1. A. A. Chialvo and J. M. Simonson, "Molecular Dynamics Simulation of the Interfacial Behavior of Short-Chain Polystyrene Sulfonate Aqueous Solutions in Contact with Graphene Surfaces in the Presence of Multivalent Cations," J. Phys. Chem. C, 112, 19521-19529 (2008).
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Ionic and Electronic Properties of Nanopores and Nanostructures

Lane Baker, Principal Investigator
Indiana University, Department of Chemistry, 800 E. Kirkwood Ave, Bloomington, IN 47405
Email: lanbaker@indiana.edu; Web: www.indiana.edu/~bakergrp

Overall research goals: The research objectives are to develop both a fundamental understanding and predictive capability related to the unique properties of structures at small scales, namely nanopores and nanoscale structures. Nanopore structures of interest include track-etch polymer and inorganic oxide membranes with tunable pore diameters that range from two nanometers to one micron. Scanned probe microscopies with specialized capabilities are utilized to study the properties of these materials.

Significant achievements: Experimental and modeled studies of transport through nanometer scale pores using scanning ion conductance microscopy (SICM) have been initiated. In these studies, a nanometer-scale pipette is rastered over a membrane of interest. When brought in close proximity to a nanometer-scale pore, ionic conductance between the nanopipette and nanopore couple. Having prior knowledge of the properties of the nanopipette, the local properties of the nanopore can be extracted with both high spatial resolution (nanometer) and high temporal resolution (200 MHz sampling rate). Application of a dithered imaging mode affords a noncontact, noninvasive imaging mode which decouples the ion currents measured at the nanopore from the feedback loop of the instrument. To date we have investigated nanopores with diameters as small as 100 nm. Ion current maps of surfaces can be analyzed quantitatively by applying GHK theory to extract information related to factors contributing to local conductivity. GHK theory is an ideal tool to apply in these studies, as the model and corrected versions of the model have been applied to transport through ion channels of small (<10 nm) dimension. Our results indicate that by considering the flux from a disk-shaped source (nanopore) to a probe (nanopipette) GHK treatment results in reliable prediction of ion currents. We are refining the model and technique to develop both a comprehensive model of transport and an ion-selective mode of imaging.

In addition to SICM, we are also developing a variant of electrochemical atomic force microscopy that incorporates fast-scan cyclic voltammetry. Our ultimate goal in this project is to map electronic conductivity and redox activity of materials at surfaces to determine structure-property relationships at the nanometer scale.

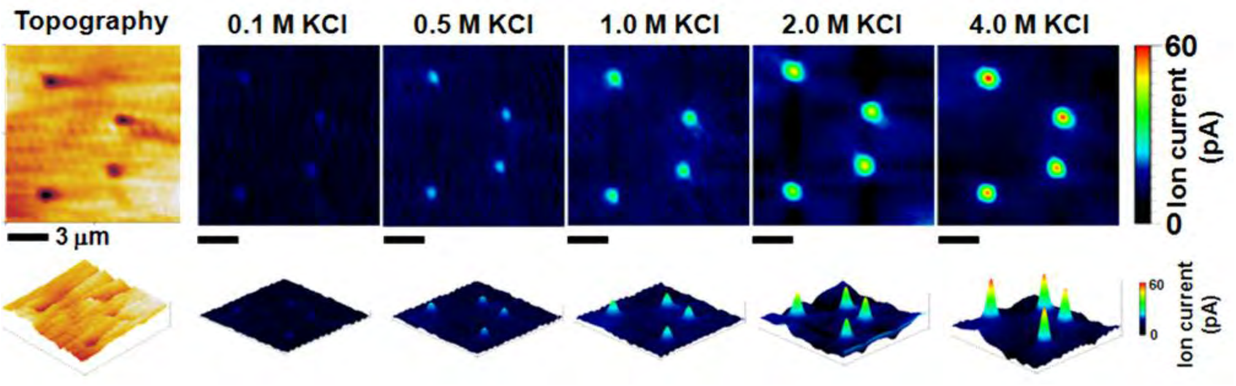

Figure 1. SICM images of ion transport through nanometer scale pores in track-etch polyimide membrane. Topography (left) and ion concentration gradient images (left to right are shown).

Science objectives for future work:

- Continue development of nanopore characterization and models using scanning ion conductance microscopy. To include investigations of single nanopores prepared in silicon nitride substrates.
- Develop an ion selective version of scanning ion conductance microscopy using an ion selective voltammetric probe. This will allow for transport properties of specific ion species to be measured with high spatial and temporal resolution.
- Integrate fast scan voltammetry with atomic force microscopy and custom conductive cantilevers. We will initially examine both transport through nanopores and intercalative properties of metal and mixed metal oxides to determine nanoscale structure-property relationships.

References to work:

1. J. Basore, N. Lavrik, L.A. Baker, "Gating with a Microelectromagnetic Trap," Adv. Mater. (2010), accepted.
2. Y. Fu, H. Tokuhisa, L.A. Baker, “Nanopore DNA sensors based on dendrimer-modified nanopipettes,” Chem Comm., **32**, 4877-4879 (2009).
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Exploring New Methods and Materials in the Formation of Selective, High-Flux Membranes for CO_2 Removal

Merlin L. Bruening, Principal Investigator
Department of Chemistry, Michigan State University, East Lansing, MI 48824
Email: bruening@chemistry.msu.edu; Web: http://www.chemistry.msu.edu/faculty/bruening/index.htm

Collaborators: Dr. Gregory L. Baker, Department of Chemistry, Michigan State University

Overall research goals: The first objective of this work is to examine the utility of atom transfer radical polymerization (ATRP) for growing ultrathin membrane skins containing poly(ethylene glycol) (PEG) side chains. Thin films allow high flux, and the presence of PEG chains favors permeation of CO_2 relative to other gases. We also aim to increase the selectivity of membrane skins and catalysts prepared by layer-by-layer deposition of polyelectrolytes. The second objective is to examine methods for disrupting the crystallization of thin films of poly(ethylene glycol methacrylates) to create highly selective membranes for removal of CO_2 from H_2 streams.

Significant achievements in 2008-2010: Removal of CO_2 is an important part of purifying H_2 produced by steam reforming of hydrocarbons. Membranes that are CO_2 selective are attractive for these separations because the H_2 remains on the feed side of the membrane and does not have to be recompressed. Poly(ethylene glycol) (PEG)-containing polymers are attractive for these separations, but crystallization of PEG chains results in minimal fluxes and selectivities. We developed the ATRP method in Figure 1 for surface-initiated copolymerization of monomers containing long and short PEG chains to avoid PEG crystallization and create membrane skins that are selective for removal of CO_2 from H_2 streams. Upon crystallization of poly(PEGMEMA-1100) films, formation of PEG helices leads to splitting of the 1150 cm^{-1} C-O-C band into peaks at 1120 and 1148 cm^{-1} and a narrowing of the CH_2 wagging peak at 1360 cm^{-1} (Figure 2A). In contrast, the FTIR spectra in Figure 2B show that *even 25 mole% of PEGMEMA-475 in a poly(PEGMEMA-475-co-PEGMEMA-1100 film is effective in preventing crystallization for at least one year*.

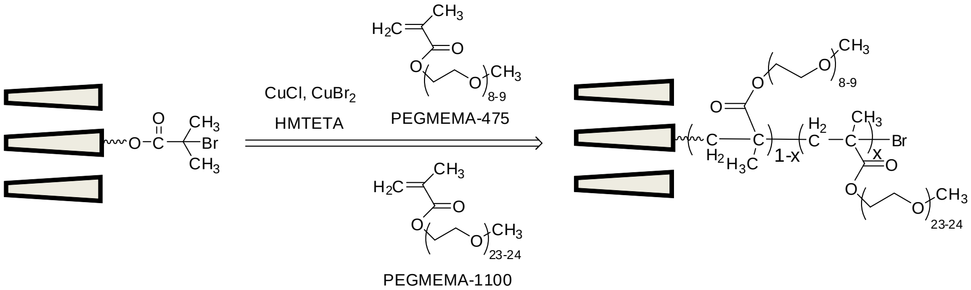

Figure 1. Surface-initiated copolymerization of PEGMEMA-475 and PEGMEMA-1100 to provide a membrane skin that remains amorphous at room temperature.

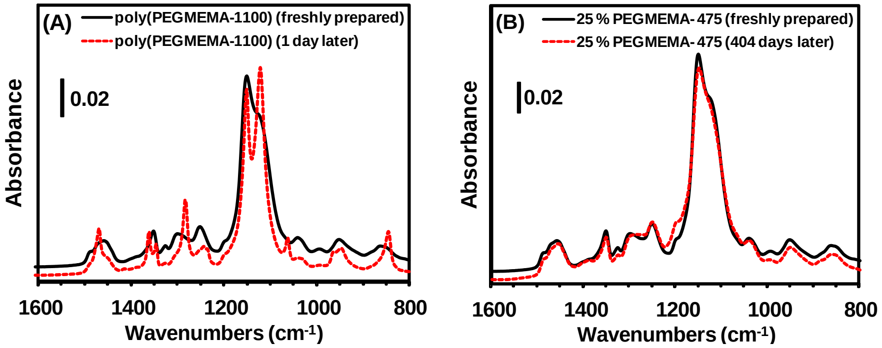

Figure 2. Reflectance FTIR spectra of (A) 60 nm-thick poly(PEGMEMA-1100) immediately after polymerization (solid black line) and 24 hours later (dashed red line) and (B) 97 nm-thick poly(PEGMEMA-475-*co*-PEGMEMA-1100) immediately after polymerization (solid black line) and 404 days later (dashed red line).

One challenge in characterizing copolymer films is determining their composition, as the two monomers may not have the same reactivity. We developed a new method for estimating the polymer composition using reflectance infrared spectroscopy. Because of complications in reflectance methods, peak intensities are not always a linear function of the concentration of a particular functional group in the film. To overcome this challenge, we employ Fresnel reflection calculations to determine IR absorption coefficients, which are a direct function of concentration. These calculations enable us to estimate the fraction of monomers containing long and short PEG chains in copolymer films. In the copolymerization in Figure 1, film composition is quite similar to the composition of the solution from which polymerization occurs.

The prevention of crystallization in copolymer films results in a room-temperature CO_2/H_2 single-gas selectivity of 12, which is equivalent to the selectivity of the best membranes in the literature (excluding facilitated transport.) Copolymer films exhibit the same selectivity as homopolymer films with long side chains, but the copolymer films do not crystallize so selectivity does not decrease over several months. Mixed gas selectivities are about 20% lower than single-gas selectivities, presumably CO_2 plasticizes the membrane. Unfortunately, the CO_2-permeability of the copolymer membranes is not as high as that of some cross-linked membranes, but the ultrathin skin maximizes permeance for a given permeability.

Work with multilayer polyelectrolyte membranes resulted in highly selective membrane skins that selectively reject divalent cations. Treatment of membranes with solutions of Fe^{3+} gives a high density of ion-exchange sites that lead to a remarkable Na^+/Mg^{2+} selectivity of 90. Such membranes may be attractive for water-softening applications.

Science objectives for 2010-2012:

- Develop the chemistry for polymerization from polymer supports to prepare highly selective membranes. Our prior research focused only alumina supports that are resistant to organic solvents.
- Examine cross-linking chemistry and changes in monomer composition to increase free volume and membrane permeability.
- Create highly charged, nanoporous membranes to begin examining selective ion transport induced by streaming potentials.

References to work supported by this project 2008-2010:

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2. S.T. Grajales, X. Dong, Y. Zheng, G.L. Baker, and M.L. Bruening, “Effects of Monomer Composition on CO_2-Selective Polymer Brush Membranes,” Chem. Mater. Submitted, March (2010).
3. M. Adusumilli and M.L. Bruening, “Variation of Ion-exchange Capacity, Zeta Potential, and Ion-transport Selectivities with the Number of Layers in a Multilayer Polyelectrolyte Film,” Langmuir **25**, 7478-7485 (2009).
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Interfacial Solvation under Aggressive Conditions

Frank V. Bright, Principal Investigator
Javid Rzayev, Co-PI
Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, New York 14260-3000
Email: chefvb@buffalo.edu; Web: http://www.chemistry.buffalo.edu/people/faculty/bright/

Overall research goals: We have set out to provide molecular-level insights into the dynamics that occur within membrane architectures when they are operated under viable H_2 purification conditions.

Significant achievements in 2008-2010: We have achieved the following research goals:

1) Developed a high-pressure total internal reflection fluorescence apparatus for measuring monolayer interfacial dynamics between 250 and 380 K up to 500 bar with picosecond time resolution (Fig. 1).

2) Determined the effects of terminal residue ($-CH_3$ vs. $-CF_3$) and CO_2 fluid density on the rotational reorientation dynamics of ‘short’ dansylated propylsilane monolayers (Fig. 2).

3) Determined the effects of chain length, surface loading, and CO_2 fluid density on the rotational reorientation dynamics of dansylated alkylsilane monolayers.

4) Determined the impact of cosolvents (MeOH, EtOH, H_2O) (1 mole%) on “2)” and “3)”.

5) Determined the effects of cross-linking strategies on “3)”.

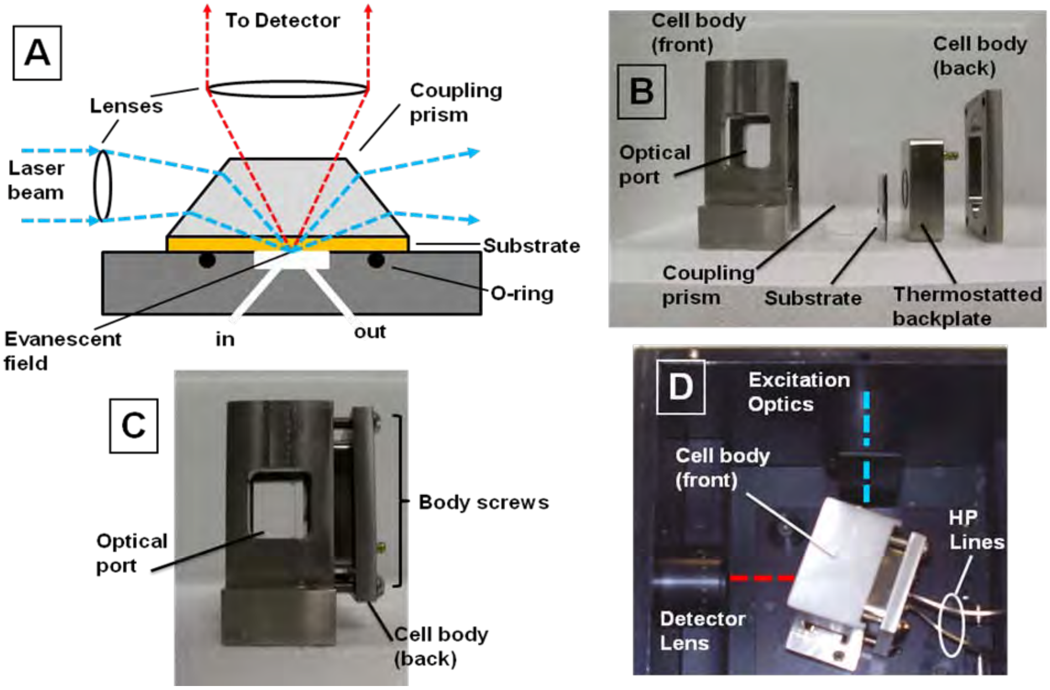

Figure 1. High-pressure total internal reflection fluoreascence system. (A) Schematic. (B) Exploded view of main components. (C) Assembled cell. (D) Top view of cell in spectrofluorometer.

A key step in obtaining pure H_2 is its separation from other gaseous molecules, mainly CO_2, that often accompany H_2 in industrial-scale reactions. Polymeric membranes represent one approach.

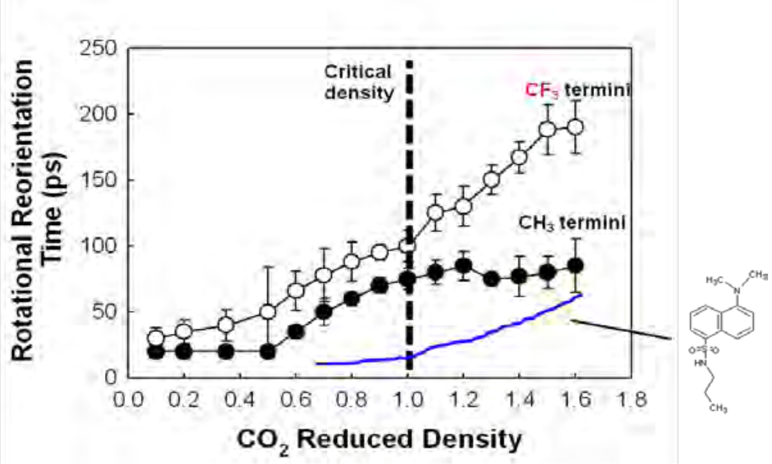

Figure 2. Density-dependent rotational reorientation times for dansyl species free in solution and at –$(CH_2)_2$-CH_3, and -$(CH_2)_2$-CF_3 modified silica.

<u>Science objectives for 2010-2012:</u>

- Determine local surface composition across density range
- Extend previous efforts to polymeric monolayers (linear, brushes)
- Implement and assess cross linking within polymeric monolayers
- Determine protein structure in ionic liquid media

<u>References to work supported by this project 2008-2010:</u>

1) T.A. McCarty, P.M. Page, G.A. Baker, and F.V. Bright, “Behavior of Acrylodan-Labeled Human Serum Albumin Dissolved in Ionic Liquids,” *Ind. Eng. Chem. Res.* **2008**, 47, 560-569.
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5) M.J. Dabney and F.V. Bright, “High-Pressure Total Internal Reflection Fluorescence,” in preparation for *Appl. Spectrosc.*.
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Synthesis and Analysis of Polymers with High Gas Permeabilities and Permselectivities

William J. Koros, Principal Investigator
Donald R. Paul, Co-Principal Investigator
School of Chemical & Biomolecular Engr., Georgia Institute of Technology, Atlanta, GA 30327
Email: wjk@chbe.gatech.edu; Web: www.chbe.gatech.edu/fac_staff/faculty/koros.php

Overall research goals: The research objectives are to provide fundamental insights leading to improved glassy polyimide gas separation membranes and to explore a new crosslinking technique for stabilizing these high-performance membranes in aggressive feed streams.

Significant achievements in 2008-2010: We discovered decarboxylation-induced cross-linking at elevated annealing temperatures (~15 ^{o}C above glass transition temperature, Tg) for a carboxylic acid-containing 6FDA-based copolyimide, 6FDA/DAM-DABA. Recently, we also reported synthesis of polyimides with different chemical structures. Our work is now concentrating on decarboxylation of 6FDA/DAM-DABA (3:2) at temperatures that are much lower than the glass transition temperature (~ 387^{o}C). This sub-Tg crosslinking capability is fundamentally interesting, but also practically significant as an avenue to enable eventual extension to asymmetric structure useful for large scale membranes. Our present results by gas permeation, thermal analysis and solvent swelling suggest that the decarboxylation-induced cross-linking of 6FDA/DAM-DABA can be carried out essentially completely at temperatures as low as 330 ^{o}C; however, under 300 ^{o}C, even for 20h, the crosslinked fraction remains low. Membranes annealed at or above 330 ^{o}C don't dissolve in the strong solvent, N-methyl pyrrolidinone (NMP) at 100 ^{o}C. On the other hand, membranes annealed at 300 ^{o}C swell at room temperature and dissolve at 100 ^{o}C in NMP. Un-annealed membranes dissolved easily in NMP at room temperature.

Permeabilities were tested for 6FDA/DAM-DABA membranes using pure gases (He, O_2, N_2, CH_4, CO_2). Results for CO_2 are shown in Fig. 1, since this is the most aggressive penetrant. The permeability actually decreases with increasing annealing temperature; however, beyond 300 ^{o}C, it actually increases with increasing annealing temperature. A plasticization response is observed for the membranes annealed at temperatures lower than 300 ^{o}C. For samples annealed above 300 ^{o}C plasticization resistance is seen up to 700 psia of pure CO_2. We are now pursuing characterization of selectivity for different gas mixtures for annealed and un-annealed membranes.

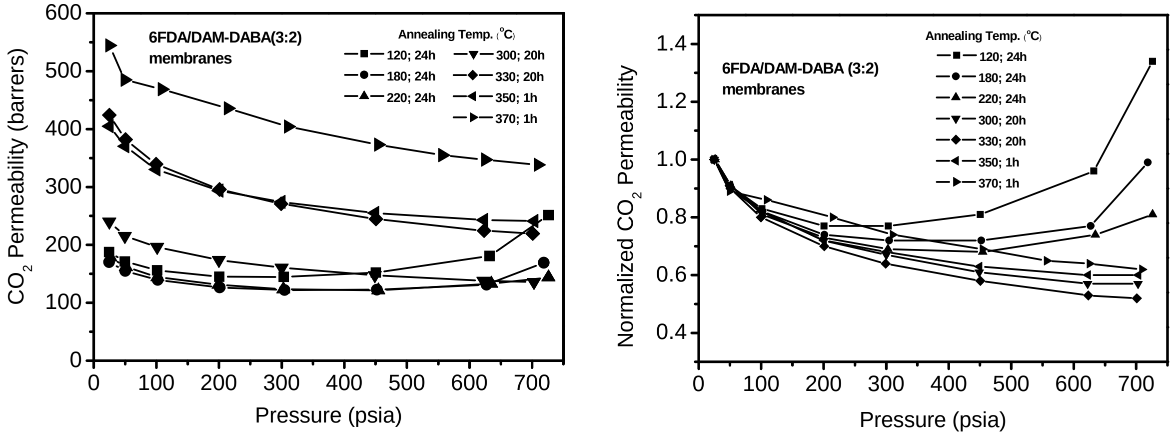

Figure 1. Permeabilities of CO_2 for membranes at 35 °C as a function of various annealing conditions. (a) Absolute permeabilities in standard units (Barrers), with 1 Barrer = 10^{-10} cc(STP)cm (cm Hg $)^{-1}$sec^{-1} cm^{-2}; b)dimensionless permeability normalized relative the absolute permeability at 200 psia feed pressure

Science objectives for 2010-2012:

- Separation performance of membranes for gas mixtures comprising CO_2 and CH_4 as well as additional heavier hydrocarbons will be measured and analyzed in terms of transport models
- Polyimide membranes with structures related to 6FDA/DAM-DABA will be annealed, tested and compared to results for 6FDA/DAM-DABA to establish structure-property relationships
- Physical aging in crosslinked and uncrosslinked samples of different thicknesses will be investigated to understand the effects of structure and thickness on aging properties.
- Aggressive CO_2 exposure responses of thin films aged for a couple of thousand hours will be investigated

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Polysaccharide Degradation and Collection via Ambient Ion Dissociation and Soft-Landing

Hao Chen, Principal Investigator
Assistant Professor
Department of Chemistry and Biochemistry
Ohio University, Athens, OH 45701
Phone: 740-249-5803; Fax: 740-597-3157
Email: chenh2@ohio.edu; Web: http://www.phy.ohiou.edu/%7Ehaochen/

Collaborators: Prof. R. Graham Cooks, Department of Chemistry, Purdue University, West Lafayette, IN

Overall research goals: The research objective is to establish a novel methodology for fast degradation of polysaccharides via ambient ionic fragmentation followed with collection of their fragments by soft landing technique. The ultimate goal is to extend this methodology for fast biofuel generation from cellulose.

Significant achievements in 2008-2010

Polysaccharides, the essential biomolecules in life, are the key starting materials or intermediates in biofuel processing which involves the gradual degradation of polysaccharides into methanol/ethanol. The traditional degradation of polysaccharides such as cellulose includes chemical and enzymatic hydrolysis.[1,2] However, these processes may not be green (e.g., using strong sulfuric acids[3]) and suffer from low degradation yield and long processing time. Thereby new routes with fast degradation rate and cleaner processing are in need. As motivated with our success in the development of ambient thermal dissociation method for dissociating peptide/protein ions at atmospheric pressure,[4-6] we propose to apply the method to degrading polysaccharides and subsequent collection of their fragments via soft landing after the dissociation event. The advantages of this protocol are that the dissociation occurs very fast (in seconds) and it does not need any acid or bacteria involved.

In our preliminary experiment, maltoheptaose (MW 1153), a linear oligosaccharide containing seven subunits of glucose, was first chosen to test the method. After the thermal dissociation and subsequent solvent washing of the tube for collection of ionic fragments that were possibly soft-landed inside the wall of the coiled tube, a solution contained the sugar fragments was obtained and analyzed by electrospray ionization mass spectrometry ESI-MS. In the acquired MS spectrum, in addition to the ion $[\text{maltoheptaose+Na-H}_2\text{O}]^+$ of *m/z* 1157.5, the fragments resulting from successive losses of glucose unit (indicated by the mass decrease of 162 Da), were observed at *m/z* 995.4, 833.3, 671.2, 509.1, 347.1, 185.1, respectively. By contrast, the control experiment was carried out under the same experiment conditions by direct electrospray of maltoheptaose in MeOH/H_2O, which only displays the intact protonated and sodiated maltoheptaose ions without any fragments observed.

Based on the preliminary data, one can see that the easy and fast ambient thermal dissociation combined with ion collection has potentials for the degradation of polysaccachrides or other biopolymers. It might find large applications in biofuel production. This is also a demonstration of a new concept for establishing preparative mass spectrometry.

Science objectives for 2010-2012:

- Optimize the ambient ion dissociation device to gain improve dissociation yield
- Seek premium dissociation conditions of polysaccharides such as using novel metal additives for catalysis
- Test the degradation of very large polysaccharides such as cellulose

References

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3. G. Braun, « α-Cellobiose Octaacetate”, *Org. Syntheses,* **2**, 24 (1943).
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Knowledge-guided Screening Tools for Identification of Porous Materials for CO_2 Separation

Maciej Haranczyk, Principal Investigator
Berend Smit, Juan Meza, Co-Principal Investigators

One Cyclotron Rd 50F-1650, Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA 94720
Email: MHaranczyk@lbl.gov ; Web: hpcrd.lbl.gov/~maciej

Collaborators: Jennifer Kloke, Gunnar Carlsson, Stanford University, Palo Alto, CA
Chris H. Rycroft, James A. Sethian, LBNL, Berkeley, CA
Rajamani Krishna, University of Amsterdam, Amsterdam, The Netherlands

Overall research goals: The goal of the project is to develop new techniques for fast screening of databases of porous materials. In our approach, the computational effort required to characterize the entire library of structures in order to perform screening is reduced to a large extent by a knowledge-based and similarity-based selection of structures to undergo characterization. The development of the proposed approach involves three steps: (1) development of structure descriptors and structure similarity measures operating on them; (2) selection and computational characterization of an initial set of structures, and then (3) knowledge extraction and execution based on variety of techniques, including similarity-based and machine learning methods.

Significant achievements in 2009-2010: We have developed a prototype version of our screening approach that allows performing similarity searches on a database of zeolite structures. This approach exploits a Similarity Principle that states that structurally similar structures are likely to have similar properties. At the same time we have run molecular simulations of an initial set of 20 zeolite structures to predict their adsorption selectivity of CO_2 with respect to methane. We found the AFX structure, with the CO2/CH4 selectivity ratio of few hundreds, to be the best in the characterized set. The identification of this one structure with desired selectivity has allowed us to test and demonstrate similarity searching at work. At the initial state of the project we have focused on screening the database of 191 known zeolite frameworks, the IZA database, and we identified a number of zeolite frameworks for CO2 separation.

Identification of similar structures to AFX was done as follows. The similarity between zeolites was determined on the basis of pore geometry and structure topology. We used data fusion to merge two dissimilariy measures: (1) difference of diameters of free spheres, which is a convenient measure of pore diameter and is expected to reflect selectivity towards CO_2; (2) distance based on structure topology obtained with the Mapper approach. Mapper extracts a simple description of 3D data in the form of simplicial complexes (simplexes, see Fig. 1, left) with far fewer points that capture topological and geometric information. The simplexes could be compared using the Gromov-Hausdorff distance measure. All pairwise (dis)similarities of known 191 zeolites were calculated. We then performed hierarchical clustering to find clusters of similar structures. The cluster containing AFX and another 10 structures was subjected to further computational characterization. Fig. 1,right presents results obtained for two selected zeolites. It can be clearly seen that these structures, similar to AFX, perform very well in CO_2 separation.

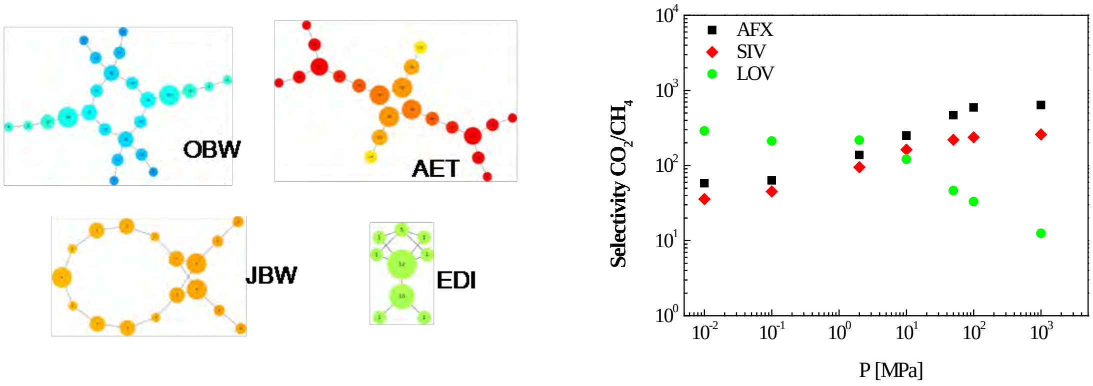

Figure 1. (left) These graphs represent the topology of four zeolite structures. Nodes of each graph are obtained by clustering of atoms of similar density and are colored according to values of density. (right) Adsorption selectivities for CO_2 as a function of pressure from equimolar binary mixture simulations of CO_2/CH_4 at 298 K.

Science objectives for 2010-2012:

- The current version of similarity searching tools as well as those zeolites indentified as having high selectivity will be used to conduct screening of a database of hypothetical zeolites.
- Development of the similarity searching approach will continue. In particular, we plan to develop a fragment-based approach which will measure similarity of zeolites by comparing occurrences of same and/or similar structural fragments (eg. specific pore connections or pore sequences).
- Execution of the structure characterization code on the DOE Leadership class computers will be enabled. Intensive structure characterizations of large numbers of zeolites will be performed. The results will be used to further improve and refine the screening technique, in particular by employing machine learning tools.

References to work supported by this project 2009-2010:

1. K. Theisen, B. Smit, M. Haranczyk, “Chemical Hieroplyphs: Abstract Depiction of Complex Void Space Topology of Nanoporous Materials”, J. Chem. Inf. Model., submitted.
2. N.E.R. Zimmermann, M. Haranczyk, M. Sharma, B. Liu, B. Smit, F.J. Keil, “Adsorption and Diffusion in Zeolites: The Pitfall of Isotypic Crystal Structures”, Micro. Mesoporous Mat., submitted.

Quantum Dots as a Probe of Charge Transport in Nanostructured Thin Films

Michael D. Barnes, Principal Investigator
710 LGRT University of Massachusetts-Amherst, MA 01003
Email: mdbarnes@chem.umass.edu

Collaborators: Dr. Paul Lahti, Chemistry University of Massachusetts-Amherst
Dr. Todd Emrick, Polymer Science & Engineering, University of Massachusetts-Amherst

Overall research goals: The principal aim of our research is to obtain a molecular-level understanding of the role of architecture and local environment in macromolecular systems in determining photonic or optoelectronic properties. Our experimental approach utilizes a combination of single-molecule imaging and spectroscopic tools combined with scanning probe microscopies whereby a high level of morphological and dynamical information can be obtained through analysis of attributes of fluorescence photons emitted from the material of interest.

Significant achievements in 2008-2010: Understanding energy and charge exchange processes in nanostructured materials is critically important for development of high-efficiency optoelectronic devices. Surface-functionalized quantum dot (QD) systems with semiconducting organic materials offer an interesting material format to explore such interactions, where the molecular architecture and choice of ligands can be used to manipulate spatial, temporal, and spectral properties of the QD luminescence. Recent work in our laboratory (as well as others) has shown that ligands with electron-donating character can profoundly affect fluorescence intensity fluctuations (blinking) and photostability in isolated QD systems. In similar systems where surfactants have been used to facilitate charge transfer between nanocrystals and organics, strong modification of QD photoluminescence intensity fluctuations (blinking suppression) have been observed. Our recent work provides compelling evidence of a Stark modified QD fluorescence spectrum combined with an induced linear polarization resulting from the electronic perturbation of a single point charge. These results suggest a new application of quantum dots as a fluorescent probe of moving charge carriers in the condensed phase.

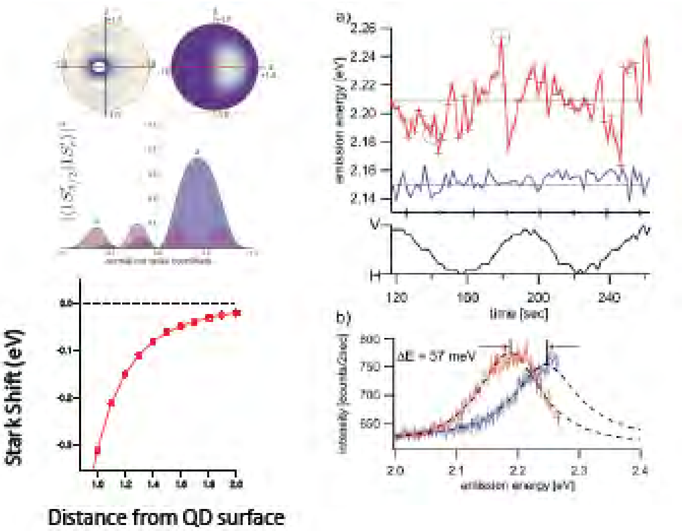

Figure 1. Simulation of point-charge induced polarization and Stark shift of QD luminescence (Left); experimental measurement of polarization-dependent Stark shift from a single CdSe-oligo ppv nanoparticle. The ≈ 60 meV (peak-topeak) shift is consistent with an average electron distance from the QD surface of 1.4 nm. (K. T. Early, et al. *Nano Letters,* submitted)

The DC Stark interaction in quantum dot systems derives from mixing of electron/hole orbitals of different symmetry using a strong linear electric field, and is manifested as a shift in luminescence wavelength. This effect has been well studied using macro-scale electrode systems that can support the large voltages (high electric fields) necessary to generate the electron-hole polarization. Figure 1 shows results of our simulations (left) and experimental measurements (right) on the effect of the electric field generated from a *single charge carrier* (free electron or proton). For a distance of a ≈ 1.5 nanometers from the surfaceof the QD, this field can induce both a significant DC Stark shift (≈ 60 meV) in the luminescence along with a strong induced linear polarization. To probe this effect experimentally, we used a QD system with conjugated organic ligands tethered to the QD surface. Photoexcitation of the ligands results in efficient charge separation in the organic that “pins” the electron near (≈ 1.3 nm) the QD surface, and we are able to measure the resulting change in QD luminescence wavelength. Because of the linear polarized nature of the ligand absorption, the observed Stark shift is correlated with excitation polarization shown in upper right of Figure 1.

Our collaboration with Paul Lahti, and Todd Emrick at UMass is ultimately focused on the synthesis and characterization of molecular-wire prototypes that present proton donating/accepting moeties with a "well-defined" spatial arrangement. The crucial technological advance represented by this work is the realization of an in-situ charge sensitive quantum dot probe that can report on distance (on a scale of 0.5 - 3 nm) and relative orientation of the moving charge, which will provide new insights into charge shuttling mechanisms in scaffolded macromolecular systems.

Science objectives for 2010-2012(style=Stand alone text heading):

- Evaluate time-resolved probes of electronically perturbed quantum dot luminescence for high-speed mobility measurements
- Explore time evolution of polarized emission in quantum dot systems; connection with QD symmetry (c-) axis orientation.
- Near-field probes of charge and energy exchange in coupled quantum dot/CdSe-opv films.

References to work supported by this project 2008-2010:

M. D. Barnes, J. Labastide, M. Odoi, K. T. Early, “Probing charge-transport in nanostructured materials with single molecules” J. Phys Chem Letters (invited *Perspective*) submitted March 2010.

K. T. Early, P. K. Sudeep, T. Emrick, and M. D. Barnes, “Polarization-driven Quantum Dot Stark Shifts in Individual CdSe-oligo phenylene vinylene Nanoparticles,” Nano Letters, submitted January 23, 2010.

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K. T. Early, P. K. Sudeep, K. D. McCarthy, T. Emrick, and M. D. Barnes, “Linear dichroism and linearly polarized emission from pseudo-spherical CdSe-oligo phenylene vinylene nanostructures” *ACS Nano* **3**, 453, (2009).

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Femtosecond Electronic Spectroscopy of Nanostructures and Their Functional Assemblies

Yingzhong Ma, Principal Investigator
P.O. Box 2008, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831
Email: may1@ornl.gov; Web: http://www.ornl.gov/sci/csd/Research_areas/lscm_group.html

Collaborators: Prof. Graham R. Fleming, University of California, Berkeley, CA
Prof. Mark C. Hersam, Northwestern University, IL
Prof. Leonas Valkunas, Vilnius University, Lithuania

Overall research goals: Fundemantal understanding of electronic coupling and energy transfer is important for solar energy utilization. The research objectives are to study ultrafast exciton dephasing and diffusive motion of localized excitons in semiconducting nanostructures and their assemblies employing femtosecond two-pulse photon echo (2PE) and frequency-resolved transient absorption spectroscopic techniques. Our goals are to determine experimentally the dephasing time scales and diffusion coefficients and lengths, and to explore their intrinsic correlations with the dimensions of system confinement. We will also seek quantitative information about exciton motion between proximal nanostructures in chosen assemblies, which should provide basic insights into the nature of electronic couplings and mechanisms governing energy transfer processes.

Significant achievements: A systematic study of ultrafast exciton dynamics was conducted in structurally distinct semiconduting single-walled carbon nanotubes (SWNTs) employing complementary femtosecond spectroscopic techniques. We performed the first and so far the only femtosecond fluorescence up-conversion experiments with sub-100 fs time resolution and tube type selectivity [1]. Detailed measurements on five different tube species under various excitation intensities enabled us to reveal a remarkable exciton-exciton annihilation process arising from the spatial confinement of this quasi-one-dimensional (quasi-1D) nanomaterial. Application of a frequency-resolved transient absorption technique further allowed us to identify novel spectroscopic and dynamical signatures of the annihilation [2] and to quantify the exciton binding energy [3].

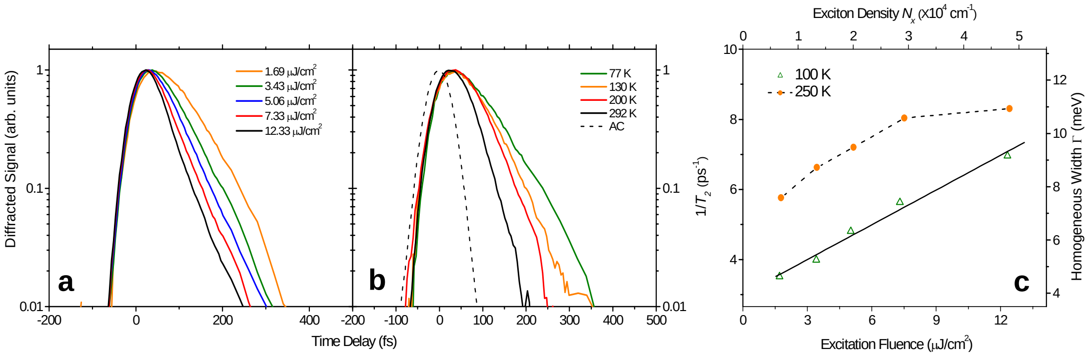

Figure 1. Time-integrated 2PE data collected by employing 45 fs laser pulses centered at 990 nm. (a) Data collected at 100 K for five different excitation intensities. (b) Data collected at 77, 130, 200 and 292 K under the lowest excitation intensity used (~1.70 μJ/cm^2). The dashed line is the autocorrelation function of the two laser pulses. All the data have been normalized at the signal maxima. (c) Exciton dephasing rates and the corresponding homogeneous line widths determined at 100 and 250 K. The solid line is the linear fit to the data obtained at 100 K, and the dashed line is drawn to guide the eye.

More recently, we carried out the first time-domain study of exciton dephasing in semiconducting SWNTs [4]. The experiment was performed using a femtosecond 2PE technique and a sample highly enriched in the (6, 5) tube. Through systematic measurements at different intensities and temperatures, we found that both exciton-exciton and exciton-phonon scattering processes have profound effects on exciton dephasing (see Figure 1a,b). Both the dephasing rates and the corresponding homogeneous line widths increase with excitation intensity, but the precise intensity dependences vary markedly with lattice temperature. At 77, 100 and 130 K, the intensity dependence is linear, whereas a clear deviation from linearity was observed at higher temperatures (see Figure 1c for representative results). Our analysis in the zero-intensity limit further identified the dominant phonon mode as an out-of-plane transverse optical mode with frequency of 847 cm^{-1}. A particularly significant finding of this study is the surprisingly long-lived exciton coherence that persists ~160 fs even at room temperature.

This long-lived exciton coherence highlights an important role of coherent excitons in the fundamental photophysics of this quasi-1D nanomaterial, which remains poorly understood. Profound effects of the coherence on ultrafast exciton dynamics have been revealed in our recent studies. For instance, we found an unusual and anomalous dependence of femtosecond time-integrated three-pulse photon echo peak shift on the intensity of the excitation laser pulses. The peak shift increases approximately exponentially with decreasing excitation intensity [5,6]. Such an intensity dependence has never been observed in molecules, molecular aggregates and complexes, or polymeric systems. We further found evidence for direct involvement of coherent excitons in non-linear exciton-exciton annihilation [7].

Future research objectives:

- Extend our investigations to both CdTe and copper-phthalocyanine nanowires to learn whether the long-lived exciton coherence is a generic phenomenon for spatially confined quasi-1D systems.
- Investigate potential correlation between key dynamical parameters (dephasing times and diffusion coefficients) and the diameter of semiconducting SWNTs through systematic studies of various structurally distinct tube species employing femtosecond 2PE and frequency-resolved transient absorption techniques.
- Determine quantitatively the diffusion coefficients and charge separation timescales for exciton migration in polymeric nanostructures. We will also seek connections between these photophysical characteristics and the overall performance of these materials in photovoltaic cells through joint efforts with materials and computational scientists.

Relevant publications:

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7. M. W. Graham, Y.-Z. Ma, A. A. Green, and M. C. Hersam, and G. R. Fleming, "Exciton annihilation and dephasing dynamics in semiconducting single-walled carbon nanotubes," Invited Paper, Proc. of SPIE, Vol. 7600 (2010).

Chemistry and Microphysics of Small Particles

Alla Zelenyuk, Principal Investigator
Timothy Vaden, Post Doctoral Associate
Pacific Northwest National Laboratory, Richland, WA 99354
Email: alla.zelenyuk@pnl.gov ; Web: http://emslbios.pnl.gov/id/zelenyuk_an.

Collaborators: Prof. Finlayson-Pitts (UCI), Prof. Mueller (SUNY), Dr. Zaveri (PNNL)

Overall research goals: The research objective is to develop and apply unique tools and methods to study the fundamental properties and processes that govern the chemistry and microphysics of particles at the nanoscale.

Significant achievements in 2006-2008: This project proceeded along three parallel pathways: 1) Extending capabilities for quantitative, high-precision, high-sensitivity, multidimensional characterization of individual aerosol particles; 2) study of the chemistry and microphysics of size-selected nanoparticles; 3) development of novel data analysis and visualization approaches.

With SPLAT II, our new generation single particle mass spectrometer, we have established unparalleled sensitivity for single particle detection, sizing precision, mass-spectral quality, and temporal resolution. We demonstrated that the two-step IR/UV approach yields reproducible and quantitative mass spectra with significantly reduced fragmentation. Most recently, we added a parallel data acquisition mode that provides quantitative measure of particle number concentration and particle asphericity parameter with 1 sec resolution, and size distributions with 60 sec resolution. We also developed a novel approach to measure the density of chemically resolved particles based on particle vacuum aerodynamic size distributions and without use of a DMA.

Taking advantage of the recently developed method for real-time identification of particle asphericity, we determined shape, phase, and precise density of α-pinene SOA particles.

We developed a depth-profiling method and demonstrated its utility to characterize the morphology of NaCl particles coated with DOP, pyrene, and SOA. We applied this method to unambiguously show that the hydrophilic SOA and hydrophobic POA form layered particles and to characterize organic layers as thin as a monolayer. In addition, we found that when homogeneously nucleated SOA particles are formed in the presence of hydrophobic organics vapors, they adsorb a surprisingly thick coating. This acquired layer increases particle mass, impacts the gas-to-particle partitioning, and affects the rates of particle evaporation and heterogeneous reactions.

The interaction between pre-existing hygroscopic salt particles and SOA was investigated using oxidized α-pinene in the presence of sodium nitrate particles in a large flow tube reactor. We find that this SOA contains a significant amount of organic nitrates. The SOA coated sodium nitrate particles exhibit a wide range of coating thicknesses. Most importantly, the data show that organic SOA coatings as thin as a monolayer cause water retention by the sodium nitrate cores.

Fundamental studies of the properties of exhaust particulates formed by a new generation research engine revealed that these particles have vacuum aerodynamic diameters between 50 to 60 nm, have a fractal dimension of 2.14±0.03, composed of the primary spherules with diameters of 15-25 nm, and have significant content of PAHs and other organics.

To take full advantage of the vast amounts of detailed multidimensional data that SPLAT II produces in addition to our data mining and visualization software, SpectraMiner, we developed and applied a new program, called ClusterSculptor. It uses a novel, visually driven, expert-steered data classification approach to aid scientists in data classification. We demonstrated that these approaches have applications far beyond the single particle mass spectrometry.

Science objectives for 2010-2012:

- Investigate the effect of pre-existing particles and their associated gas-phase component on the mechanism of formation and chemical and physical properties of SOA-containing particles.
- Investigate the effect of size, composition, shape, and morphology on particle reactivity, hygroscopicity, CCN and IN activity.
- Quantify the chemical, microphysical properties and transformation dynamics of fractal soot.
- Continue development and application of novel approaches to multidimensional data analysis.

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Investigation of Transport Mechanisms in Surface Modified Inorganic Membranes

J. Douglas Way[1], Principal Investigator
Mark T. Lusk[2], Co-Principal Investigator
Mayur Ostwal, Post-Doctoral Fellow
[1]Dept. of Chemical Engineering and [2]Dept. of Physics, Colorado School of Mines, Golden, CO 80401
Email: dway@mines.edu; Web: http://www.mines.edu/Academic/chemeng/faculty/dway

Overall research goals: The objective of this project is to synthesize, characterize, and investigate the transport mechanisms in surface modified inorganic membranes for the separation of CO_2 from other light gases such as N_2 and H_2. In particular, chemical modification of mesoporous silica with 3-aminopropyl-triethoxy silane, allows selective transport of CO_2 over N_2 at 373 to 393 K via a "chained carrier" transport mechanism.

Significant achievements in 2008-2010: The CO_2/N_2 selectivity of mesoporous (4 nm) silica membranes is enhanced by surface modification using APTS (3-aminopropyl-triethoxy silane). Unmodified silica membranes exhibited Knudsen diffusion behavior and are nitrogen selective. Gas separation experiments were performed on the modified membranes for both pure gas and mixed gases for a range of temperatures and feed gas compositions. As shown in Figure 1 below, mixed gas separation factors as high as 10 for CO_2 over N_2 were observed at 393 K and CO_2 partial pressures of 15 kPa; whereas for pure gases (CO_2 partial pressure of 303 kPa), no separation was seen. The hypothesized transport mechanism is the reaction of CO_2 with surface amine groups to form a carbamate species and subsequent surface "hopping" of carbon dioxide. The CO_2 binding at ambient conditions is sufficiently strong to greatly inhibit the surface diffusion of CO_2. However, as the temperature increases, the CO_2 permeance increases and selective transport of CO_2 is observed. The influence of driving force on the CO_2 permeance is highly non-linear, and permeance increases with decreasing CO_2 partial pressure in the feed gas. NMR studies performed on the bare support and modified membrane shows the support has been modified by APTS. Characterization of the APTS/silica membrane with adsorbed CO_2 by NMR shows the presence of a carbamate species and thus supports the hypothesized reaction mechanism or facilitated solid-state CO_2 transport. The binding energy for CO_2 adsorption is 15.5 kcal/mol and activation energy for CO_2 diffusion/hopping from one amine group to another of APTS is 7.2 kcal/mol as computed using ab-initio Density Functional Theory (DFT). Figure 2 shows the molecular models used for the calculation of CO_2 binding energy. Based on these data, our hypothesis is that the selectivity of APTS membranes can be increased by reduction in the pore size to minimize transport of gases other than CO_2.

Science objectives for 2010-2012:

- Investigate the effect of reducing the effective pore size of the substrate on CO_2 transport and CO_2/N_2 mixed gas selectivity. Technical approaches will include reduction of the mesoporous silica pore diameter using atomic layer deposition and increasing the alkyl chain length of the amine silane.
- Using DFT simulations, examine the effect of amino silane structure on the binding energy of CO_2. This will include electron withdrawing and donating substituent groups, multiple amine functionalities, and the comparison of primary, secondary, and tertiary amines. Candidate silanes will be chosen from those that are available commercially: http://www.gelest.com/
- Investigate the feasibility of using mesoporous carbon membranes, derived from pyrolysis of polymer percursors, as substrates with a pore diameter range of 1 to 3 nm for fabricating higher selectivity amine silane membranes. Adsorbents selective for CO_2 have been reported in the

literature synthesized by modifying activated carbon, molecular sieve carbon, and carbon nanotubes with APTS or similar amino silanes.

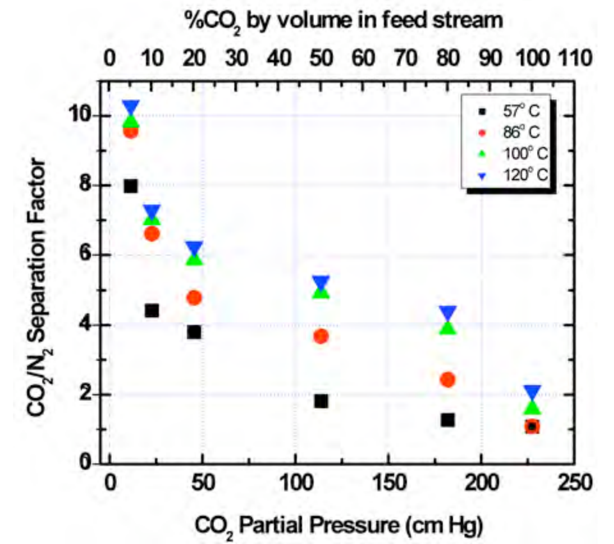

Figure 1. Effect of temperature and gas composition on CO_2/N_2 separation factor of APTS silica membrane

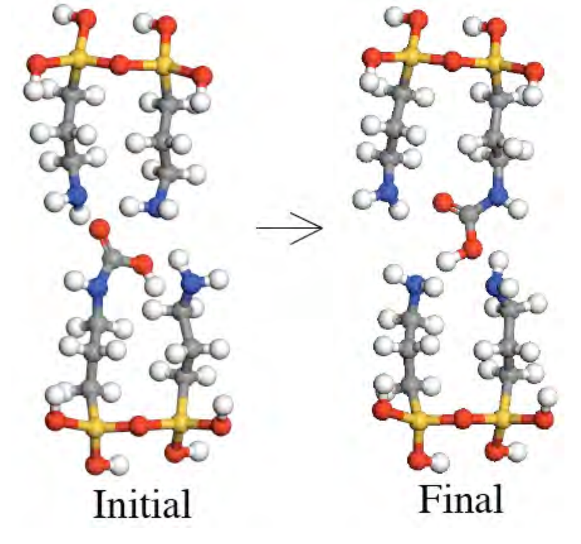

Figure 2. Double-inverted amine silane groups for DFT simulation of CO_2 binding energy

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Session 7 – Analysis and Material Properties

Analysis of the Metabolites of Lipids in Microalgae by Two-Dimensional HPLC

Georges Guiochon
Department of Chemistry, University of Tennessee, Knoxville, TN, 37996-1600
Email: Guiochon@utk.edu

Collaborators: Jacob N. Fairchild, Department of Chemistry, University of Tennessee
Dr. Krisztian Horvath, Department of Chemistry, University of Tennessee
Gengen He, Department of Microbiology, University of Tennessee

Overall research goals: The research objectives are to identify a maximum number of the metabolites involved in the synthesis of lipids by selected microalgae, to elucidate the relative role of these compounds in these syntheses, and to unravel the important chemical pathways of these reactions. The work is done in cooperation with a group of biochemists. The ultimate goal would be to find ways to orient and accelerate the production of raw materials for the production of biofuels.

Significant achievements in 2008-2010: In 2008-2009, we completed our development of highly effective separations of protein digests by two-dimensional liquid chromatography [1-9]. Our new project consists in applying the same analytical method to the separation and identification of the metabolites of microalgae, particularly those involved in the synthesis of lipids. To begin a project of this importance we need to develop several techniques, including (1) a method of production of sufficient amounts of selected microalgae; (2) an analytical procedure for the extraction of the metabolites from the lyzing products of the filtrates of culture solutions; (3) an analytical procedure for the separation of the metabolites by two-dimensional chromatography (2D-LC); (4) the development of methods for the detection, identification, and quantitation of these chemicals.
Although significant progresses have been made in the four sets of problems, the coordination of their solutions has just begun. (1) We selected *Botryococcus Braunii* because it has 50 to 80% of its weight in Triterpenes and grow also a *Prochlorococcus*. We found these microalgae to grow more slowly that we anticipated. In spite of significant support by colleagues in the UT Department of Microbiology, we have so far obtained only limited amounts of dry cell material. (2) To progress further, we are using the same procedures as a biochemist colleague and analyze the metabolites of *Escherichia Coli*. (3) We are developing and testing a comprehensive off-line 2D-LC procedure [2] involving the successive use of a strong cation exchange and a hydrophobic interaction column (see experimental conditions in Figure 1). Detection is carried out by selective reaction monitoring (SRM) in mass spectrometry, successively in the positive and the negative modes. The fractions collected from the eluent of the first separation column are successively analyzed on the second column. Typical examples are reported in Figure 1. The total analysis time is 1.5 hours and the peak capacity about 200. Sensitivity is limited by the large dilution due to the very principle of liquid chromatography. This explains why SRM must be used and why full-scan mass spectrometry detection cannot be used for identification purposes.

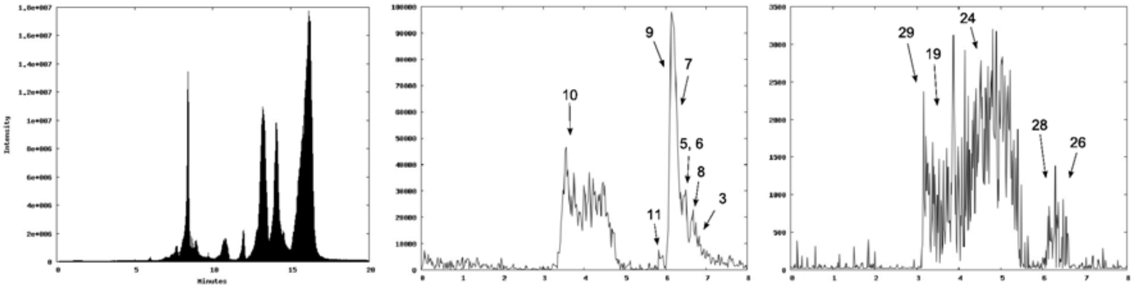

Figure 1. 2D-LC analysis of metabolites of *Escherichia Coli* on (1) a strong cation exchange column (SCE) eluted at 0.2 ml/min, with a 2 to 35% acetonitrile (ACN) gradient in a water solution of NH_4 TFA at pH=3.2 and (2) on a hydrophobic interactions (HILIC) column eluted at 0.25 ml/min, with a 75 to 50% gradient of ACN in a water solution of NH_4 HCO_2^-. Left, chromatogram on the SCE column; enter, chromatogram of the 4th fraction on the HILIC column, with positive ion detection in MS; right chromatogram of the 4th fraction on the HILIC column, with negative ion detection in MS

Science objectives for 2010-2012(style=Stand alone text heading):

- Further work is needed and will be done to improve the quality of the separations by spreading the eluted components over a larger range of elution times and increasing the number of first-separation fractions and the efficiency of the second separation. This will be done by adjusting more finely the experimental conditions, particularly the composition of the solvents used in gradient elution. We will investigate the trade-off between separation power and analysis time.

- We need to reduce the degree of dilution of the compounds eluted during the two steps of the separation, in order to decrease the detection limits and improve the detection sensitivity. Methods of concentrating the fractions collected from the first separation before their injection into the second column will be investigated.

- Having succeeded in markedly improving the performance achieved in the analyses of the metabolites of *Escherichia Coli* by increasing the number of components detected, we will extend the methodology to the analysis of the metabolites of *Botryococcus Braunii*. This requires that we become able to produce significant amounts of the different microalgae necessary.

- The lyzates of *Botryococcus Braunii* should contain also numerous hydrocarbons and lipids, which we will need to analyze. New off-line 2D-LC analytical procedures will be developed for this purpose.

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Bipolar Electrode Focusing for Concentration Enrichment and Analyte Separations

Richard M. Crooks, Principal Investigator
Eoin Sheridan, Postdoctoral Associate
Robbyn K. Anand, Graduate Student
Department of Chemistry and Biochemistry, 1 University Station, A5300, The University of Texas at Austin, Austin, TX 78712-0165
Email: crooks@cm.utexas.edu ; Web: http://research.cm.utexas.edu/rcrooks/

Collaborators: Dzmitry Hlushkou and Ulrich Tallarek, Department of Chemistry, Philipps-Universität Marburg, Hans-Meerwein-Strasse, 35032 Marburg, Germany

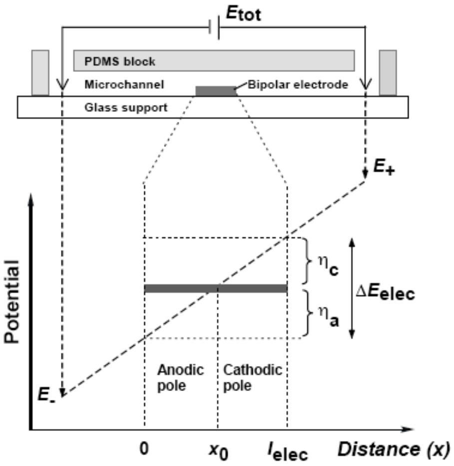

Figure 1. Schematic representation of the PDMS/hybrid device (side view, cross section) containing a gold BPE. At bottom, a diagram of the potential drop in solution, the BPE potential, and resulting overpotential.

Overall research goals: The research objectives of this project are the development of a simple method for the rapid enrichment and separation of analytes within a microchannel. This goal is achieved through the formation and control of an electric field gradient (EFG) resulting from the faradaic reactions occurring at a bipolar electrode (BPE) on the floor of a PDMS/glass microchannel.

Significant achievements in 2008-2010: When a sufficiently large potential is applied across a fluid-filled microchannel containing a gold BPE, the solution potential difference across the length of the BPE induces faradaic reactions at its ends (Figure 1). The resultant EFG generates a unique electrophoretic velocity for each analyte depending on its lateral location and electrophoretic mobility. Each analyte will focus at a unique location at which its electrophoretic velocity is opposite in direction and equal in magnitude to the bulk solution flow (driven by electroosmosis).

Recently, we demonstrated the simultaneous separation and enrichment of three anionic fluorescent dyes into discreet bands (Figure 2). This is significant because this approach is a simple means of avoiding band broadening during separation and is potentially applicable to a wide range of analytes.

Working with our collaborators, we have been able to produce simulations of the electric field profile within the microchannel. These simulations have allowed us to better understand previously unexplored underlying principles. Recently, for example, we have employed an array of 15 microband electrodes (Figure 3) to obtain a map of the EFG. Any two of these microbands may be connected externally by a conductive wire or an ammeter to form a BPE. The potential difference between neighboring pairs of the remaining microbands is a measure of the local electric field strength. Our experimental results confirm simulations (Figure 4). We have found that by coating the internal walls of the microchannel with a surfactant such as Pluronic F108, the EFG is steeper allowing significantly greater enrichment of a single analyte (2500-fold).

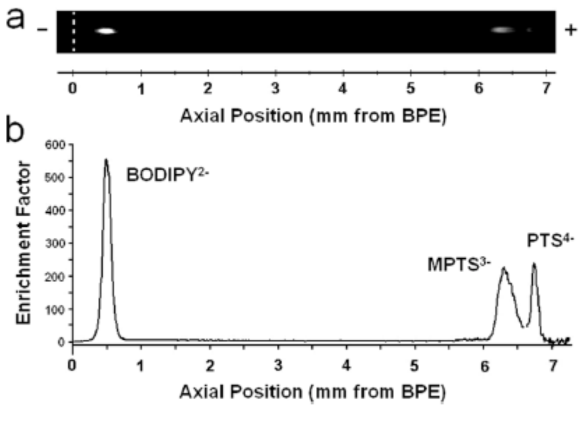

Figure 2. a) Fluorescence micrograph (top view) showing separation of BODIPY disulfonate (BODIPY^{2-}), methoxypyrene trisulfonate (MPTS^{3-}), and pyrene tetrasulfonate (PTS^{4-}) in 5.0 mM TRIS (pH 8.0) 200 s after application of E_{tot} = 40 V in a 12 mm-long Pluronic-modified channel. B) Plot of enrichment factor vs axial location corresponding to part a.

Using these microband arrays, the enriched band may be transported within the microchannel by rapid switching of the connected microbands forming the BPE. This development might make it possible to deliver discrete, concentrated packets of analyte for on-chip analytical applications.

Another significant development that we have recently made is the ability to monitor the formation, and position of an enriched band of analyte by tracking the current passing through the BPE. We have shown that the BPE current increases significantly upon formation of an enriched band, and decreases linearly as the band is pushed away from the cathodic edge of the BPE by pressure driven flow. This principle has been demonstrated with two fluorescent dyes, and could enable monitoring the enrichment of non-fluorescent species.

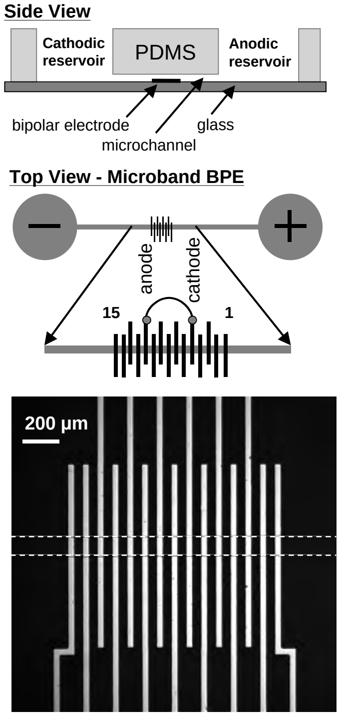

Figure 3. Side and top view schematics of the PDMS/glass hybrid microfluidic device with 15 microband electrodes. Optical image of the electrodes. Dashed lines denote the microchannel.

Science objectives for 2010-2012:

- Exert fine control over the EFG to suit individual analytes, separations, and applications.
- Miniaturization of device components by one and two orders of magnitude to investigate surface effects and ascertain applicability of BPE focusing in nanofluidics.
- Monitoring the evolution of the EFG during analyte enrichment to better understand the increased BPE current upon formation of an enriched band.
- Development of a BPE-based electrochemical detection method that can be integrated into the microchannel.
- Delivery of enriched analyte off-chip.

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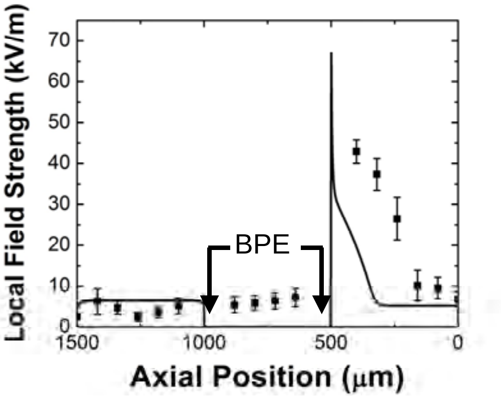

Figure 4. Numerical simulation (solid line) of the axial electric field at 3 µm above the channel floor. Experimental data (squares) measured as the potential difference between neighbouring microband electrodes. The BPE is located from x = 500 to 1000 µm.

Inelastic Neutron Scattering (INS) Studies of Oxide Nanoparticles

Nancy L. Ross, Principal Investigator
Elinor C. Spencer, Postdoctoral Research Associate
Dept. Geosciences, Virginia Tech, Blacksburg, VA 24061
Email: nross@vt.edu; Web: www.crystal.vt.edu/crystal/nlr/index.html

Collaborators: Dr. Alexandra Navrotsky, NEAT ORU, UC Davis, CA
Dr. Brian Woodfield, Dept. Chem., Brigham Young Univ., UT
Dr. Juliana Boerio-Goates, Dept. Chem., Brigham Young Univ., UT
Dr. Alexander I. Kolesnikov, SNS, ORNL, Oak Ridge, TN

Overall research goals: The research objectives are to evaluate the influence of nanoparticle structure and composition on the thermodynamic properties of water confined to their surfaces and to investigate the extent of the magnetic heat capacity intrinsic to magnetic nanomaterials. The large incoherent neutron scattering cross-section of hydrogen relative to transition metals and the absence of selection rules facilitate the use of inelastic neutron scattering (INS) techniques to probe the dynamics of water adsorbed on the surface of the particles. Furthermore, INS spectra of magnetic nanoparticles allow evaluation of the magnetic heat capacity associated with the particles themselves.

Significant achievements in 2008-2010: Analysis of the INS spectra of 7 nm TiO_2 rutile collected on HRMECS (IPNS) on $TiO_2 \cdot 0.37H_2O$ and $TiO_2 \cdot 0.22H_2O$ showed that the hydrodynamics of the confined water is influenced strongly by the intermolecular interactions between the water and the nanoparticle surface. The level of hydration does not have a significant influence on the thermodynamic properties of the rutile-TiO_2 nanoparticles. INS spectra collected on SnO_2 cassiterite showed that the water confined on the surface is suppressed relative to that in ice-Ih, but less strongly constrained than in TiO_2 rutile suggesting that TiO_2 has stronger H_2O-surface interactions.

INS spectra collected on 1-2 nm nanoparticles of SnO_2 with 1.07 ±0.04 moles H_2O at ARCS (SNS) suggested that the 1-2 nm sample with the larger surface area contains mainly dissociated water in the form O-H groups. Follow-up studies of INS spectra collected at TOSCA (ISIS) confirm that structure of water confined on 1-2 nm SnO_2 particles is different from that of larger particles. This result has implications for the thermodynamic properties of

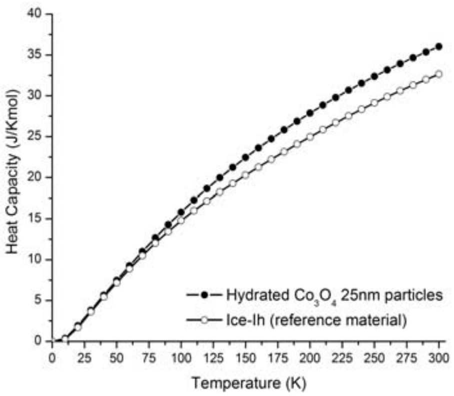

Figure 1: Isochoric heat capacity of hydration layers on the surface of 25nm Co_3O_4 .

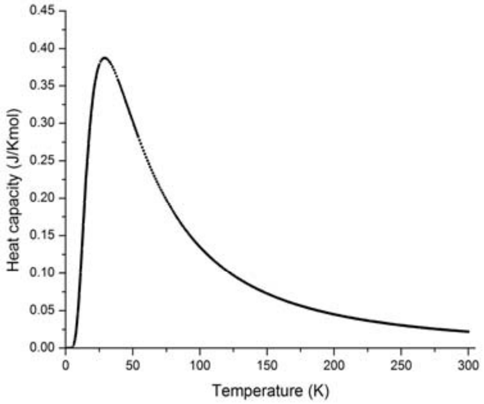

Figure 2: Magnetic contribution to the heat capacity of 25nm Co_3O_4 calculated from INS data.

the hydrated nanoparticle. Further analyses are underway to unravel the effects of particle size, hydration level, and structure and dynamics of water adsorbed on the nanoparticles.

An INS spectrum at 11K of 25 nm Co_3O_4 with 1.83 wt.% H_2O was recently collected on TOSCA (ISIS). Figure 1 shows the vibrational heat capacity that was calculated from the phonon density of states encompassing the translational (0-40 meV) and librational (60-120 meV) bands of water. In addition, the low-energy (5 meV) magnetic excitation peak permitted the magnetic contribution to the heat capacity of the antiferromagnetic particles to be determined (Fig. 2). We plan to build on the success of this experiment by exploring the influence of temperature on the magnetic contribution to the heat capacity.

Science objectives for 2010-2012:

- Complete synthesis CoO and Co_3O_4 nanoparticles with well-defined water contents and differing particle sizes and collect INS spectra on TOSCA (ISIS) and ARCS (SNS): (i) to compare the hydrodynamics and thermodynamic properties of water confined on their surfaces; (ii) to investigate the influence of the magnetic state of the Co_3O_4 and CoO lattice on the properties of the hydration layers.
- Collect variable temperature INS data on SEQUOIA (SNS) between 5-250K on Co_3O_4 nanoparticles in order to: (i) calculate the magnitude of the magnetic heat capacity as a function of the magnetic state of the particles and (ii) study the influence of temperature on the heat capacity of the hydration layers present on the surface of the Co_3O_4 nanoparticles.
- Begin exploring the ZnO-CoO system to study properties of bulk materials *vs*. nanomaterials and the effect of size on solid solubility, phase transitions, and magnetism.

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Laser-Material Interactions (ablation) for Chemical Analysis

Richard E. Russo, Principal Investigator
Xianglei Mao, Scientist
Vasillia Zorba, Post Doc
Lawrence Berkeley National Laboratory, University of California, Berkeley CA 94720
Email: rerusso@lbl.gov; Web: http://teamd.lbl.gov/

Overall research goals: The objectives of this research are to elucidate fundamental mechanisms underlying laser ablation processes as they relate to chemical analysis. Ablation processes include laser material-interactions, mass ejection, laser-plasma interactions, plume/plasma dynamics, and particle formation.

Significant achievements in 2008-2010: A primary objective in laser ablation solid sampling is to achieve performance metrics comparable to those of liquid nebulization. The precision and accuracy of the $^{238}U/^{232}Th$ ratio were evaluated from nebulization and repetitive pulsed laser ablation with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Nanosecond (ns) and femtosecond (fs) pulsed lasers at 266 nm wavelength were utilized for the ablation studies (Figure 1). We found that similar figures of merit were obtained when we compared fs-laser ablation to liquid nebulization, even though ~4000 times less sample was required with ablation sampling.

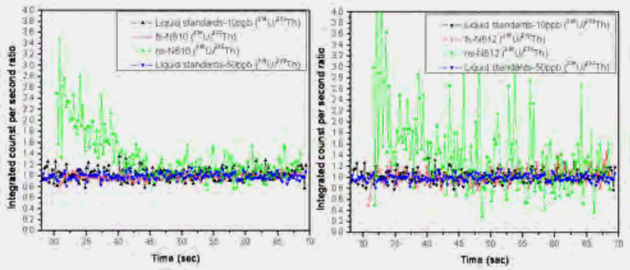

Figure 1. Comparison of the response ratio $^{238}U/^{232}Th$ for the different sample introduction approaches, for NIST 610 and NIST 612.

Laser Induced Breakdown Spectroscopy (LIBS) was used for chemical analysis with a goal to identify the minimum crater size from which spectral emission could be measured in the optical far-field. The crater size, defined as the full width at half maximum (FWHM) of the feature beneath the original substrate, can be as low as 450 nm for the lower energies implemented and this was the smallest diameter for which spectral emission could still be detected in this system. (Figure 2**)**. The corresponding ablated mass was 220 10^{-18} gr for Na and 4.2 10^{-15} gr for K.

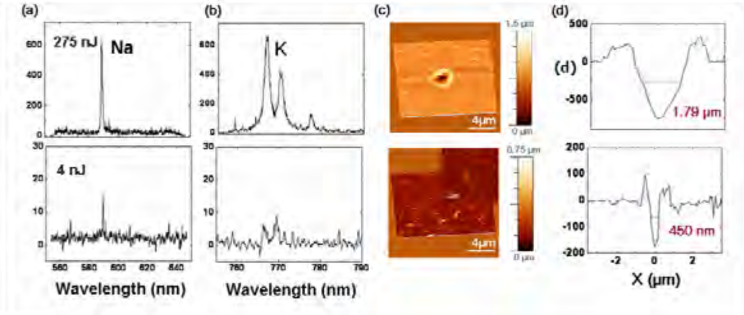

Figure 2. Mica substrate containing 0.62% Na_2O and 9.87% K_2O: LIBS spectral emission generated by a single 400 nm, 100 fs laser pulse at different incident energies in the (a) 550-650 nm and (b) 750-800nm spectral region. (c) AFM surface maps of the corresponding craters and (d) their surface profiles.

In order to further reduce crater dimensions, we studied near-field laser ablation of Si through sub-wavelength apertures, using fs laser pulses. The laser beam (400 or 800 nm) was coupled to an

Near-field Scanning Optical Microscope (NSOM) fiber probe. We found that laser wavelength is important both for the size and type of features that can be obtained, which can be tuned between craters and protrusions (Figure 3). Under optimal conditions craters as small as 30 nm in FWHM with a depth of ~1 nm were obtained.

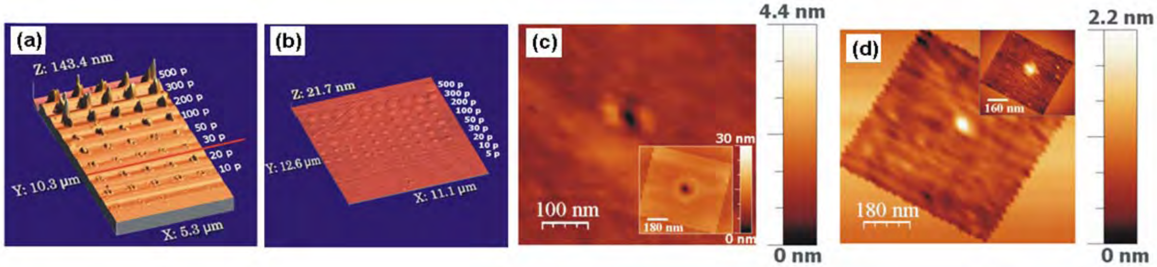

Figure 3. AFM surface map of a near-field fs laser processed Si surface at (a) 400 nm, and (b) 800 nm, for different number of laser pulses. The smallest structures that could be formed at (c) 400 nm, and (d) 800 nm.

Science objectives for 2010-2012:

- Advance experimental and theoretical understanding of ultrafast pulsed laser material interactions as related to chemical analysis
- Elucidate laser material interaction mechanisms as function of spatial scale (macro to nano)
- Extend laser-based chemical analysis to the nanoscale through far-field femtoseocond and near-field laser ablation.
- Propose and analyze processes for measuring spectral emission or enhancing ionization for mass spectrometry as mass removal approaches 10^8 atoms or less.

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Laser-Material Interactions Relevant to Analytic Spectroscopy of Wide Band Gap Materials
DE-FG02-04ER-15618

J. Thomas Dickinson, Principal Investigator
Stephen C. Langford, Postdoctoral Research Associate
Sharon George and Enamul Kahn, Graduate Students
Department of Physics and Astronomy, Washington State University, Pullman, WA 99164-2814
Email: jtd@wsu.edu; Web: www.wsu.edu/~jtd/

Collaborators: Dr. Wayne Hess, PNL, P.O. Box 999, K8-88, Richland, WA 99352
Dr. Lynn Boatner, ONRL, P.O. Box 2008, MS6056, Oak Ridge, TN 37831-6056
Dr. Stefano Orlando, Consiglio Nazionale delle Ricerche, Italy
Dr. Kenichi Kimura, Research Institute, National Printing Bureau, Japan
Several Research Groups at Washington State University

Overall research goals: To characterize laser-materials interactions relevant to laser-based sampling and chemical analysis of wide bandgap materials. Since absorption in these materials is often mediated by defects, they are a major focus. We also focus on thermal, chemical, and physical interactions/mechanisms responsible for matrix effects and mass-dependent transport/detection at surfaces and interfaces.

Significant achievements in 2008-2010:
ZnO nanoparticles formed during 193-nm irradiation.[3,5] In the course of particle emission measurements in vacuum, we discovered an unexpected gray/black coloration on single crystal ZnO. ZnO is generally resistant to defect formation by laser irradiation. Optical spectroscopy showed evidence for metallic zinc, which subsequently proved to have formed particles typically 20 nm in diameter on the surface, shown in Fig. 1. The ZnO in this study was provided by Dr. Lynn Boatner, ONRL; Wayne Hess of PNNL assisted with TEM and x-ray diffraction work that verified the presence of metallic Zn nanoparticles. These nanoparticles reflect 193-nm radiation strongly and thus limit absorption at low fluences. We carefully determined in detail the laser-driven processes leading to the delivery of metallic Zn to the crystal surface.[11] The production of these particles is initiated by photo-induced vacancy formation in the near surface region which also serve as a source for copious laser desorption of atomic Zn, O, as well as singly charged Zn^+ and O^+.

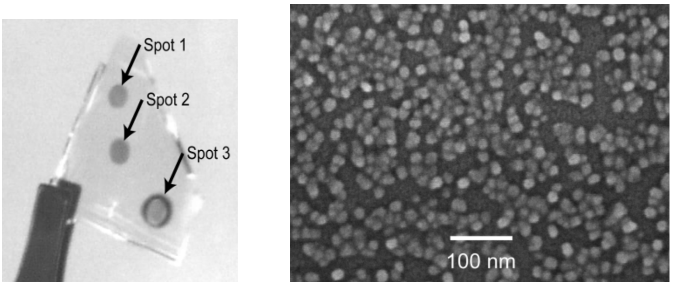

Figure 1. Optical and scanning electron images of single crystal ZnO after exposure to 193-nm laser radiation. Spot 1 on the left was produced by 2000 pulses at a fluence of 210 mJ/cm^2. The particles on the right (typically 20 nm in diameter) were produced on the irradiated surface exposure to 1000 pulses at the same fluence.

Pre-Breakdown Optical Atomic Emissions from ZnO irradiated at 193 nm. In a related study, we find that in recent measurements of atomic line emission (ALE) from single crystal zinc oxide at 193 nm, we observe spectral emission lines from atomic zinc that cannot be attributed to collisional excitation nor optical breakdown (the normal origin of a visible "plume" above a laser irradiated surface). These emissions are confined to the triplet 4p manifold; breakdown and collisional excitations would excite transitions on the singlet manifolds as well. The effect is dramatic: decay of the dominant triplet excitations yields a brilliant blue emission in front of the irradiated spot (a few time resolved images shown in Fig.2, left hand side and middle). As the fluence is raised to a value ~three times the threshold for exciting the triplet excitations (right hand side of Fig.2), the onset of avalanche breakdown/collisional excitation (plume formation) is marked by the appearance of a bright white continuum which decays on time scales of microseconds to broad Zn spectral lines and then to non-broadened lines (corresponding to left hand side/middle of Fig. 2). The white plume and broadened spectral features are consistent with Stark broadening normally accompanying breakdown. A major addition (with breakdown) is the appearance of the singlet transitions completely missing from the pre-breakdown emissions.

We propose that in the absence of breakdown, the $3d^{10}4p(^2P^\circ_{3/2})5s$ autoionizing state at 103,001 cm^{-1} is reached via a two-photon excitation at 193 nm. The radiative decay of a nearby set of autoionizing states ($3d^{10}4p^2$, near 80,000 cm^{-1}) is believed to produced bound states almost exclusively in the triplet manifold.[28] Such a scheme would explain the radiation observed here. These excitations lies *above* the ionization energy of atomic zinc (75,769 cm^{-1}), which could easily (but in our opinion, wrongly) be ignored as a source of excitation. The spectra associated with the images on the left and middle show only triplet emissions which we propose are excited by *collisionless* processes. A detailed mechanism for the low fluence ALE has been developed.

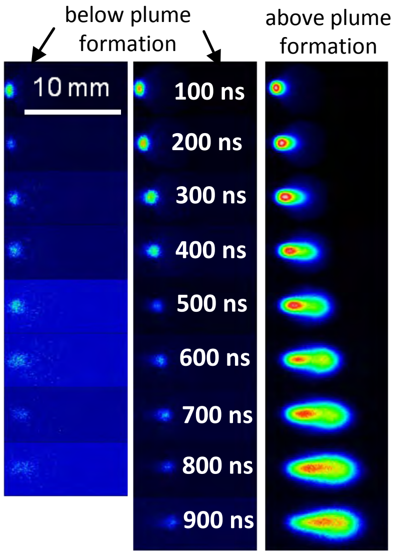

Figure 2. Images of time resolved light emission from single crystal ZnO exposed to193 nm excimer laser pulses at fluences below (left) 1.2 J/cm^2 and above (right). Times == times after laser pulse.

Other areas of progress include: (i) Studies of negative ion formation during excimer laser irradiation of alkali halides and fused silica.[1,8,9], (ii) in situ VUV spectroscopy of fused silica and calcium fluoride, and (iii) polymer decomposition[4] with emphasis on the role of defects in the photodecomposition process.

Science objectives for 2010-2012:

- *Continued studies of the fundamental mechanisms for the release of atoms and radicals from UV irradiated solid surfaces;* including single crystal wide bandgap semiconductors such as ZnO and TiO_2. Formation of excited species similar to the Zn* described will be carefully examined
- *Studies of in-situ VUV absorption to measure transient defect densities* in wide bandgap materials. Through time resolved studies we are trying to measure the rates (on a ps time scale) for the formation of vacancy related defects in alkaline earth halides. We will try to look at surface reflection spectroscopy to examine similar processes in the wide bandgap semiconductors.
- *Effect of sidechain substitutions on laser interactions with fluorinated polymers at 157 nm.* The decomposition chemistry of partially fluorinated polymers contrasts markedly with that of PTFE. We are characterizing the product distributions and kinetics to compare with calculations of the photochemical

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Abstracts Not Presented

Ion-Surface Interactions and Ion Soft Landing

R. Graham Cooks, Principal Investigator
560 Oval Drive, Department of Chemistry, Purdue University, West Lafayette, IN 47907
Email: cooks@purdue.edu; Web: http://aston.chem.purdue.edu/

Collaborator: Dr. Julia Laskin, Pacific Northwest National Lab, Richland, WA julia.laskin@pnl.gov

Overall research goals: Understanding of collisions of low energy molecular ions at surfaces, especially ion soft landing (SL). Fundamental studies include (i) searches for ion-initiated organic reactions and their mechanisms, (ii) understanding of surface charge neutralization mechanism and (iii) the study of desorption electrospray ionization (DESI) mechanisms, especially as informed by using surface charge imaging. Tasks with practical potential include (i) creation of catalytic materials with high reactivity and (ii) improvement in secondary ion mass spectrometry (SIMS) yields through appropriate surface ion treatment.

Significant achievements in 2008-2010: Deposition of homogenous hydrogenation catalysts (e.g. Wilkinson catalyst) by SL was shown to provide intact ions at surfaces. Deposition of metal-salen complexes onto inert fluorocarbon substrates was used to create catalytically active organometallic species. The intact deposition of a catalytically active site together with associated ligands, suggested by studies of homogeneous catalysis, was a major objective of the present proposal. Slow redox reactions occur in the ion/surface interface (Fig. 1); the deoxygenation of the oxo-vanadium complex previously observed only in highly acidic non-aqueous solvents occurs on the surface in the UHV environment when a suitable acid is provided by ion soft landing. Exposure to O_2 reverses the process.

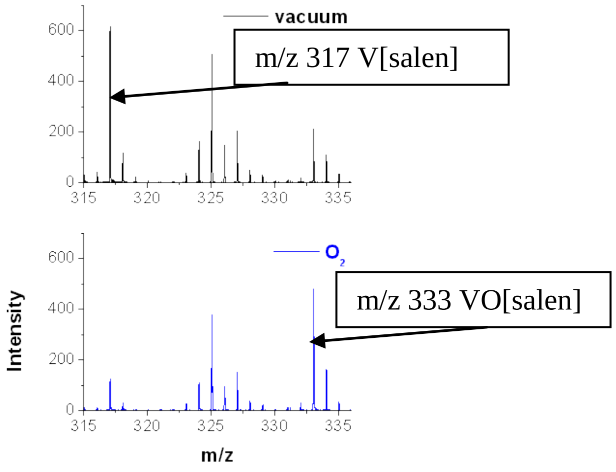
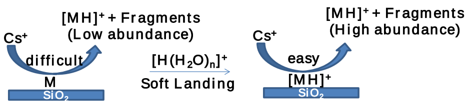


Fig.1. In situ TOF-SIMS mass spectrum after VO(Salen) and Ni(Salen) dimer ions were deposited sequentially on an F-SAM surface. The surface is kept in vacuum and then exposed to atmospheric molecular oxygen for one hour. The relative ratio intensity plot of ion peaks of m/z 333 $[VO(Salen)]^+$ to m/z 317 $[V(Salen)]^+$ shows that oxidation occurs at the surface and is reversible as the surface is exposed to oxygen or to vacuum.

Molecular ion yield enhancement in static SIMS is demonstrated using soft landing of protonated water clusters $[H(H_2O)_n]^+$ (mostly n=4 but up to >100). SIMS yield enhancements in the cases of several amino acids and peptides were demonstrated. The charge must be retained at the surface to give the enhancement and the mechanism proposed is shown in Scheme 1.



Scheme 1: SIMS yield enhancement by ion soft landing

Charge retention and neutralization mechanisms on surfaces after ion soft landing were investigated using image current measurements. For electrically conducting substrates, complete charge loss/charge neutralization occurred, apparently through a rapid recombination mechanism with mobile electrons. For polytetrafluoroethylene (PTFE) surfaces, the dominant charge loss process is via charge transfer to gas-phase or surface adsorbed water. The charge neutralization kinetics shows a typical autocatalytic behavior, Figure 2. A mechanism involving water absorption and proton transfer to water clusters is proposed. For the special case of the Rhodamine B cation, without a free proton, the neutralized product is the hydroxylated molecule, as indicated by SIMS analysis.

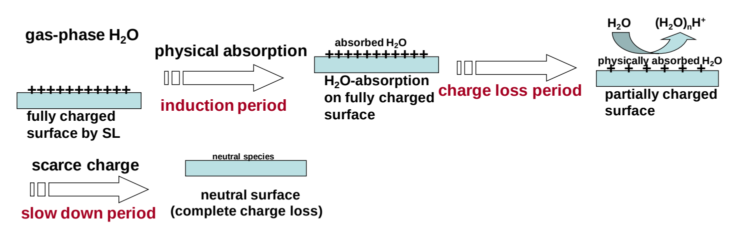


Fig 2. (left) Charge neutralization kinetics $[YGGFL+H]^+$ on PTFE at 0.017 mTorr H_2O pressure (above) proposed processes

Science objectives for 2010-2012:

- In situ surface-enhanced Raman spectroscopy (SERS) will be setup and used to characterize surfaces modified surface by SL.
- Cesium ion initiated reaction will be further investigated in other reaction systems.
- Investigation on surface charge neutralization will continue, the protonated water clusters will be further verified by mass spectrometer and other spectroscopic techniques.
- Studies on organic metallic ion deposition to pursue the objective of creating epoxidation and hydrogenation catalysts.

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Participants and Abstracts Index

Participant List and Abstracts Index

Last Name	First Name	Affiliation	E-mail address	Page
Asta	Mark	University of California, Davis	mdasta@ucdavis.edu	51
Austin	Daniel	Brigham Young University	dea@byu.edu	37
Baker	Lane	Indiana University	lanbaker@indiana.edu	61
Barnes	Michael	University of Massachusetts	mdbarnes@chem.umass.edu	73
Basaran	Osman	Purdue University	obasaran@purdue.edu	33
Belfort	Georges	Rensselaer Polytechnic Institute	sorels@rpi.edu	43
Bohn	Paul	University of Notre Dame	pbohn@nd.edu	53
Bright	Frank	State University of New York	chefvb@buffalo.edu	65
Bruening	Merlin	Michigan State University	bruening@chemistry.msu.edu	63
Buratto	Steve	University of California	buratto@chem.ucsb.edu	23
Chen	Hao	Ohio University	chenh2@ohio.edu	69
Crooks	Richard	University of Texas at Austin	crooks@cm.utexas.edu	83
Dickinson	Tom	Washington State University	jtd@wsu.edu	89
Diebold	Gerald	Brown University	Gerald_Diebold@Brown.edu	49
Fang	Ning	Iowa State University	nfang@iastate.edu	41
Farnsworth	Paul	Brigham Young University	paul_farnsworth@byu.edu	9
Freeman	Benny	University of Texas	freeman@che.utexas.edu	25
Futrell	Jean	Pacific Northwest National Lab	jean.futrell@pnl.gov	
Garrett	Bruce	Pacific Northwest National Lab	bruce.garrett@pnl.gov	
Goeringer	Douglas	Oak Ridge National Lab	goeringerde@ornl.gov	35
Guiochon	Georges	University of Tennessee	guiochon@utk.edu	81

Haranczyk	Maciej	Lawrence Berkeley National Lab	mharanczyk@lbl.gov	71
Harris	Joel	University of Utah	harrisj@chem.utah.edu	3
Hieftje	Gary	Indiana University	hieftje@indiana.edu	31
Higgins	Daniel	Kansas State University	higgins@ksu.edu	55
Houndonougbo	Yao	Eastern Washington University	yhoundonoug@ewu.edu	51
Hupp	Joseph	Northwestern University	j-hupp@northwestern.edu	21
Ito	Takashi	Kansas State University	ito@ksu.edu	55
Kertesz	Vilmos	Oak Ridge National Lab	kerteszv@ornl.gov	35
Koros	William	Georgia Institute of Technology	wjk@chbe.gatech.edu	67
Laird	Brian	University of Kansas	blaird@ku.edu	51
Laskin	Julia	Pacific Northwest National Lab	julia.laskin@pnl.gov	7
Lee	Young-Jin	Ames Laboratory	yjlee@iastate.edu	19
Ma	Yingzhong	Oak Ridge National Lab	may1@ornl.gov	75
Marceau	Diane	U. S. Department of Energy	Diane.Marceau@science.doe.gov	
McLuckey	Scott	Purdue University	mcluckey@purdue.edu	11
Miller	John	U. S. Department of Energy	john.miller@science.doe.gov	
Miller	Jan	University of Utah	jan.miller@utah.edu	39
Millman	William	U. S. Department of Energy	william.millman@science.doe.gov	
Ozolins	Vidvuds	UCLA	vidvuds@ucla.edu	51
Pederson	Mark	U. S. Department of Energy	mark.pederson@science.doe.gov	
Britt	Phillip	Oak Ridge National Laboratory	brittpf@ornl.gov	
Rahn	Larry	U. S. Department of Energy	larry.rahn@science.doe.gov	
Rohlfing	Eric	U. S. Department of Energy	Eric.Rohlfing@science.doe.gov	

Ross	Nancy	Virginia Tech	nross@vt.edu	85
Russell	David H.	Texas A&M University	russell_asst@mail.chem.tamu.edu	17
Russo	Richard	Lawrence Berkeley National Lab	rerusso@lbl.gov	87
Schmidt	Jordan	University of Wisconsin	schmidt@chem.wisc.edu	47
Schwartz	Daniel	University of Colorado	daniel.schwartz@colorado.edu	5
Shaw	Robert	Oak Ridge National Lab	shawrw@ornl.gov	1
Simonson	J. Michael	Oak Ridge National Lab	simonsonjm@ornl.gov	59
Smit	Berend	UC Berkeley	Berend-Smit@Berkeley.edu	45, 71
Smith	Emily	Ames Laboratory	esmith1@iastate.edu	41
Snurr	Randall	Northwestern University	snurr@northwestern.edu	21
Spencer	Ross	Brigham Young University	ross_spencer@byu.edu	9
Trimpin	Sarah	Wayne State University	strimpin@chem.wayne.edu	27
Vertes	Akos	George Washington University	vertes@gwu.edu	15
Way	Doug	Colorado School of Mines	dway@mines.edu	79
Weiss	Paul S.	UCLA	stm@ucla.edu	13
Whitten	William	Oak Ridge National Lab	whittenwb@ornl.gov	1
Winograd	Nicholas	Penn State University	nxw@psu.edu	29
Yaghi	Omar	UCLA	lissett@chem.ucla.edu	51, 57
Yeung	Edward	Ames Laboratory	yeung@ameslab.gov	19, 41
Zelenyuk	Alla	Pacific Northwest National Lab	alla.zelenyuk@pnl.gov	77