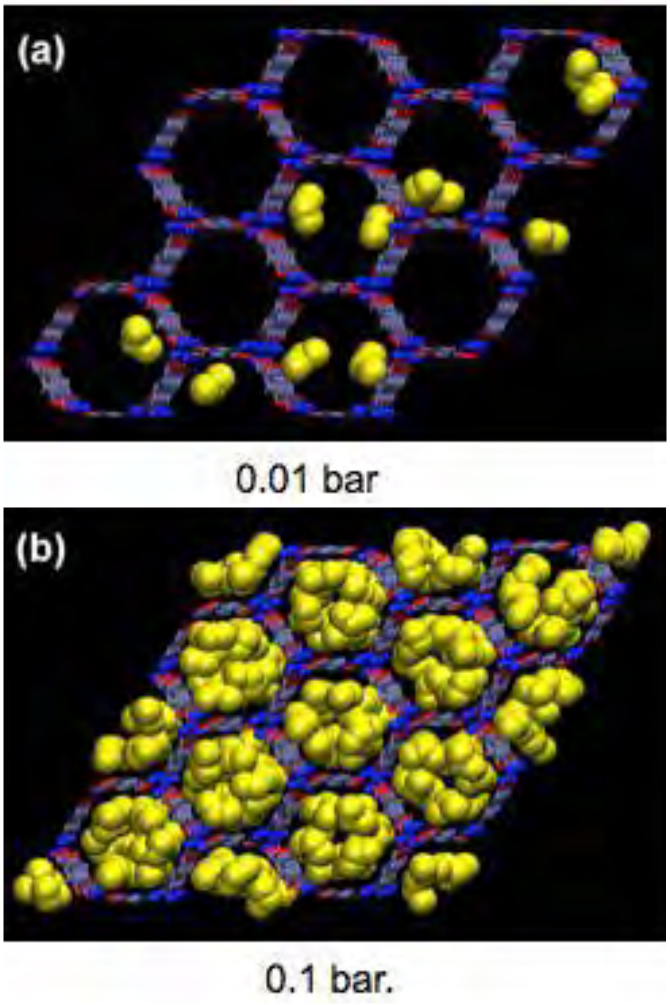
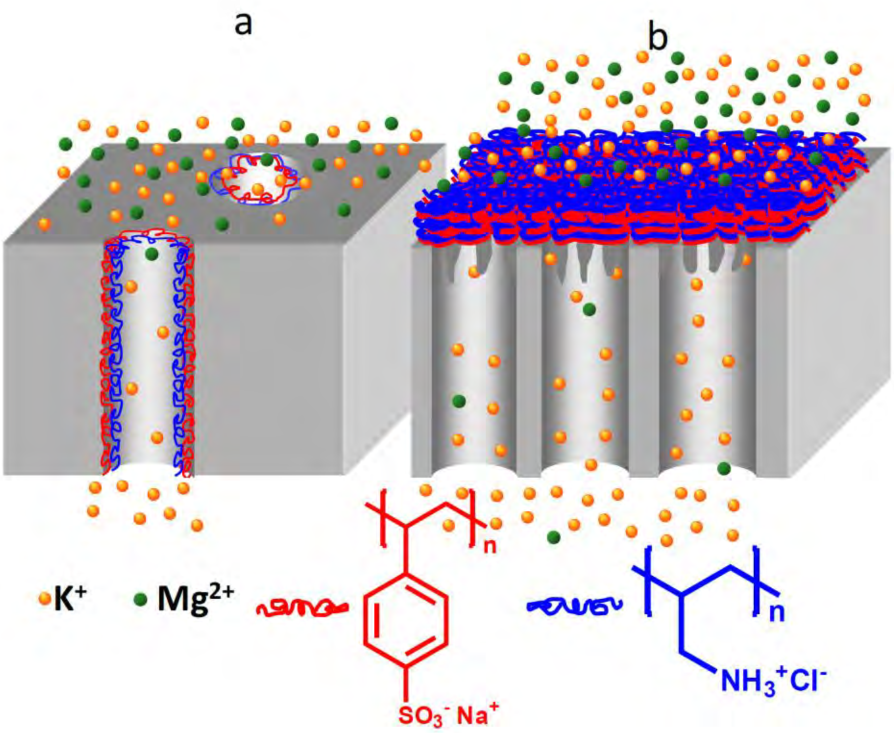
2012 DOE Separations and Analysis Research Meeting





Westin Annapolis Hotel
Annapolis, MD
April 22–25, 2012

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

Research Meeting

Westin Annapolis Hotel
Annapolis, MD
April 22–25, 2012

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 depicts simulations showing basis for emergent behavior in the separation of propylene from propane by MOF-74 by Joseph T. Hupp, Randall Q. Snurr, SonBinh T. Nguyen, Omar K. Farha, et al. (see page 9 of this book and *Angew. Chem. Int. Ed. 2012, 51, 1857–1860*). The image on the right shows a schematic drawing of (a) a track-etched membrane with pores coated with a PSS/PAH film and (b) a porous alumina membrane with a $(PSS/PAH)_n$ film on its surface by Merlin Bruening, et al. (see page 61 of this book and *Langmuir 2008, 24, 7663–7673*).

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Foreword

This abstract booklet provides a record of the U.S. Department of Energy biennial research meeting in separations and analysis science. This year the meeting is co-chaired by Dr. Emily Smith (Ames Laboratory) and Professor William J. Koros (Georgia Institute of Technology). This meeting is sponsored by the Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences and includes invited presentations from DOE ARPA-E, Pacific Northwest National Laboratory, and the Center for Gas Separations to Clean Energy Technologies, an Energy Frontier Research Center. Related research funded in the BES Computational and Theoretical Chemistry Program is also represented. Also featured in this meeting is a poster presentation from an early career researcher invited 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 Emily Smith and Bill Koros in organizing and conducting this 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 Tim Ledford 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.

Larry A. Rahn
Mark Pederson

Agenda

2012 Separations and Analysis Research Meeting
Westin Annapolis Hotel, Annapolis, MD April 22–25, 2012

Sunday, April 22 2012

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

Session 1 – Imaging Mass Spectrometry – Julia Laskin, Chair

7:40 – 8:00	p.m.	Welcome – Larry Rahn, Emily Smith, Bill Koros
8:00 – 8:25		Professor R. Graham Cooks – Preparation of Chemically Functionalized Surfaces through Ion Soft Landing and Other Ion Chemistry in the Mass Spectrometer
8:25 – 8:50		Professor Nicholas Winograd – Strong-Field Ionization of C_{60} Sputtered Neutral Biomolecules using fs IR Radiation
8:50 – 9:15		Dr. Gary J. Van Berkel – Sampling, Ionization and Energy Transfer Phenomena in Mass Spectrometry

Monday, April 23

7:30 – 8:00	a.m.	**Continental Breakfast**
8:00 – 8:25		John Miller – DOE Update

Session 2 – Carbon Capture I – Shannon Mahurin, Chair

8:30 – 9:15	a.m.	**Invited Speaker** – Dr. Karma Sawyer – Bridging Basic Science and Gas Separation Applications
9:15 – 9:40		Professor Joseph T. Hupp – Coordination-Chemistry-Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities
9:40 – 10:05		Dr. De-en Jiang – Advanced Ionic Liquids and Carbon-Based Porous Materials for Capture of Carbon Dioxide
10:05 – 10:30		**Break**

Session 3 – Carbon Capture II – Jordan R. Schmidt, Chair

10:30 – 11:15	a.m.	**Invited Speaker** – Professor Jeffrey Reimer – NMR Characterization of Metal-Organic Frameworks for Carbon Capture
11:15 – 11:40		Professor Laura Gagliardi – Bridging the Gap between Quantum Chemistry and Classical Simulations for CO_2 Capture
11:40 – 12:05		Dr. Maciej Haranczyk – Knowledge-Guided Screening Tools for Identification of Porous Materials for CO_2 Separation

Introduction of Invited Early Investigator – Bill Koros, Chair

12:05 – 12:10	p.m.	Professor Aaron Esser-Kahn – Microvascular Materials for Ultra-High Specific Surface Area Membranes
12:10 – 1:10		**Working Lunch**
1:10 – 4:00		**Interaction Time** – Put up posters for Poster Sessions

Monday, April 23 (Cont'd)

Poster Session 1

4:00 – 6:00 p.m. Poster Session 1 – with no-host bar

P1-1 **Invited Poster –** Professor Aaron Esser-Kahn – Microvascular Materials for Ultra-High Specific Surface Area Membranes
P1-3 Professor Jordan R. Schmidt – Robust, Transferable, and Physically Motivated Force Fields for Gas Adsorption in Nanoporous Systems
P1-5 Professor Eric J. Schelter – A Physicochemical Method for Separating Rare Earths: Addressing an Impending Shortfall
P1-7 Dr. Scott A. McLuckey – Selective Covalent Bond Formation in Gas-Phase Ion/Ion Reactions and Spectroscopy of Cold Gaseous Polyatomic Ions
P1-9 Professor Raymond Gorte – The Development of Nano-composite Electrodes for Solid Oxide Electrolyzers and Fuel Cells
P1-11 Professor David Keffer – Multiscale Modeling of the Relationship between Nanostructure of Hydrated Proton Exchange Membranes and Proton Conductivity
P1-13 Dr. Julia Laskin – Ion-Surface Interactions in Mass Spectrometry
P1-15 Professor David H. Russell – Developing Nanoparticle-Based Efficient Analyte Capture and Ionization
P1-17 Professor Stephen Creager – Fluoropolymers, Electrolytes, Composites and Electrodes
P1-19 Professor Richard M. Crooks – Separations and Analysis using Bipolar Electrodes
P1-21 Professor Paul B. Farnsworth – Ion Production and Transport in Atmospheric Pressure Ion Source Mass Spectrometers
P1-23 Dr. Olga Ovchinnikova, Gary Van Berkel, and Vilmos Kertész – Nanoscale Molecular Cartography: Combining Mass Spectrometry with Atomic Force Microscopy

6:00 – 7:15 **Working Dinner**

Session 4 – Membranes and Hydrogen – Raymond Gorte, Chair

7:30 – 7:55 p.m. Professor Frank V. Bright – Interfacial Solvation under Aggressive Conditions
7:55 – 8:20 Professor Steven L. Regen – Hyper-thin Membranes for Hydrogen Purification
8:20 – 8:45 Professor Theodore Tsotsis – Nanoporous Membranes for Hydrogen Production: Experimental Studies and Molecular Simulations
8:45 – 9:10 Professor Gregory A. Voth – Computer Simulation of Proton Transport in Fuel Cell Membranes

Tuesday, April 24

7:30 – 8:00 a.m. **Continental Breakfast**

Session 5 – Chemical Imaging – Joel Harris, Chair

8:00 – 8:45 **Invited Speaker** – Dr. Hong-fei Wang – New Opportunities of Surface Nonlinear Vibrational Spectroscopy in Spectral, Structural and Dynamic Interactions at the Interfaces for Separation and Analysis
8:45 – 9:10 Professor Michael D. Barnes – Chemical Microscopy of Conjugated Organic Nanomaterials

Tuesday, April 24 (Cont'd)

9:10 – 9:35	Professor Josef Michl – Imaging of Conformational Changes
9:35 – 10:00	Dr. Emily Smith – Chemical Analysis of Nanodomains
10:00 – 10:30	**Break**

Session 6 – Membrane Separations – Sheng Dai, Chair

10:30 – 10:55 a.m.	Professor Benny D. Freeman – Fundamental Structure/Property Studies of Thermally Rearranged Polymers for Use as Gas Separation Membranes
10:55 – 11:20	Professor William Koros – Synthesis and Analysis of Membrane Materials with High Permeabilities, Permselectivities and Potential for Economical Large-Scale Energy-Intensive Separations
11:20 – 11:45	Professor Merlin Bruening – Towards Separations of Stable Isotopic Ions in Homogeneous, Highly Charged Nanopores
11:45 – 12:10	Professor Georges Belfort – Combinatorial and High Throughput Membrane Synthesis and Testing: Tailoring Membrane Surfaces to Applications
12:10 – 1:00	**Working Lunch**
1:00 – 4:00	**Interaction Time**

Poster Session 2

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

P2-2	Professor Paul W. Bohn – Molecular Aspects of Transport in Thin Films of Controlled Architecture
P2-4	Professor Takashi Ito – Molecular-Level Investigation of Diffusion Behaviors within Cylindrical Nanoscale Pores
P2-6	Dr. Richard E. Russo – Laser-Material Interactions (Ablation) for Chemical Analysis
P2-8	Professor Akos Vertes – Nanophotonic and Atmospheric Pressure Ion Production in Imaging Mass Spectrometry
P2-10	Dr. Yingzhong Ma and R.W. Shaw – Ultrafast Electronic Spectroscopy of Individual Nanostructures and Complex Ensembles
P2-12	Professor Joel Harris – Analytical Spectroscopy Methods for Liquid/Solid Interfaces
P2-14	Dr. Shannon Mahurin – Gas Separations using Room Temperature Ionic Liquids
P2-16	Dr. Ning Fang – New Ways of Tracking Nanoparticles
P2-18	Professor Daniel K. Schwartz – Mapping Non-covalent Surface Functionality using Single Molecule Probes
P2-20	Dr. Young-Jin Lee – Mass Spectrometric Imaging of Plant Metabolites
P2-22	Dr. Robert W. Shaw – Nanoparticle Imaging, Assembly, and Chemistry
P2-24	Professor Paul S. Weiss – Local Spectroscopies for Subnanometer Spatial Resolution Chemical Imaging

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

Wednesday, April 25

7:30	– 8:00	a.m.	**Continental Breakfast**

Session 7 – MS Analysis Science – Paul B. Farnsworth, Chair

8:00	– 8:25	a.m.	Dr. Alla Zelenyuk – Chemistry and Microphysics of Small Particles
8:25	– 8:50		Professor Gary M. Hieftje – Fundamental Studies of the Inductively Coupled Plasma and Glow Discharge
8:50	– 9:15		Professor Osman A. Basaran – Electrohydrodynamic Tip Streaming
9:15	– 9:45		**Break**

Session 8 – Surface Chemistry and Properties – Takashi Ito, Chair

9:45	– 10:10		Brian F. Woodfield – Energetics of Nanomaterials
10:10	– 10:35		Professor Jan D. Miller – Surface Chemistry Issues in the Development of Nonsulfide Flotation Technology

Session 9 – Closeout Session – Dr. Emily Smith, Prof. Bill Koros, Chairs

10:45	– 12:00		Presentation of program summaries and discussion
12:00	– 1:00	p.m.	**Working Lunch** – boxes for lunches available for those who have to leave early
1:00	– 3:00		Open Discussion and take down posters

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Session 4 – Membranes and Hydrogen

Session 5 – Chemical Imaging

Session 6 – Membrane Separations

Poster Session 2

Session 1 – Imaging Mass Spectrometry

Preparation of Chemically Functionalized Surfaces through Ion Soft Landing and their Utilization in Heterogeneous Reactions (DE-FG02-06ER15807)

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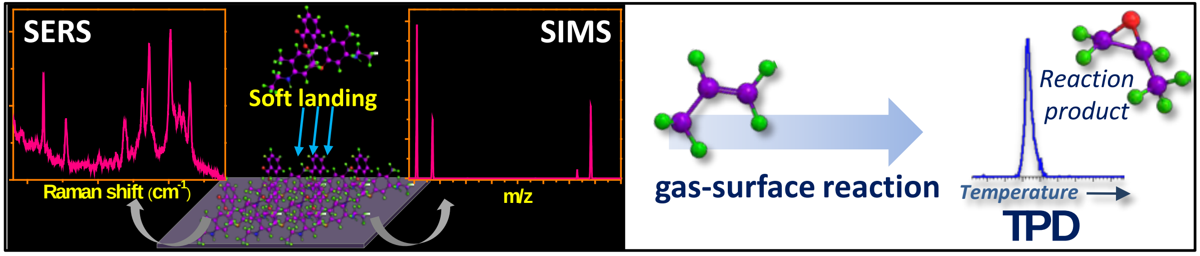
Overall Research Goals: One objective of this work is to create surfaces with appropriate chemical functionalities via soft landing (SL) of molecular or cluster ions and to characterize the surfaces in situ using secondary ion mass spectrometry and Raman spectroscopy. A subsequent goal is to perform heterogeneous reactions at the functionalized surfaces and to employ temperature programmed desorption to investigate the surface chemistry. A final goal is to generate and characterize model catalytic surfaces.

Significant Achievements in 2010-2012:

Completion of instrumentation: The soft landing (SL) instrument at Purdue can be used to mass-select particular ions and to soft land them at low energy onto a selected surface in high vacuum and characterize the deposited materials by in situ secondary ion mass spectrometry (SIMS). Recently the system has been modified with new capabilities that include: (i) a new high vacuum compatible, low cost in situ Raman analysis capability with 2D imaging capabilities and (ii) the ability to expose the characterized surface to vapor phase reagents and perform temperature programmed desorption (TPD) analysis in situ. One advantage of the design is the fact that all measurements can be conducted without breaking vacuum; one can analyze the functionalized surfaces in their native form. Following SL and again after utilization of the surface, any combination of in situ Raman and in situ SIMS can be performed. In situ 2D Raman spectral imaging was achieved using a manual x,y,z micrometer stage and gold nanoparticles were used to achieve surface enhancements of up to 10^6.

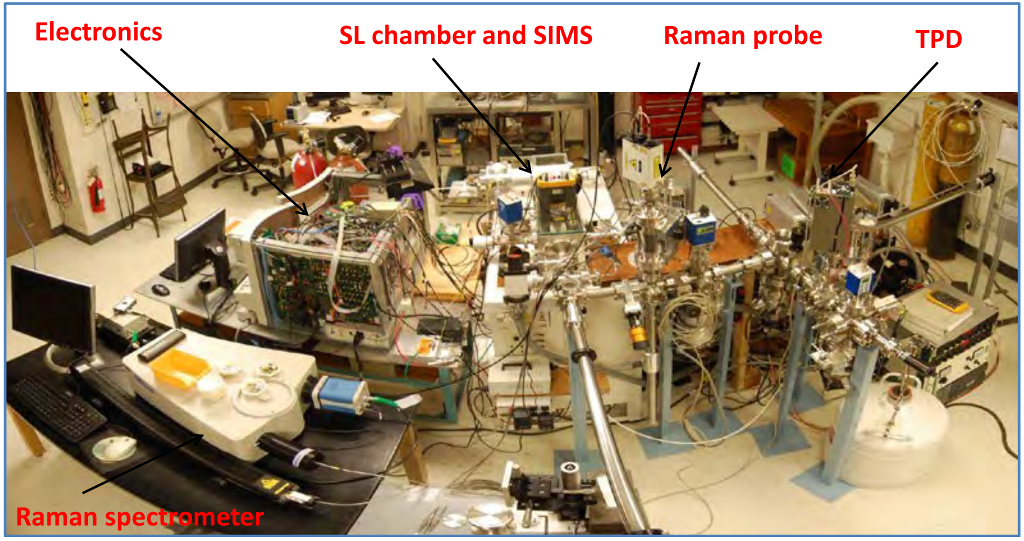


In situ analysis capabilities of the Purdue SL instrument

Chemically Functionalized Surfaces: With the new instrumentation and characterization tools, we have studied a number of systems. Cations/protonated ions derived from Rhodamine 6G, crystal violet, methyl red, and peptides as well as negative ions derived from fluorescein, copper phthalocyanine and methyl orange have been soft landed onto various surfaces and their structures and charge states investigated using SERS and SIMS. Well-defined molecularly specific SERS features are observed in as little as 15 min of ion deposition. An alternative of SL, reactive landing has been used to tailoring surfaces with biomolecules for the preparation of biosensors and substrates for cell adhesion. Lysine containing peptides have been successfully attached to dithiobissuccinimidyl nitrobenzoate (DSNB) surfaces.

Superior carrier mobility of inorganic materials and the processability of organic materials is expected to be incorporated into organic-inorganic hybrid materials. Graphene oxide (GO) is a 2D nanomaterial with interesting electrical and chemical properties. We have modified thin films of GO with functional molecules such as copper phthalocyanine and phorphine using the SL procedure. This route has advantages over solution phase methods as the structure of the GO film is preserved the desired chemical patterns can be generated on the surface.

Temperature Programmed Desorption (TPD): The TPD system is being tested and preliminary experiments have been completed. An ongoing experiment is the preparation of an organometallic catalyst surface through SL and use of this surface for ethylene epoxidation. Investigation of heterogeneous reactivity, including catalysis, of particular soft landed surfaces at ambient pressure with vapor phase reagents is being carried out through the examination of the post-exposure changes in surface chemistry.



Photograph of Purdue SL instrument

Science objectives for 2012-2014:

- Reaction of a model heterogeneous catalyst prepared by ion SL, characterized by SERS and SIMS, studied in reaction chamber and analyzed by TPD.
- Re-examination of the surface after heterogeneous reaction to confirm catalytic cycle.
- Charge state/structural differences in surfaces prepared by ion SL.

References to work supported by this project 2010-2012:

1. Jobin Cyriac, Guangtao Li and R Graham Cooks "Vibrational spectroscopy and mass spectrometry for characterization of soft landed polyatomic molecules" *Analytical Chemistry*, 2011, 83, 5114–5121.
2. Liang Gao, Guangtao Li, Jobin Cyriac, Zongxiu Nie and R. Graham Cooks "Imaging of surface charge and the mechanism of desorption electrospray ionization mass spectrometry" *Journal of Physical Chemistry C*, 2010, 114, 5331-5337.
3. Guangtao Li, Jobin Cyriac, Liang Gao and R Graham Cooks "Molecular Ion Yield Enhancement in Static Secondary Ion Mass Spectrometry by Soft Landing of Protonated Water Clusters" *Surface and Interface Analysis*, 2011, 43, 498-501
4. Wen-Ping Peng, Grant E. Johnson, Ivy C. Fortmeyer, Peng Wang, Omar Hadjar, R. Graham Cooks and Julia Laskin "Redox chemistry in thin layers of organometallic complexes prepared using ion soft landing" *Physical Chemistry Chemical Physics*, 2011, 13, 267–275.
5. Jobin Cyriac, Michael S. Wleklinski, Guangtao Li, Liang Gao, and R. Graham Cooks "In situ Raman Spectroscopy of Surfaces Modified by Ion Soft Landing" *Analyst*, 2012, 137, 1363-1369.
6. Jobin Cyriac, T. Pradeep, R. Souda, H. Kang and R. G. Cooks (2012) "Low energy ion collisions at molecular solids" *Chemical Reviews*, 2012, (*Under Revision*).
7. Guangtao Li, Jobin Cyriac, Liang Gao, and R. Graham Cooks "Neutralization of Surface Cations during Ion Soft Landing: Mechanistic Studies and Analytical Implications" 2012 *(Submitted)*.

Strong-field ionization of C_{60} sputtered neutral biomolecules using fs IR radiation

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Overall research goals: The main objectives of this program are to increase the capabilities and better understand the fundamentals of cluster secondary ion mass spectrometry (SIMS), by employing laser photoionization. The emphasis is on elucidating the cluster/solid interaction, improving sensitivity in two and three dimensional imaging, and advancing bioimaging applications.

Significant achievements in 2010-2012: Work with fs IR strong field ionization is ongoing. Post-ionization was applied to the study of depth profiling fundamentals, by investigating a model system of guanine vapor deposited on silver. Comparison of the SIMS and simultaneously acquired neutral depth profiles (Figure 1) highlight the influence of matrix effects on the secondary ion signal at the surface, and interfacial regions. Evidence of near surface, dynamically created preformed ions (DCPI) is observed, supported by the sudden increase in the protonated SIMS signal in the first 10 nm of the profile, most likely caused by the bombardment induced generation of free protons in the top layers of the sample. In addition, the neutral data allows the direct observation of how ionization effects influence the accurate determination of important depth profiling parameters such as the sputter rate, depth scale calibration, altered layer thickness, and the interface width. The results of the study are believed to be general, and to highlight the need for suitable correction schemes for cases when neutral data are not available.

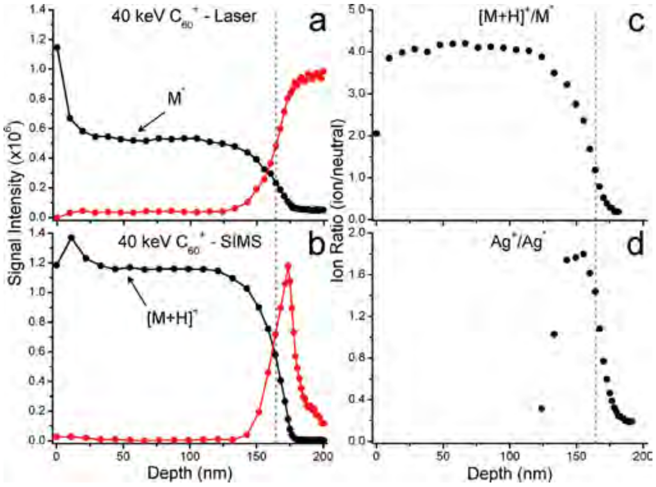

Figure 1: The signal intensity is monitored as a function of depth for (a) the photoionized M° (black) and Ag° (red) neutral species and (b) the secondary $[M + H]^+$ (black) and Ag^+ (red) ions. Ion ratios observed as a function of depth for (c) the $[M + H]^+$ secondary ion signal divided by the M° photoionized neutral signal and (d) for the Ag^+ secondary ion signal divided by the Ag° photoionized neutral signal. The vertical dotted line indicates the interface between the guanine thin film and Ag substrate measured by AFM.

One such method, which attempted to correct for the surface fluctuation in the secondary ion signal, was evaluated in a related post-ionization study. The model guanine system was once again employed, with the near surface secondary ion depth profile being fit by a previously proposed erosion dynamics model, and compared to the neutral signal from the same depth range. The comparison allowed for the deconvolution of the effects of chemical damage accumulation and ionization enhancement, which both affect the secondary ion signal at the start of the depth profile. The successful use of the erosion dynamics model to predict the near surface signal in guanine, prompted its application in the analysis of trehalose depth profiling.

In the middle of 2011, a new laser system was brought online which increased the intensity available to post-ionization experiments to 10^{15} W/cm^2, in the 1.2-2.4 µm wavelength range. Initial experiments confirmed earlier work showing softer ionization mechanisms occurring at longer wavelengths. Model systems – xenon gas, sputtered indium clusters, and gas phase histamine – served as initial calibration standards, and preceded biologically relevant studies. To date, the intact ionization of a number of sputtered biomolecules - stearic acid, beta-estradiol, cholesterol, and the Gly-Gly-Gly peptide – has been observed, and the post-ionization experiment has been successfully applied to the analysis of mouse brain tissue (Figure 2).

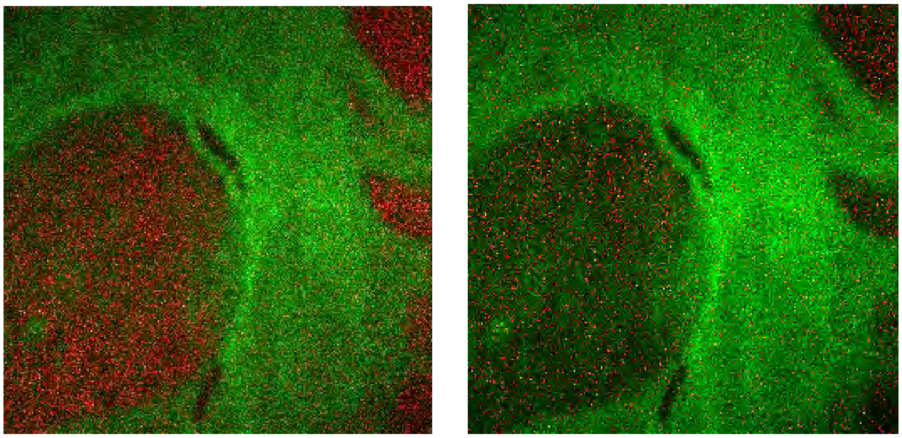

Figure 2: 750 µm field of view images of mouse brain tissue, produced by post ionization with a focused 1400 nm beam. Cholesterol fragments at m/z 220-230 (left image) and molecular ion (right image) in red, and phosphatidylcholine fragment (m/z 58.1) in green.

<u>Science objectives for 2012-2014</u>:

- Fundamental studies of strong field ionization mechanisms in biologically relevant molecules
- The application of strong field post-ionization to the study of hydrocarbon production by *B. braunii* algae
- Tissue imaging of mouse brain using strong field post-ionization

<u>Selected references to work supported by this project 2010-2012:</u>

1. D. Willingham, D. A. Brenes, A. Wucher and N. Winograd, "Strong-field Photoionization of Sputtered Neutral Molecules for Molecular Depth Profiling", *J. Phys. Chem. C*, **114**, 5391-5399 (2010).
2. D. Willingham, D. A. Brenes, N. Winograd and A. Wucher, "Investigating the fundamentals of molecular depth profiling using strong-field photoionization of sputtered neutrals", *Surface and Interface Analysis*, **43**, 45-48 (2011).
3. A. Kucher and N. Winograd, "Strong-Field Ionization of C_{60}-Sputtered Neutral Molecules Using 10^{15} W/cm^2 of fs IR Radiation", *Surface and Interface Analysis*, submitted (2012).

Sampling, Ionization and Energy Transfer Phenomena in Mass Spectrometry

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Overall research goals: The overarching goal of the research within this proposal is to advance the capacity of mass spectrometry (MS) to study and characterize the reactions and molecular products of redox transfer processes and to study and characterize with nanometer spatial resolution molecular constituents of surfaces under real world conditions.

Significant achievements in 2010-2012: We discovered a new surface sampling method to quantitatively concentrate, mix, and react samples extracted with nanoliter volumes of solvent from multiple sub-millimeter size areas on a surface. Spatially resolved surface sampling of this type has potential analysis applications in multiple energy related fields including battery and biomass characterization. This spatial resolved surface sampling advance could lead to a real-world sample introduction interface for existing and future microfluidic sample analysis platforms. The liquid microjunction surface sampling probe (LMJ-SSP) plug generation mode of operation decouples sampling from immediate continuous downstream detection, which enables in probe sample manipulation prior to detection. The ability to extract and completely mix individual samples within a fixed volume at the sampling end of the probe was demonstrated and a linear mass spectral response to the number of equivalent analyte spots sampled was observed. The ability to efficiently extract reagents into the same plug volume and run reactions within the probe was demonstrated using the color and mass changing chemical reduction of the redox dye 2,6-dichlorophenolindophenol with ascorbic acid. With the present optically transparent probe, more sophisticated spectroscopic interrogation of the sample plugs is possible. The LMJ-SSP in plug generation mode provides a simple means to interact with and sample from a macroscale surface while maintaining microfluidic analyte and solution flow control.

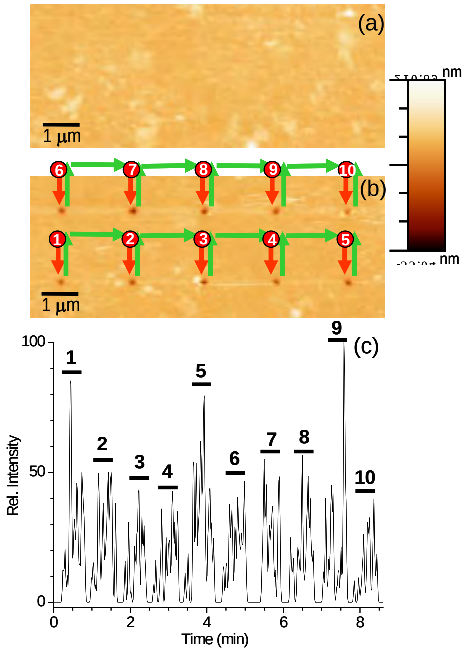

Figure 1. AFM topography of a caffeine thin-film surface (a) pre-heating and (b) post-heating the surface for 30 s per spot in a 5 x 2 array. (c) MS/MS ion current chronogram (5 pt gaussian smooth) for caffeine (m/z 195 → 138, normalized collision energy 35%) recorded during the 30 s per spot sampling of the 5 x 2 array. The red and green arrows in (b) correspond to the movement of the AFM probe while the probe is at 350 ^{o}C, and at ambient temperature 25 ^{o}C respectively. Crater numbers in (b) correspond to MS chronogram peaks in (c) with the line below the numbering in (c) representing the 30 s heating interval during which the AFM probe is on the caffeine thin-film surface.

Chemical analysis and topographic imaging at the nanoscale was demonstrated by combining atomic force microscopy and proximal probe thermal desorption with secondary ionization mass spectrometry. By using a nanometer scale probe tip from an atomic force microscope coupled to an electrospray ionization mass spectrometer (ESI-MS), atmospheric pressure proximal probe thermal desorption ESI-MS was demonstrated to provide sub-micrometer (0.25 µm) spatial identification of the model analyte caffeine with high sensitivity (10 amol, 2 fg) and topographic maps of the surface (Figure 1). This novel analytical platform provides multimodal spatially resolved molecular chemical analysis of surfaces under real world conditions. Such a combined AFM/MS platform could be used to co-register local nanomechanical measurements and topography using AFM with MS-based chemical profiling of specific surface features. Because the AFM measurements and surface sampling and ionization are carried out at atmospheric pressure, this system provides great versatility in the type of samples that can be analyzed relative to techniques that might achieve similar spatial resolution, but require operation at high vacuum. We anticipate this new analytical tool will have broad application for determining the spatial distribution of target molecules in many complex systems including plant tissue and interfaces in energy storage and conversion devices.

Science objectives for 2012-2014:

- Understand, advance and create means to transfer chemical species at 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, nanoscale surface sampling/ionization and mass spectrometry based chemical imaging.
- Understand and implement the means to overcome the compromise between an optimum solution/electrolyte composition for electrochemistry and that needed for mass spectrometry to improve the utility of online electrochemistry/mass spectrometry.
- Understand and implement the means to efficiently ablate, desorb, or extract surface species and then efficiently collect and transport at atmospheric pressure (AP) the neutrals or subsequently the ions created, with emphasis on micro- and nanoscale liquid extraction, thermal desorption, or laser ablation/desorption approaches to surface sampling with molecular or elemental MS detection.

References to selected work supported by this project 2011

1. M. S. ElNaggar, G. J. Van Berkel, “Liquid Microjunction Surface Sampling Probe Fluid Dynamics: Characterization and Application of an Analyte Plug Formation Operational Mode,” J. Am. Soc. Mass Spectrom. **22**, 1737-1743 (2011).
2. M. S. ElNaggar, C. Barbier, G. J. Van Berkel, “Liquid Microjunction Surface Sampling Probe Fluid Dynamics: Computational and Experimental Analysis of Coaxial Intercapillary Positioning Effects on Sample Manipulation,” J. Am. Soc. Mass Spectrom. **22**, 1157-1166 (2011).
3. V. Kertesz, G. J. Van Berkel, “Electronic Control of Analyte Electrolysis in Electrospray Ionization Mass Spectrometry Using Repetitively Pulsed High Voltage,” Int. J. Mass Spectrom. **303**, 206-211 (2011).
4. O. S. Ovchinnikova, V. Kertesz, G. J. Van Berkel, “Combining Laser Ablation/Liquid Phase Collection Surface Sampling and High-Performance Liquid Chromatography Electrospray Ionization Mass Spectrometry,” Anal. Chem. **83**, 1874-1878 (2011).
5. O. S. Ovchinnikova, V. Kertesz, G. J. Van Berkel, “Combining Transmission Geometry Laser Ablation and a Non Contact Continuous Flow Surface Sampling Probe/Electrospray Emitter for Mass Spectrometry-Based Chemical Imaging,” Rapid. Commun. Mass Spectrom. **25**, 3735-3740 (2011).
6. O. S Ovchinnikova, V. Kertesz, V. G. J. Van Berkel, “Molecular Surface Sampling and Chemical Imaging Using Proximal Probe Thermal Desorption/Secondary Ionization Mass Spectrometry,” Anal. Chem. **83**, 598-603 (2011).
7. O. S. Ovchinnikova, M. V. Nikiforov, J. A. Bradshaw, S. Jesse, G. J. Van Berkel, “Combined Atomic Force Microscope-Based Topographical Imaging and Nanometer Scale Resolved Proximal Probe Thermal Desorption/Electrospray Ionization-Mass Spectrometry,” ACS Nano **5**, 5526-5531 (2011).

Session 2 – Carbon Capture I

ARPA-E Carbon Capture Portfolio

Bridging Basic Science and Gas Separation Applications

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Abstract:

The U.S. has 1493 coal-fired power plants, 336 gigawatts (GW) of rated power generation capacity. In 2006, these plants produced ~70% of U.S. fossil-fuel derived electricity, ~50% of total electricity and ~1.9 gigatonnes (Gt) of CO_2, about 1/3 of total U.S. emissions. To substantially reduce the CO_2 emissions from the U.S. stationary power sector, these plants must either be shut-down or retrofitted for post-combustion CO_2 capture.

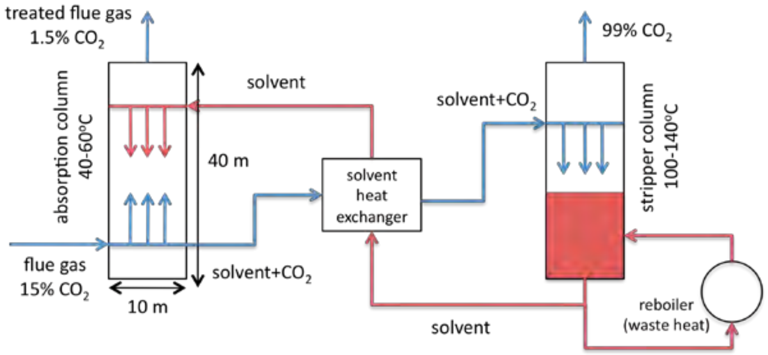

Figure 1. Schematic of a state-of-the-art CO_2 absorption system used for post-combustion capture based on the report DOE/NETL-

The state-of-the-art CO_2 separation technology, 30% monothanolamine (MEA), is outlined in Figure 1. Despite decades of research and development, numerous challenges remain that hinder the feasibility retrofitting coal-fired power plants with this technology. In this presentation, the advantages and disadvantages of this approach will be reviewed to illustrate the opportunities for new technical approaches. The primary challenge is the energy required to regenerate the solvent in the stripper column at 100-140^{o}C(Figure 1). To achieve these high temperatures, steam is diverted from the turbines that generate electricity at the plant, resulting in a large parasitic energy penalty that further adds to the cost of capture. While this problem is difficult, the fact that the energy for the MEA process are more than a factor of 5 higher than the thermodynamic minimum indicates that there is still room for improvement. Several agencies within the Department of Energy are taking a coordinated approach to revolutionize this important area. In addition to the Office of Science programs discussed at this meeting and applied research and field demonstrations funded by the Office of Fossil Energy, the Innovative Materials and Processes for Advanced Carbon Capture Technology (IMPACCT) program at the Advanced Research Projects Agency – Energy (ARPA-E) seeks to identify promising early stage separation concepts that, if successful, will drastically reduce the parasitic energy penalty for CO_2 capture.

Several of these promising new concepts, such as phase-changing ionic liquids, non-aqueous solvents, metal-organic framework sorbents, and multicomponent membranes, will be discussed. Part of an ARPA-E project includes evaluation of potential pathways to take new technology to market. Despite the lack of clear carbon pricing signals, there are applications such as enhanced oil recovery (near term) and synthetic fuels (longer term) that are stabilizing the economics of larger-scale demonstration projects and providing additional value for separate d CO_2. In addition to the IMPACCT program, other ARPA-E programs in energy-related separation technologies such as thermal storage, HVAC, and natural gas storage for vehicles will be highlighted in this presentation.

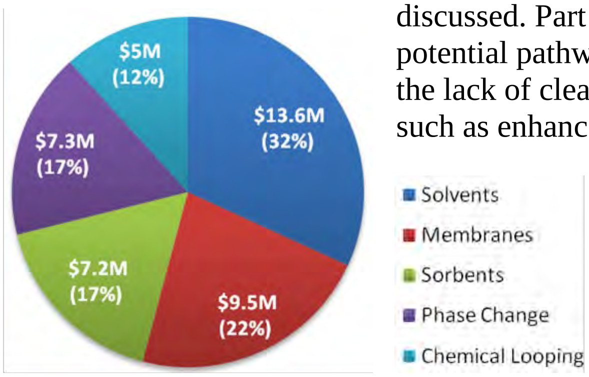

Figure 2. Carbon capture projects from FOA-1 and IMPACCT: $42.7M in federal funding / $58M

References:

1. EIA (2007), Net Generation by Energy Source by Type of Producer
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Coordination-Chemistry-Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities

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Overall research goals: The research objectives are design, understand, and utilize new materials having nanoscale porosity – specifically, new metal-organic frameworks – to achieve energy-efficient separations of technologically-relevant or DOE-mission-relevant chemical mixtures, especially mixtures of gases and/or vapors (e.g. alkane/alkene, xenon/krypton, etc.).

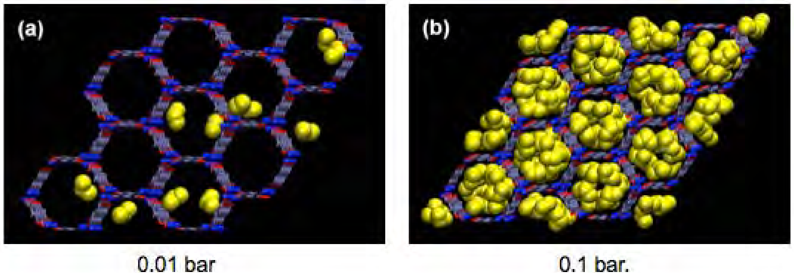
Significant achievements in 2010-2012:

Much of our recent work is described in the 18 papers cited below. Three developments are highlighted here.

1) A key development, described in part in papers 5, 18, and 21, has been the use of computational modeling to discover new MOFs, or identify existing MOFs, showing potentially superior chemical separation capabilities. Subsequent experimental syntheses have confirmed the effectiveness of the approach. The computational approach provides a means for evaluating many more candidate materials than could ever be examined experimentally. The following video also provides a description of the work (a portion of which was supported by this program):
http://www.youtube.com/watch?v=QaKSekjAnqY

2) There has been considerable uncertainty and controversy over whether BET analyses of gas sorption (a standard technique for mesoporous materials) accurately report on internal surface areas for microporous and ultra-microporous (pore diameters below 0.7 nm) MOF materials. We simulated nitrogen and argon isotherms in MOFs and zeolites having ultra-micropores and used the simulated isotherms as pseudo-experimental data to evaluate the BET method for these structures. BET surface areas calculated from the simulated N_2 and Ar isotherms agree well with the accessible surface areas obtained directly from crystal structures in a geometric fashion. However, this is only true when the BET analysis was performed using the appropriate pressure range based on published "consistency criteria"; the BET analysis underestimates the surface area if it is done in the "standard" BET pressure range.

3) A third result we wish to highlight is the discovery of emergent collective behavior by propylene in various M-MOF-74 compounds, resulting in exceptional thermodynamic selectivities for separation of propylene and propane (e.g. S = 46 at 1 bar, with higher values anticipated at higher pressures).



0.01 bar
0.1 bar.

Figure 1. Simulations showing basis for emergent behaviour in the separation of propylene from propane by MOF-74

Science objectives for 2012-2014:

- Build and capitalize upon, for efficient chemical separations, new MOFs featuring accessible metal sites featuring unusually low coordination numbers.
- Develop additional examples of emergent collective behavior by sorbates within MOFs as a means of achieving high selectivity in chemical separations.
- Exploit computational screening techniques to identify MOFs for desired chemical separations.

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Fundamental Studies of Novel Separations

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Collaborator: Dr. Eugene Mamontov, SNS, Oak Ridge National Laboratory

Overall research goals: The overall goal of this project is to investigate fundamental issues of chemical separation phenomena at the gas-solid, and gas-liquid interfaces of nanostructured architectures and unconventional separation media that selectively bind or transport target molecular species via tailored interactions. Currently, the systems of study include novel nanoporous materials and ionic liquids with a focus on carbon capture.

Significant achievements during 2010-2012:

(1) We show that superbase-derived protic ionic liquids (PILs) with low melting points are capable of reversibly capturing CO_2 with an extremely high capacity (more than 1 mol per mole ILs). In addition, both polarities and basicities of these PILs can be easily tuned using CO_2 and N_2 as the "switch," which opens up their potential applications in separation and catalysis.

(2) We show that the CO_2 solubility, selectivity, and permeance could be optimized for CO_2/N_2 separation through controlled introduction of the nitrile functionality into the anion. Molecular simulations indicated that the symmetric $[B(CN)_4]$ anion is unique in giving high CO_2 solubility by interacting weakly with the cation and hence allowing easier creation of cavity for close contact with CO_2. This insight has great implications in designing new ionic liquids for CO_2 capture.

(3) We succeeded in a strategy to tune the enthalpy of CO_2 absorption by tunable basic ionic liquids, which were prepared by neutralizing weak proton donors with different pKa values with phosphonium hydroxide. Based on the relationship between the stability, the enthalpy of absorption, absorption capacity, and the basicity of ILs, highly stable ILs for CO_2 capture with desirable absorption enthalpy and high capacity were achieved.

(4) We developed a synthesis method to make functional porous carbon and carbon-oxide composite materials using conventional ILs. This unique method does not require the ILs to have cross-linkable groups and instead, utilizes the space confinement of ILs inside oxide networks to convert ILs with no carbonization yields into efficient carbon precursors with carbonization yields approaching theoretical limits.

(5) We show that an ammonia activation process that introduces nitrogen functionality into a hierarchically-structured mesoporous carbon can be used to significantly enhance the separations capabilities of the material for CO_2/N_2 and C_3H_6/N_2 separation. This process enhances separations by introducing additional microporosity to the carbon framework and by adding nitrogen-containing groups to the carbon surface.

Science objectives for 2012-2014:

- Pursue multi-dimensional gas separations using three dimensional hierarchical carbon architecture with mesoporous networks coated with microporous skins.
- Develop highly porous nitrogen-doped mesoporous carbon materials based on ionic-liquid precursors for CO_2 separation; understand the role of nitrogen with molecular simulation.

- Achieve optimal chemical binding and transport kinetics of gas molecules by task-specific ionic liquids for improved gas separations, including olefin/paraffin and CO_2/N_2.
- Design, synthesis, and test of ionic liquids with high CO_2 solubility for membrane separations in a supported liquid membrane setup.

Selected publications supported by this project 2010-2012

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Session 3 – Carbon Capture II

NMR Characterization of Metal-Organic Frameworks for Carbon Capture

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Metal-organic frameworks (MOFs) represent a new class of crystalline materials that exhibit record-setting porosity without sacrificing chemical "tenability" control of surface chemistry. Although considered for many uses, these materials show great promise for CO_2 $^{\text{capture}}$. In this talk I will describe how various solid-state NMR methods provide multiple length scale characterization of MOF local bonding structure, inform us on the dynamics of adsorbed CO_2 molecules, and provide an opportunity for high-throughput screening of surface area.

Multivariate MOFs (MTV-MOFs), which have multiple linkers distributed throughout the crystal, are a relatively new category of MOFs developed by Professor Omar Yaghi's research group. The MTV-MOFs adopt the same crystalline structure as the standard MOF-5, but have improved gas adsorption properties when comprised of the "right" proportion of linkers. I will describe how 2D NMR correlation and nuclear dipolar recoupling methods determine the local arrangement of these linkers; this approach is analogous to those used to determine secondary and tertiary structure of proteins. Our findings suggest that the different linkers are adjacent to each other in a single pore (Figure 1a), consistent with a random distribution of linkers based solely upon the initial synthesis composition. The NMR results provide unambiguous guidance for molecular simulations which, based upon a random distribution of linkers, predicts an optimal ratio of linkers for the best CO_2 capture performance.

Certain MOFs with open metal sites, e.g. MOF-74, have superior CO_2 capture capacities. In these materials we investigated the ^{13}C NMR of adsorbed $^{13}CO_2$. The lineshape and relaxation of CO_2 at variable temperatures provide rich information regarding CO_2 dynamics, including characterization of uniaxial rotation around the metal site at low concentrations (Figure 1b). Desorption processes with differing activation energies have been observed from NMR relaxation times. We find that MD simulation is in agreement with these NMR results.

Finally, characterization of MOFs using conventional BET adsorption for surface area measurement requires time-consuming experimental procedures and imposes a bottleneck for high-throughput discovery of new MOFs. ^{1}H-NMR relaxation can quickly probe the structure of many types of fluid-filled porous media, yet application of relaxometry to MOFs presents a unique challenge given MOFs with chemically functionalized, nanometer-sized pores. We are developing a robust procedure to correlate MOF surface area with solvent relaxation times (Figure 1c) using isoreticular expansion of a zirconia-based MOF, UIO66, as a proof-of-concept. Relaxometry is being performed using a single-sided NMR-MOUSE, a platform amenable to robotic automation for high-throughput synthesis. This new technique should provide a robust screening technique to direct further, more detailed characterization of newly synthesized MOFs and remove the characterization bottleneck.

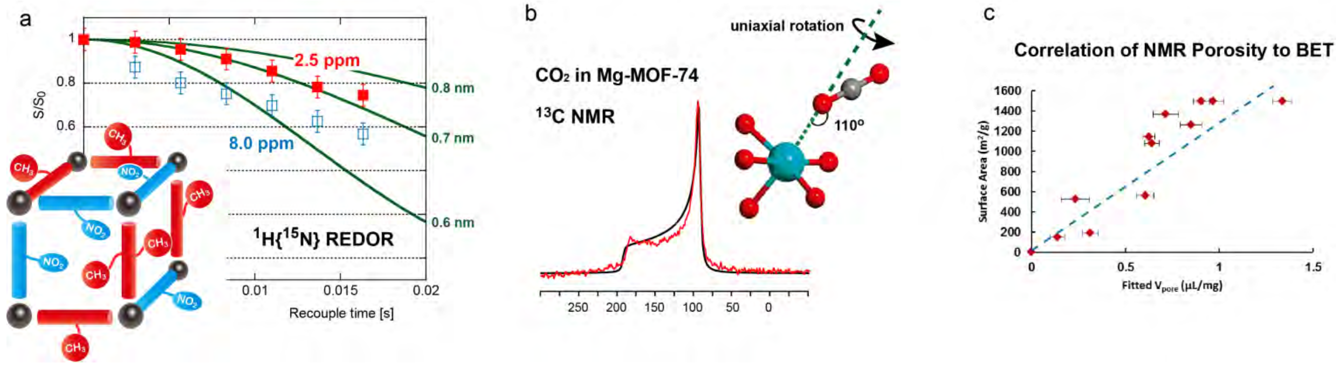

Figure 1. (a) ^{1}H-^{15}N REDOR that verifies the proximity of two different linkers in MTV-MOF. (b) ^{13}C NMR of CO_2 in MOF-74 which shows CO_2 undergoes uniaxial rotation at the open metal site. (c) Surface areas of a variety of MOFs, zeolites, and porous silicas correlated to NMR relaxometry observables.

Postdoctoral fellow Dr. Xüé-Qiān Kǒng (Sean), graduate student Joseph Chen, and visiting student Wen Ding (Xiamen University, China) conducted this work. We are grateful for our collaborations with Hexiang Deng of Professor Omar Yaghi's group (UCB and LBNL), Kenji Sumida, Mary Anne Manumpil of Professor Jeffrey Long's group (UCB and LBNL), as well as Fangyong Yan and Jihan Kim of Professor Berend Smit's group. Research funding for our MOF NMR studies is provided as part of the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001015. High-throughput screening studies are supported by the Advanced Research Projects Agency - Energy (ARPA-E), U.S. Department of Energy DE-AR0000103.

Bridging the gap between quantum chemistry and classical simulations for CO_2 capture

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Overall research goals: The research objective is to develop a computational methodology based on quantum chemical calculations to obtain classical force fields that can be employed in simulations of CO_2 capture within Metal Organic Frameworks (MOFs). At present the development of force fields for MOFs is still very empirical, and relies on the availability of accurate experimental data. In the quantum chemical community high-level methods have been developed which allow us to systematically study the nature of the various interactions. We plan to derive intermolecular potentials describing the interaction of CO_2 with MOFs directly from ab initio calculations. These potentials will offer the options of transferability and systematic improvement.

Significant achievements in 2011-2012: We have started working on this project in the fall of 2011. The goal is to employ the NEMO (Non-Empirical MOdel potentials) approach to intermolecular forces for the study of the interaction of CO_2 with MOFs. We have previously employed the NEMO force field to determine accurate *structural properties* of isolated molecules in solution. Since our long-term goal is to determine *thermodynamic properties* of gases in MOFs, and eventually to predict optimal material *design*, we have checked if the NEMO force field parameters can determine energetic properties accurately. We have started to develop CO_2-CO_2 parameters and MOF-CO_2 parameters for well-studied MOFs.

We have investigated Mg-MOF-74. During the formation of this metal organic framework not only does the metal coordinate with the linker, but also with solvent molecules. Subsequent activation removes the solvent molecules and creates open Mg sites, which have strong affinity for CO_2. At present the interactions of CO_2 with these open Mg sites are so poorly understood that state of the art force fields underestimate the adsorption of CO_2 in Mg-MOF-74, at carbon capture conditions, by as much as two orders of magnitude. We have developed a NEMO force field for Mg-MOF-74 and similar systems, using high-level quantum chemical calculations. This force field accurately takes into account the chemistry of the open metal sites. Monte Carlo simulations based on this force field shed some light on the interpretation of thermodynamic data of this system.

Science objectives for 2012-2014:

- We will employ the same approach to study the interaction of Mg-MOF-74 with other gases, like N_2, CO and CH_4.
- We will consider different M-MOF-74 types of material, in which M=Ni, Zn and Fe. We will determine the absorption properties of these different materials and try to understand, by inspection of the electronic structure of the various metals, which one is more selective towards CO_2.
- We will extend the NEMO procedure in such a way that it can be employed in combination with different electronic structure theories, ranging from MP2, the method currently employed to

study Mg-MOF74 to multi-reference wave-function methods and DFT.

- We will apply the NEMO method to study also CO_2 capture in ionic liquids.

References to work supported by this project 2010-2012(style=Stand alone text heading):

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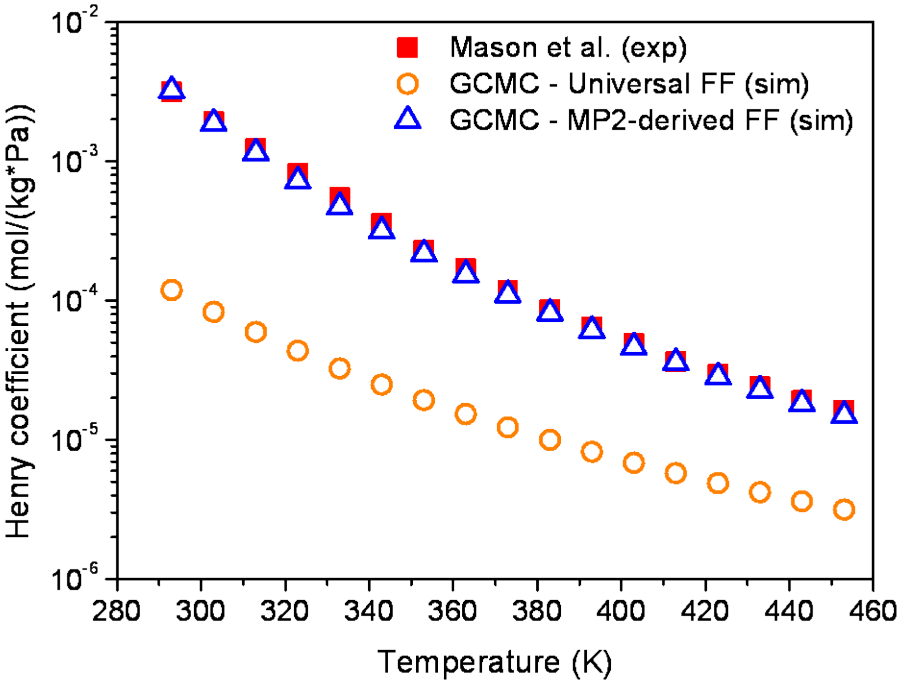

Figure 1. CO_2 Henry coefficient: experiment; our prediction (MP2) and prediction from conventional UFF.

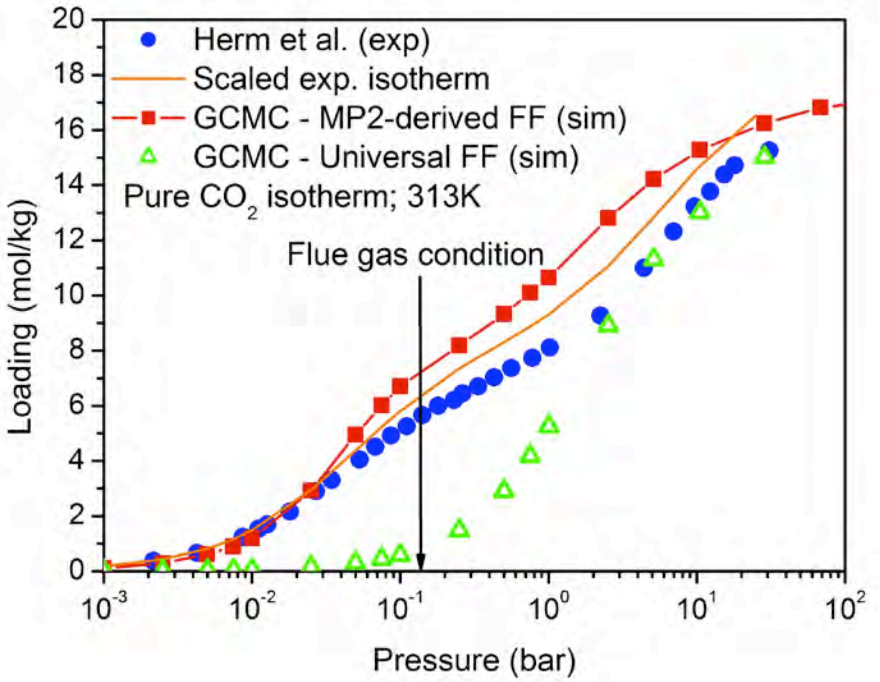

Figure 2. CO_2 Loading: experiment; our prediction (MP2) and prediction from conventional UFF.

Knowledge-guided screening tools for identification of porous materials for CO_2 separation

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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.

Significant achievements in 2010-2012: Our approach to screening of materials relies upon purpose-built applied mathematics and material informatics algorithms and the corresponding software tool, Zeo++, by which we can describe, compare, and search large sets of materials in an unsupervised manner. Zeo++ utilizes the Voronoi decomposition, a computational geometry technique which provides a representation of a material's void space as a network of restricting apertures between structure atoms. The resulting Voronoi network can be used to calculate structure descriptors, e.g. restricting pore diameters, dimensionality of channel systems, accessible volume and surface area. Most importantly, it serves as a starting point for the development of a novel structural descriptor which encodes the entire shape of a material's void space: the Voronoi hologram (Fig 1). The Voronoi hologram is a histogram representation of the guest-accessible portion of the Voronoi network. Its development allowed us to establish a framework for efficient navigation through the chemical space of all-silicious zeolites.

Similarity between Voronoi holograms can be quantified using an appropriate similarity coefficient. Since similar materials exhibit similar holograms, by identifying similar holograms we can identify families of similar structures. We can also select structures which have dissimilar holograms, thereby obtaining a maximally diverse and representative sampling of a dataset. As a result, we can filter large databases to identify only those materials with sufficient dissimilarity in their structures, so as to limit the performing of wasteful calculations upon highly similar structures. For example, out of the ca. 135000 zeolites from Prof. Deem database, we identified a set of 172 diverse structures, for which CO_2 adsorption performance was determined. A number of these structures were found to exhibit a high Henry coefficient for CO_2. Moreover, within this set, common substructural features were detected. It was determined that the identified features are highly preferential CO_2 binding sites, contributing more than 90% of the Henry coefficient (Fig. 2; a site can dominate the Henry coefficient as the site's contribution is proportional to the exponent of the site's CO_2 binding energy).

Finally, to utilize this knowledge, we developed a computational method which allows for identification of these preferential binding sites within materials, without the need for molecular simulation. Our approach is based on analyzing materials' topology and pore geometry. First, we identify substructural fragments which are similar to those occurring in preferential CO_2 binding sites in the diverse set, and then rank materials based on the predicted strength of these sites by a CO_2 docking and scoring procedure. Our analysis conducted on the ca. 135000 set indicates that within the highest ranked 10% of materials, we obtain a set in which strong CO_2 binding sites are correctly identified in 90% of structures, and so these are also the structures with the highest Henry coefficient. Moreover, our algorithms are two orders of magnitude faster than our GPU-based molecular simulation. In other words, with the current prototype approach ***we can identify ca. 900 best performing structures out of the top 1000 of the 135000 set of zeolites by performing molecular simulations for as little as 1172 materials!***

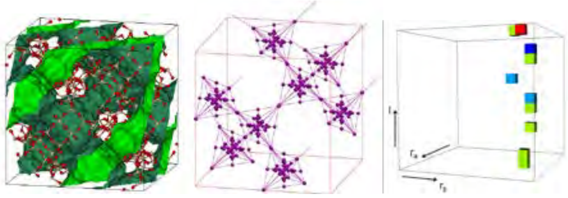

Fig. 1. FAU zeolite (l-to-r): pore landscape, the Voronoi network representation and the corresponding hologram

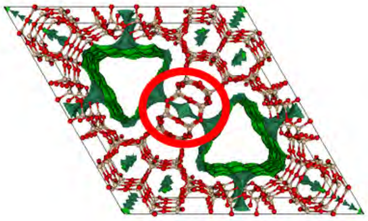

Fig. 2. A preferential binding site highlighted in a zeolite

Science objectives for 2012-2014:

- Development of Zeo++ will continue to include new structural, geometric and topologic descriptors of the void space in porous materials. This will enable new generation of similarity and diversity techniques as well as QSPR and data-mining studies.
- To enable screening studies including weakly interacting guest molecules such as methane, which pose a challenge to the current formulation of our similarity searching.
- Extension of the current approach to include materials with diverse chemistry (e.g. MOFs). This will involve supplementing Voronoi networks with additional information on atoms and chemical groups present on the pore surface.

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Poster Session 1

Microvascular Materials for Ultra-High Specific Surface Area Membranes

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Overall research goals: The research objectives of our lab are to develop new methods, using sacrificial patterning techniques, to create ultra-high specific surface area materials. The high specific surface area is achieved by packing microchannels in 3-dimensions. The membranous material can then be molded into high surface area structures for use in separations. The micro-channel structures can also be used to drive separation processes in liquids to release absorbed gases. Fundamental study of the mechanisms of transport, the interplay of molecular design and function and surface based reactivity are all of interest.

Significant achievements in 2010-2012: Our research group only began in 2011, so many achievements are yet to come. However, we have developed a technique for making compact packed patterns in 3-dimensional membranes. The technique creates structures similar to hollow-fiber membranes, but with two distinct differences. First, the fibers can be arranged in pre-designed packing patterns. This patterning allows for control over the edge-to-edge distance between channels and gives us the ability to create compact packing of membrane structures with increased specific surface area. Second, it allows for the creation of hollow membranes without the use of spinning, providing the ability to access several new membranous materials that might otherwise not benefit from being from increased surface areas. We have also been able to directly visualize the reactivity of gases with liquids at a membrane-liquid interface and note that varying the membrane structure has a direct influence on the reactivity at the interface.

Additionally, we have been exploring new methods for utilizing waste heat as a source of energy for separations in liquid/gas reactions. We have been working towards using radiant heat to remove CO_2 from gas dissolved in liquid. We believe these types of reactive structures could be used to drive separations in two-component systems.

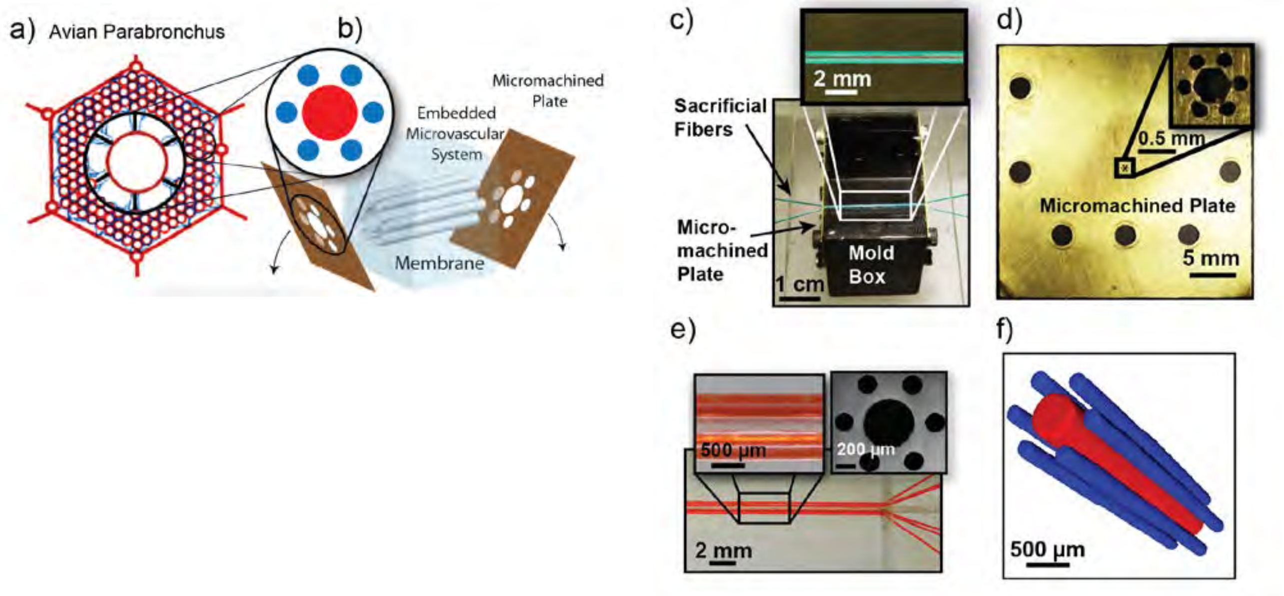

Figure 1. Inspiration, development, and synthesis of 3D microvascular exchange unit. a) Anatomic

schematic of avian parabronchi hexagonal airflow passages. Gas exchange occurs with unidirectional flow through a hierarchical array of hexagonal units composed of air and blood capillaries. b) Synthetic method for creating parabronchus-like capture units using VaSC. Channels are arranged in a hexagonal pattern via laser micromachined end-caps. c) A laser etched micromachined end-cap used for fiber patterning. d) Sacrificial fibers patterned with a mold box utilizing micromachined end-caps. e) A representative sample composed of hexagonally arranged channels (filled with dye for visual clarity) with a cross-sectional SEM image. f) Representative µCT image of a 3D microvascular gas exchange unit with 200 µm outer channels and a 500 µm central channel.

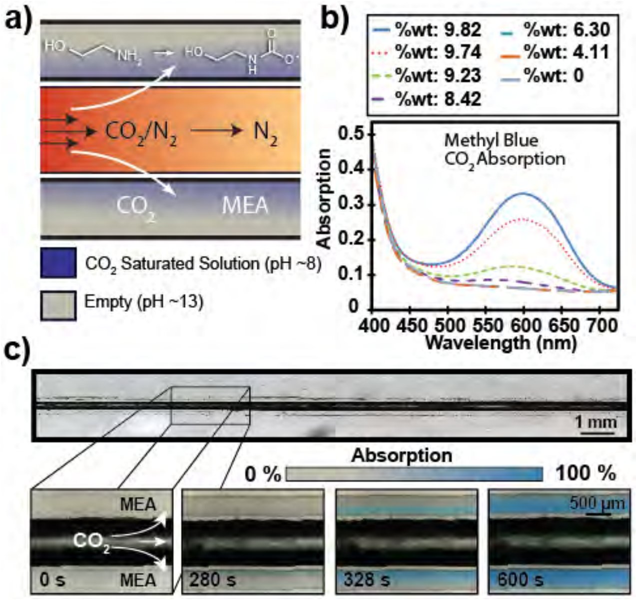

Fig. 2 Experimental capture process and visualization of CO2 reactivity. a) Schematic of the overall reaction taking place as CO2 permeates through the membrane and reacts with MEA. b) UV-Vis spectrum of MEA with indicating dye over absorption range of 0-10% weight. c) Time-lapsed visualization of capture process. The dye in MEA shifts from clear yellow to blue as CO2 is absorbed due to the pH change. A clear spatiotemporal pattern moving through the channel radiating from the central CO2 source is exhibited.

Science objectives for 2012-2014:

- Develop densely compact structures with specific surface area structures that exceed 20,000 m^2/ m^3. Use these structures to selectively capture and then separate gas from mixed gas streams.
- Cast structures in variety of permeable materials. Compare previously synthesized materials with new structural rearrangements.
- Expand the variety of liquids used as capture agents and the ability to use waste heat sources for gas separations.
- References to work supported by this project 2010-2012:

1. No Previous Support, However references to work mentioned have been included.
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Robust, Transferable, and Physically-Motivated Force Fields for Gas Adsorption in Nanoporous Systems

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Overall research goals: The research objective of this work are to develop the theoretical framework necessary to generate transferable and physically-motivated classical force fields for complex systems, and apply these methodologies to the specific case of gas adsorption in nanoporous metal-organic framework systems.

Significant achievements in 2010-2012: We have developed a novel approach to force field development based on symmetry adapted perturbation theory (SAPT) calculations. Our force fields are physically-motivated in that they contain explicit terms for each of the various fundamental classes of intermolecular interactions: exchange repulsion, electrostatics, polarization, and dispersion. Each of these is described using a physically-appropriate functional form, and fit *individually* to the corresponding term in the SAPT energy decomposition. This approach strongly mitigates the possibility of spurious (or fortuitous) error cancelation, yielding force fields that are robust and give the right answer, for the right reason.

We validated our methodology using two well-characterized systems: bulk CO_2 and bulk N_2. We developed our model based *exclusive* on SAPT calculations on CO_2 (N_2) dimers and timers and then benchmarked these models against bulk data. We find quantitative agreement with a host of structural, thermodynamic, and dynamic properties. Since these models have not been empirically tuned to reproduce bulk properties, and are also polarizable, they are also ideally suited for use in studying gas adsorption in heterogeneous, polar environments such as MOFs.

Building upon these encouraging preliminary results, we utilized a parallel methodology to develop physically-motivated force fields for the interaction of CO_2 with zeolite imidazolate framworks ZIF-8 and -71. Here we utilized SAPT calculations on validated ZIF clusters models interacting with a single CO_2, generating specific force fields tailored to each ZIF system. These force fields were validated via the adsorption isotherms, which are in quantitative to semi-quantitative agreement with the corresponding experimental measurement – with no empirical parameters or “scalings”. These results demonstrate that our SAPT-based approach is sufficiently accurate to enable truly predicative computational studies of gas uptake in related nanoporous systems.

One significant limitation of the above work is that it requires time consuming parameterization for each MOF system. In contrast, we very recently enhanced our methodology to allow us to generate robust, physically-motivated, and *transferable* force fields for a related family of functionalized MOFs. We find that using a single, self-consistent parameter set, we can reproduce the CO_2 and N_2 uptake for a wide variety of ZIFs. This approach combines the accuracy of our tailored, system-specific force fields with the convenience of “generic” force fields (DREIDING, UFF). In a complementary effort, we also recently developed a novel rapid simulation / screening methodology. This *rigorously exact* lattice-model based is ~10-100 times faster than corresponding Monte Carlo simulations, facilitating predictive high-throughput computational screenings!

In parallel with these efforts, we have been exploring the implications of common flue gas contaminants (NO_x, SO_x, H_2O) on flue gas separation utilizing MOFs, including their impact on MOF stability. We previously explored binding of both contaminants and CO_2 to several MOFs with CUS, including Mg-MOF-74 and MIL-101. We find that many of these contaminants bind extremely strong, in some cases over 100 kJ/mol. As such, despite the small contaminant concentrations (10-100 ppm, assuming that post-combustion CO_2 separation would occur after normal flue gas scrubbing), the equilibrium occupation of such CUS would actually favor the contaminant over CO_2. This phenomenon is likely unique to MOFs with CUS, since as the binding energies of CO_2 and contaminants both increase, the differential binding energy also increases, eventually favoring contaminant binding over CO_2 binding despite the dramatic difference in concentrations. We are currently working to estimate regeneration temperatures necessary to desorb these contaminants, but the strong binding suggests that extreme conditions may be required. This work raises important issues that must be addressed to ensure the robustness of MOFs in realistic flue gas working conditions.

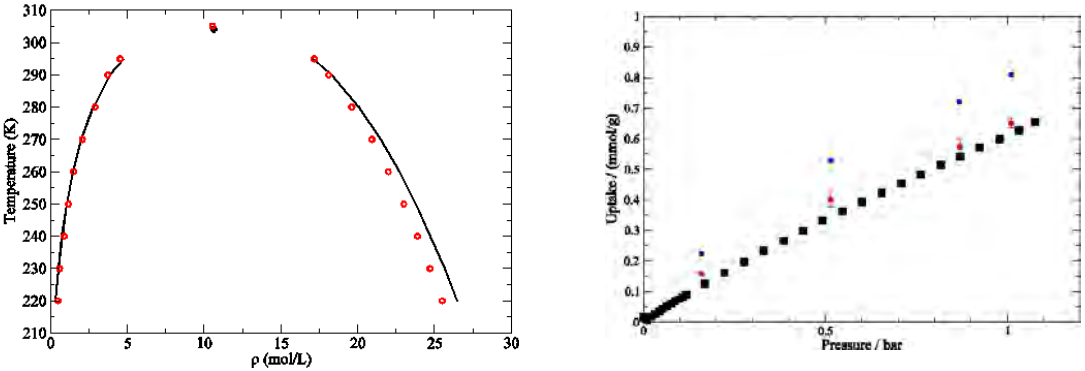

Figure 1. (Left) Predicted phase diagram for our "SYM" CO2 model (points) vs. experiment (solid); the model is essentially entirely fit from first-principles. (Right). Applying the same approach, we generated a force field for ZIF-71/CO_2 (red) – with no empirical parameters -- yielding semi-quantitative agreement with the experimental isotherm (black). The standard UFF force field results are shown in blue.

Science objectives for 2012-2014:

- Refine methodologies for generating *transferable*, physically-motivated force fields from SAPT calculations, focusing specifically on the crucial dispersion and exchange parameters; also extend our approach to account for interaction with coordinately unsaturated sites. These developments are of wide ranging importance well beyond MOFs, facilitating the generation of a modern"universal" force field for condensed phase simulation.

- Enhance lattice model simulation techniques to better account for adsorbate-adsorbate interactions, pushing the domain of applicability into the high pressure regime.

- Utilize the synergy of the prior two developments to address challenging and relevant problems in MOF materials, including: elucidation of synergistic effects in mixed ligand MOFs; transport simulations; and high throughput screening methodologies.

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A Physicochemical Method for Separating Rare Earths: Addressing an Impending Shortfall

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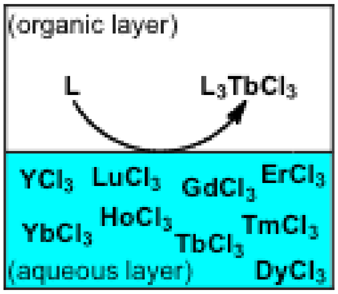
Overall Research Goals: The overall objective of this proposal is to chemically separate Ce, Pr, Nd and Tb ions with extractants that bind those individual metal ions selectively using oxidative intermediate valence effects.



Proposed selective biphasic extraction of terbium from an aqueous solution of heavy rare earth elements.

Achievements since August 2011: An important economic and technological choke point in rare earths mining and extraction is the separations chemistry of those elements. Rare earths separations are accomplished industrially using contiguous, counter-current liquid-liquid extraction. Chinese suppliers currently dominate the global market for rare earth elements because of cheap labor costs, established infrastructure to perform separations and weak environmental regulations. In response to the market imbalance for these important strategic elements we are developing new methodologies for separating targeted high value rare earth ions. Selective separations schemes that take advantage of unique electronic structure effects are expected to improve the economics for separations of high value rare earths including Pr, Nd, Tb, and Dy by producing less waste and consuming less energy.

Since August 2011 we have expanded on and improved the synthetic chemistry of a family of organo-nitroxide ligands for use as extractants. The electrochemical properties of the nitroxides have been determined and their electronic structures have been evaluated using Density Functional Theory (DFT). We have also shown the compounds bind rare earth ions effectively and demonstrated intra-complex redox chemistry. Of the complexes that have been prepared, the cerium congeners exhibit extraordinary reducing electrochemical redox events and unusual charge transfer bands in their optical spectroscopy. We are working to correlate this data to direct spectroscopic observables comprising metal valence.

Science Objectives for 2012–2013:

- To establish correlations of cerium valences with physicochemical properties including bond distances, optical charge transfer band energies, electrochemistry, magnetism and XANES spectroscopy
- The application multi-reference quantum chemistry methods, specifically Complete Active Space Self-Consistent Field (CASSCF) approaches, to cerium complexes
- Expansion of the synthetic methodology to *trans*-cerium lanthanide ions
- Establish ‘proof-of-principle’ selective separations for rare earth ions

Selective Covalent Bond Formation in Gas-Phase Ion/Ion Reactions and Spectroscopy of Cold Gaseous Polyatomic Ions

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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, such as those relevant to bio-fuels. 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. We have also devoted considerable effort in the characterization of dipolar DC collisional activation.

Significant achievements in 2010-2012:

Dipolar DDC in Linear and 3-D Ion Traps. We implemented means to apply dipolar DC to opposing electrodes in 3-D and linear ion traps. By displacing ions from the ion trap center, it is possible to expose them to RF heating in a controlled fashion. This constitutes a novel means for ion trap collisional activation in that it is not m/z-dependent as is conventional resonance excitation. This provides a collisional analog to infra-red multi-photon ionization. During the course of the work, we found that the higher order fields associated with so-called ‘stretched’ ion traps leads to faster heating than is predicted based on pure quadrupolar fields. This effect allows for higher ion temperatures to be achieved when higher order fields are present.

Ion/ion Charge Inversion. We have been exploring the use of ion/ion charge inversion reactions as means for selective screening of mixtures and for increasing the absolute charges of ions. We use multiply-charged reagent ions to effect charge inversion of singly charged analyte ions. We have noted that the charge state of the reagent ion plays a major role in charge inversion efficiency. For example, when a range of reagent charge states is available, an intermediate charge state typically proves to provide the highest charge inversion efficiency. In this reporting period, we developed a model to allow us to predict which reagent charge states should provide the highest efficiency. We found that the drop in efficiency at high charge states is not a result of the dynamics of the reactions, as we had initially expected. Rather, the electrostatic repulsion of the ion/ion reaction products leads to significant scattering of the products and consequent loss of the charge-inverted analyte ions.

Specific covalent bond formation via ion/ion chemistry. We have discovered several ion/ion reactions that lead to covalent bond formation with specific functional groups. These discoveries have shown that it will be possible to effect selective reactions in tandem mass spectrometry using ion/ion reactions. Examples of reactions include Schiff base formation upon the reaction of an aldehyde with a primary amine, the reaction of primary amines and guanidinium groups with N-hydroxy succinimide esters, and the reaction of carboxylic acid groups with carbodiimide reagents. We have also found that the particularly strong dipole-dipole interactions of sulfonates phosphates with protonated basic sites allow for the selective charge inversion of particular analyte classes. These and other reactions promise to provide a new dimension of specificity to tandem mass spectrometry.

Science objectives for 2010-2012:

- We plan to study mechanistic aspects of the ion/ion reactions that we have already found to give rise to covalent reactions. All such reaction require the formation of a long-lived complex. The covalently-bound products are often observed only after dissociation of the complex. In these cases, it is not clear whether the ion activation process is needed to overcome reaction barriers or if the reaction has already occurred in the complex.
- In parallel with our mechanistic studies, we will seek to expand the functional groups for which we can effect covalent reactions. For example, we are interested in developing selective reactions for thiols, alcohols, aldehydes, ketones, etc.
- 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 hope to be able to initiate cold ion spectroscopy and photodissociation studies in collaboration with my colleague Tim Zwier, who has longstanding expertise in the spectroscopy of cold neutral species generated via supersonic expansion. Our initial work will focus on lignins, which are particularly relevant to bio-fuel research.

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The Development of Nano-Composite Electrodes for Solid Oxide Electrolyzers and Fuel Cells

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Overall research goals: The objectives of this work have been to understand the chemistry of oxide-oxide interfaces in the air and fuel electrodes of both solid oxide electrolyzers (SOE) and fuel cells (SOFC), with the goal of determining how interactions at these interfaces affect electrode microstructure and electrochemical function.

Significant achievements in 2010-2012: We have made the following important contributions towards the understanding of electrode function in SOFC:

- We have demonstrated that the loss in SOFC performance with time is often due to coarsening of the perovskite and subsequent loss of surface area. Interlayers of ceria do not prevent this deactivation.
- The enhanced performance of SOFC cathodes with addition of a large number of promoters is often associated with textural changes in the electrode, not to catalytic effects.
- In composite SOFC cathodes, the ionic conductivity of the electrolyte phase strongly affect performance, while the ionic conductivity of the perovskite phase does not. The structure and surface areas of both phases strongly influence the electrochemical properties.
- For SOFC anodes, the use of ceramic conductors with various metal catalysts can provide excellent performance for both hydrogen and methane fuels.
- Sintering of the metal catalysts can serious deactivate the electrochemical performance of SOFC anodes. The use of core-shell catalyst, specifically Pd@ceria, can alleviate this problem.
- HBr electrolysis can be carried out with good efficiency using an electrolyte made from molten bromides in a porous YSZ scaffold.

Science objectives for 2012-2014

- Techniques will be developed to characterize the surface vacancy sites on perovskites that are used for SOFC cathodes and for Ion Transport Membranes. Specifically, we will be studying the adsorption of reactive molecules and the use of various spectroscopies in order to measure the concentration of these sites in doped $LaFeO_3$.
- Oxygen-exchange rates will be studied on both doped $LaFeO_3$ electrodes formed by infiltration into porous YSZ scaffolds and on epitaxial $LaFeO_3$ films on YSZ crystals by correlating surface vacancies with electrochemical activity in order to establish whether these surface vacancies are indeed the active sites.
- The effect of modifying the electrodes by ALD of various compounds will be examined to understand the role that various promoters have on electrochemical performance.

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Multiscale Modeling of the Relationship Between Nanostructure of Hydrated Proton Exchange Membranes and Proton Conductivity

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Overall research goals: The research objectives are to use multiscale simulation techniques to understand at the molecular level the relationship between the structure of hydrated proton exchange membranes and the resulting transport properties. A secondary goal is to distill this understanding into a predictive theory relating proton conductivity to hydrated membrane nanostructure.

Significant achievements in 2010-2012: The first significant achievement of this period was the development and implementation of a reactive molecular dynamics (RMD) algorithm that allowed us to simulate both the structural ("proton hopping") and vehicular (center-of-mass translation of the hydronium ion) components of charge diffusion in a variety of aqueous systems, including bulk solutions, solutions confined in carbon nanotubes and hydrated Nafion Proton Exchange Membranes (PEMs). These simulations allowed us to observe the impact of decreasing hydration on the individual mechanisms for charge transport. We observe that the influence of nanoscale confinement and high acidity in PEMs have a much stronger negative impact on the structural component than on the vehicular component.

The second significant achievement of this period was the development of a truly integrated multiscale modeling approach that allowed us to connect nanoscale structure to experimental measurements of proton conductivity in PEMs. The approach invoked molecular dynamics (MD) simulations to characterize the free volume of the aqueous domain and the interfacial surface area within the hydrated PEMs. Short time mean square displacements of water from MD simulations were fit to long-time Confined Random Walk (CRW) simulations that yielded cluster sizes, cluster-to-cluster hopping probabilities and intrinsic intracluster diffusivities. The combined MD and CRW were used to parameterize a percolation theory, which accounted for diminishing connectivity of the aqueous domain with decreasing water content. Taken together, this combined approach is able to reproduce experimentally determined proton conductivities across the full range of hydration in Nafion as well as in cross-

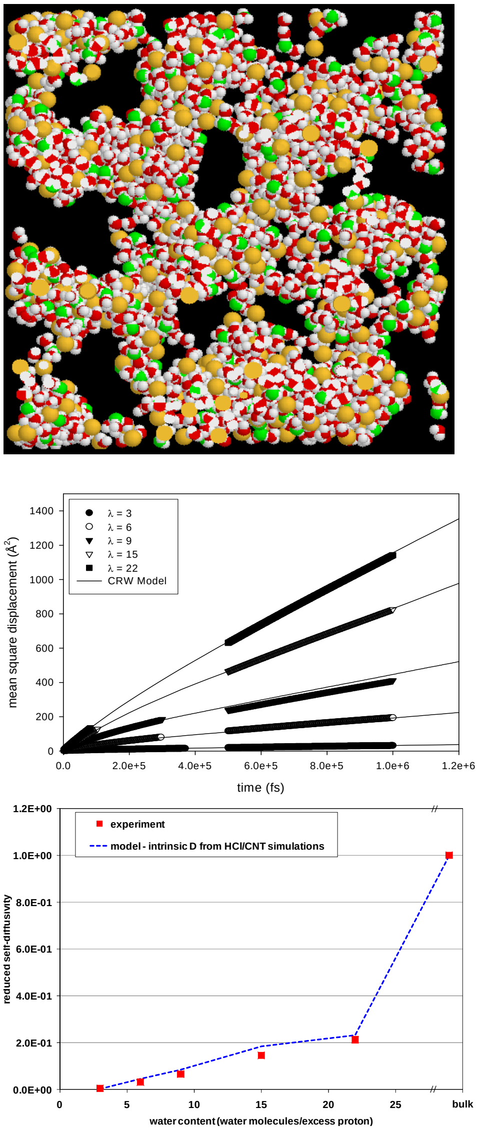

Figure 1. Characterization of aqueous domain in hydrated PEMs from MD simulation (top) combined with MD/CRW simulations yielding water mean square displacements (middle) and percolation theory yield a quantitative agreement with experiment for the proton conductivity in Nafion across the full range of hydration (bottom).

linked and sulfonated polycyclohexadiene (xs-PCHD) PEMs.

The third significant achievement of this period is the publication of a comprehensive set of MD simulations of Nafion and the Short-Side Chain (SSC) perfluorosulfonic acid (PFSA) PEM as a function of hydration. These simulations form a definitive characterization of the local structure of the membranes as a function of side chain length and degree of hydration.

Science objectives for 2012-2014:

- Demonstrate general applicability of multiscale approach to predicting proton conductivity to hydrated membranes composed of cross-linked and sulfonated PCHD of varying composition, including comparison of homopolymer, block copolymer with PEG, and blends with PEG.
- Demonstrate general applicability of multiscale approach to predicting proton conductivity in decorated amorphous silica membranes.
- Demonstrate general applicability of multiscale approach to predicting lithium ionic conductivity in graphitic anodes of varying nanostructure used in Li-ion batteries.

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Ion-Surface Interactions in Mass Spectrometry

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Overall research goals: The objective of our research is to achieve a fundamental understanding of the interactions of complex molecules with surfaces and develop new approaches for selective modification of substrates using beams of mass-selected hyperthermal ions. In addition, we are developing approaches to analyze complex mixtures such as organic aerosols, petroleum, and biofuels directly from solid substrates using ambient ionization mass spectrometry. This research addresses analytical challenges relevant to a broad range of applications within the Department of Energy (DOE) mission areas.

Significant achievements in 2010-2012: Surface-induced dissociation (SID) experiments examined the role of the charge and radical on the energetics and mechanisms of dissociation of large floppy molecules and non-covalent complexes. Our results indicate that entropy plays a major role in dissociation of large complex molecules. Charge-directed fragmentation often occurs in competition with charge-remote fragmentation; the competition between these processes is often determined by differences in entropy effects.

We conducted first studies focused on selective deposition of catalytically active organometallic complexes and metal clusters on surfaces. Our studies demonstrated that proton loss by protonated molecules deposited onto on surfaces efficiently acidifies the surface. Fundamental understanding of charge reduction on surfaces is important for controlling the acidity of the monolayer and studying proton-mediated reactivity of molecules deposited on substrates. Furthermore, we demonstrated that collision-induced dissociation may be used for preparation of catalytically active molecules that do not exist in solution for subsequent deposition on substrates. In addition, we developed a new ambient ionization technique, nanospray desorption Electrospray ionization (nano-DESI), for sensitive analysis of molecules and complex mixtures on surfaces. The technique was demonstrated for complex organic mixtures including crude oil and ambient organic particles.

Science objectives for 2012-2014:

- Examine the effect of charge, composition, and surface coverage on the charge loss by monolayer-protected gold clusters and polyoxometalate complexes deposited on substrates;
- First studies of the energetics and dynamics of dissociation of gold clusters;
- Explore the utility of nano-DESI for characterization of organic matter important for understanding carbon cycling and sequestration in terrestrial ecosystems.

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Developing Nanoparticle-based Efficient Analyte Capture and Ionization

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Overall research goals: Research objectives focus on developing novel platforms, *i.e.*, gold nanorods (AuNR), polymer-encapsulated AuNP and sol-gel processed thin films, for capture and enrichment of low abundance membrane active molecules from complex mixtures. Capture functionality is achieved by tailoring the surface chemistry of the materials with a specific functional groups that mimic a cellular surface, while retaining the optically active nanostructure.

Significant achievements in 2010-2012: A ‘strategy’ for selective capture/ionization of specific compound classes based on chemical derivatization of AuNRs and infrared laser desorption ionization (IR-LDI) was developed. IR-LDI is performed at wavelengths (1064 nm) that overlap with the longitudinal surface plasmon resonance (L-SPR) mode of AuNR. The wavelength of the L-SPR band can be tuned by controlling the AuNR aspect ratio (length-to-diameter); L-SPR band for AuNR (aspect ratio of 5:1) is centered at approximately 840 nm, which overlaps with the 1064 nm Nd:YAG laser irradiation. The results of these studies are critically important for designing selective mass spectrometry based biomarker discovery and imaging/spatial profiling mass spectrometry experiments.

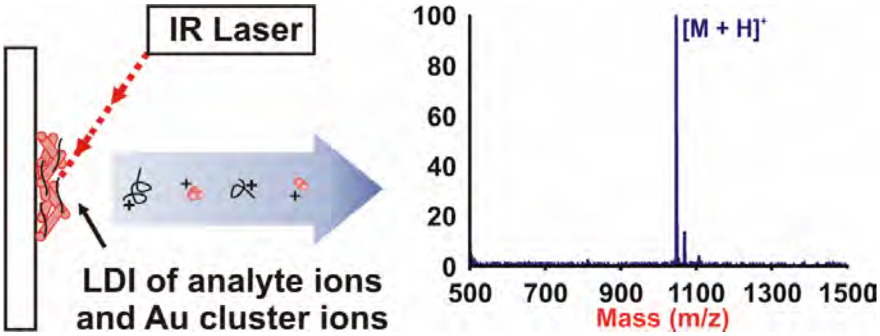

Figure 1. A schematic representation illustrating the use of AuNR in L-SPR-IR-LDI-MS in which the analyte is mixed with nanorods in solution, spotted onto the sample plate, and dried prior to analysis. The figure shows L-SPR-LDI mass spectrum of Angiotensin II, m/z = 1046.5 Da using 4-ATP capped gold nanorods.

The success of the analyte capture described above led to the fabrication of a label-free mass spectrometry and optical detection based biosensor platform for the detection of low abundance lipophilic analytes from complex mixtures. The biosensor consists of a lipid layer partially tethered to the surface of a AuNR. The effectiveness of the biosensor is demonstrated for the label-free detection of a lipophilic drug from aqueous solution and of a lipopeptide from serum. These results demonstrate, for the first time, the successful application of a hybrid lipid capped AuNR biosensor for the capture and label-free detection of membrane active drugs by MS.

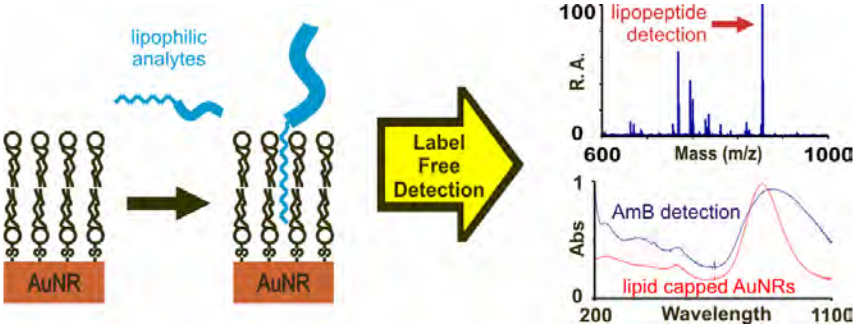

Figure 2. Capture of the lipopeptide (Myristoyl-Lys-Arg-Thr-Leu-Arg) from calf serum with lipid-capped AuNRs. The lipopeptide was captured from an 11 nM lipopeptide from 3 mg/mL serum solution. Optical detection of capture of the AmB by the lipid capped AuNRs is confirmed by the absorbance at 300-500 nm and perturbation of the longitudinal surface plasmon resonance band of the gold nanorods.

A mass spectrometry platform composed of a porous thin film embedded with AgNP is currently under investigation. The porous thin films are prepared by using sol-gel methods that yield optically active platforms that are used for LDI various analytes spotted directly to the surface. This type of platform is not selective for a single class of compounds (olefins), but rather is capable of analysis of several types of plant-derived compounds, *i.e.*, peptides, lipids, and sterols.

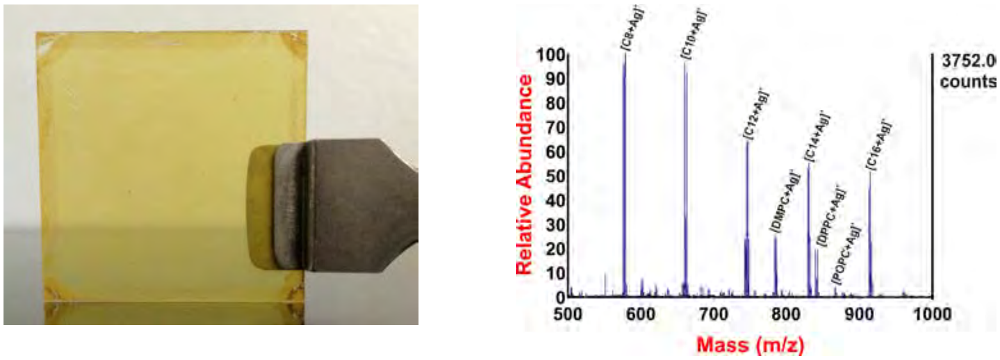

Figure 3. A typical silver nanoparticle film (left) and analysis of a triglyceride and phosphatidylcholine mixture (right) from the surface of a film. Note: Concentration of analytes spotted on the surface range from ~6pmol - ~11 pmol; POPC is the only olefin in the mixture.

Science objectives for 2012-2014:

Develop multiplexing platforms for capture-enrichment of multiple low abundance analytes for MS analysis.

Incorporate specificity by functionalizing the surface of the nanorod with lipids containing reactive headgroups.

Investigate the use of sol-gel prepared thin films embedded with metal nanoparticles as platforms for flexible detection of a number analytes by mass spectrometry analysis.

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Fluoropolymers, Electrolytes, Composites and Electrodes

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Overall research goals: The overall objective of this research project is to provide new electrolyte membranes and electrode materials consisting of integrated catalysts and fluorinated electrolytes for use in PEMFC power sources.

Significant achievements in 2010-2012: During the period 2010-2012, work toward the overall project objective was pursued in four topical areas, as follows; (1) low equivalent weight (EW) perfluoro-sulfonimide (PFSI) ionomers; (2) telechelic perfluoro-cyclobutyl (PFCB) ionomers; (3) mesoporous nanocomposite carbon supports for use in PEMFC electrodes; and (4) electrospun PFCB mats for use in PEMFC stacks. Significant achievements in these four topical areas are summarized below.

In topic 1, fluoro-ionomers having equivalent weights between 600 and 900 g / equiv were prepared and processed into membranes. The materials are co-polymers of tetrafluoroethylene with trifluorovinyl ether (TFVE) co-monomers having fluorosulfonimide protogenic groups. Some polymers were partially crosslinked using difunctional TFVE units during the polymerization, and others consisted of blends of low and high EW ionomers. Ionic conductivities are generally improved relative to Nafion PFSA ionomers, with the best conductivities generally corresponding to the lowest EW ionomers. Figure 1 presents representative data on three ionomer blends consisting of low EW ionomers which provide regions having low EW / high IEC, blended with high EW ionomers which provide dimensional stability and prevent excessive swelling.

In topic 2, oligomeric PFCB ionomers having a high degree of sulfonation within the main chain and end groups consisting of phenylphosphonic acid (PPA) groups were prepared. One intended application for these ionomers involves attachment onto catalyst support surfaces via the PPA end groups, to allow for a robust integration of very low EW ionomers into electrodes, when such ionomers would otherwise wash out of the electrode with product water.

In topic 3, a wide range of mesoporous carbon catalyst supports was prepared using resorcinol / formaldehyde chemistry for making RF sols (which produce carbon upon high-temperature pyrolysis) containing silica sols as templating agents, and also zirconia nanoparticles as anchoring agents for PPA-based ionomer electrolytes. Extensive characterization of support materials was accomplished using electron microscopy / EDX, nitrogen porosimetry, and X-ray diffraction. Platinum deposition was demonstrated for all supports, and electrolyte immobilization was demonstrated for supports containing integrated zirconia, using electrolytes having PPA groups. This work had identified a new strategy for integrating electronic and ionic conduction within catalyst supports in PEMFC power sources.

Finally, in topic 4, an electrospinning approach to making nonwoven fibrous mats of PFCB-based polymers was demonstrated. This work could hold promise for controlling water transport within PEMFC membrane-electrode assemblies.

Science objectives for 2012-2014

- Continue exploring use of crosslinking / blending strategies to prepare PFSI-based proton-exchange membranes having high ionic conductivity over a wide range of humidity and temperature. The work will ultimately seek to achieve the conductivity / humidity targets set in the high-temperature membranes program from DOE-EERE, and will extend to include studies of MEA fabrication using project membranes and testing in both fuel-cell and electrolyzer applications.

- Extend work on combinations of mesoporous carbon composite catalyst supports and telechelic ionomers to include supported catalysts and MEA fabrication and testing.
- Pursue new synthetic strategies to prepare fluorinated anion-exchange materials for use as membranes and electrode ionomers in alkaline exchange membrane fuel cells and electrolyzers.
- New applications areas for PFSI and anion exchange membranes and ionomers in lithium ion and redox flow battery applications will be pursued.

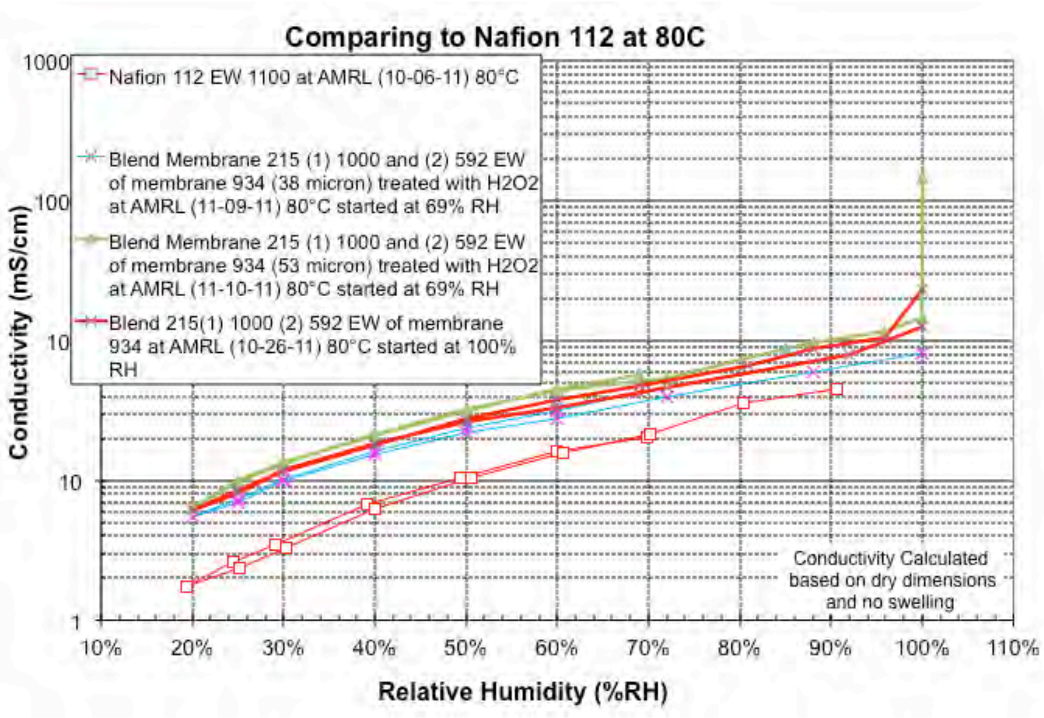

Figure 1. Three data sets of ionic conductivity vs. relative humidity for three PFSI ionomer blends. Benchmark data for a Nafion 112 membrane is also included for comparison. All three ionomer blends show higher conductivity than the Nafion sample, with the largest difference exhibited at the lowest RH values. These blends show a good combination of high conductivity retention at low RH from the low EW component, and good dimensional stability from the high EW component.

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Separations and Analysis using Bipolar Electrodes

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Overall research goals: The research objectives of this project are to further the understanding and development of bipolar electrodes (BPEs) for the separation and analysis of materials. Two aspects of the project are the focus of the current project: (1) understanding how BPEs can be used for screening electrocatalyst candidates; and (2) using BPEs as valves for steering enriched analyte bands.

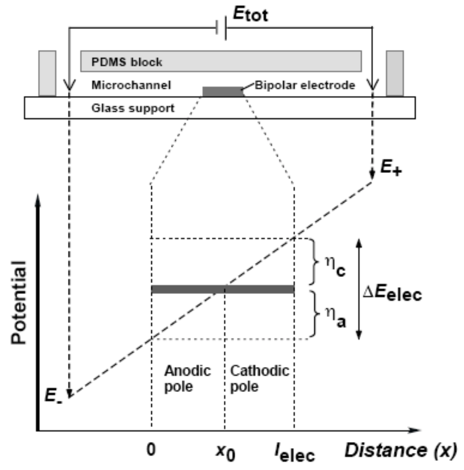

Figure 1. Schematic representation of the PDMS/hybrid device (side view, cross section) containing a gold BPE. At bottom, a diagram of the potential drop in solution, the BPE potential, and resulting overpotential.

Significant achievements in 2010-2012: When a sufficiently large potential is applied across a fluid-filled microchannel containing a BPE, the potential difference across the length of the BPE induces faradaic reactions at its poles (Figure 1). This provides a means for simultaneously controlling the potential of large arrays of electrodes using a simple power supply. We have developed multiple methods for reading out the state of such arrays in parallel, using, for example, electrogenerated chemiluminescene and electrodissolution of Ag band electrodes.

As an example of how BPEs can be used to address a specific DOE need, we have integrated them into a platform for rapid screening of electrocatalysts for the oxygen reduction reaction (ORR). As shown in Figure 2, ORR electrocatalyst candidates are deposited onto the cathodic poles of BPEs. The anodic poles consist of parallel Ag microbands that are in electrical contact with one another and with the ORR catalyst via an underlying indium tin oxide (ITO) support (Figure 2a). The BPE array is then placed into a microchannel containing an electrolyte solution. When a sufficiently high potential (E_{tot}) is applied across this microchannel via a pair of driving electrodes, the ORR occurs at the cathodic pole of each BPE and the Ag microbands undergo electrodissolution (Figure 2b). This process continues until the dissolution of the Ag microbands ceases. The efficiency of each ORR catalyst is determined by the number of Ag microbands remaining: the more bands that dissolve, the better the catalyst. Figure 3 shows micrographs of a small BPE array before and after a screening experiment. Before screening (Figure 3a), the micrograph shows three identical BPEs that have Pt, ITO, and Au cathodes. After screening (Figure 3b), the most Ag bands have dissolved for the Pt electrocatalyst, and hence it is the most effective ORR catalyst.

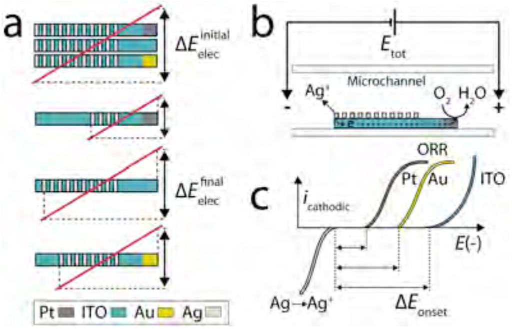

Figure 2. (a) Experimental scheme for the ORR catalyst screening on BPEs showing the initial condition of the BPEs (top) and the final number of Ag microbands (bottom). (b) Scheme showing the configuration of the microchannel device. (c) Schematic representation of the thermodynamic properties of the catalyst screening system shown in part (a).

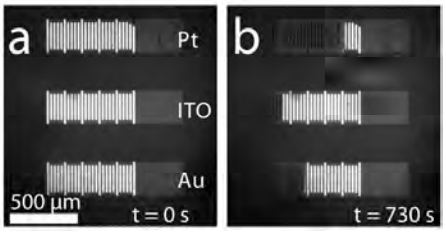

Figure 3. Optical micrographs of 3 BPEs having the indicated electrocatalysts on the cathodic pole. (a) before screening; (b) after screening.

We have previously shown that BPEs can be used to enrich analytes up to a factor of at least 500,000. The next step in that project is to move these enriched bands to locations where they can be analyzed. Rather than use the types of valves and pumps one normally associated with microfluidic devices, we sought to use BPEs. If successful, this would greatly simplify device design and fabrication, becuase BPEs are already present in the device to induce enrichment. Specifically, the method we propose has the ability to enrich and separate a mixture of charged analytes, and then deliver them into secondary microchannels without the use of valves, pumps, or other complicated components. We have investigated three different BPE configurations for implementing the gating function, and the most successful of these will be discussed in the presentation.

Science objectives for 2012-2014:

- The catalyst screening system will be improved and expanded. Specifically, the ITO support will be replaced with pyrolyzed photoresist carbon electrodes to increase device stability and performance in strongly acidic media. We also plan to replace the Ag reporting system with an electrochromic material that will not compromise the integrity of nearby catalyst candidates. We are also designing a method for physically separating the anodic and cathodic poles. The size of the array will also be increased, and appropriate large-scale spotting methods will be developed. Finally, a complete theoretical treatment of the thermodynamics and kinetics for the screening device will be developed.
- We plan to develop a two channel device for simultaneous enrichment of anions and cations. If successful, this system may be capable of desalination.

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4. B. A. Zaccheo; R. M. Crooks "Self-Powered Sensor for Naked-Eye Detection of Serum Trypsin" *Anal. Chem.* **2011**, *83*, 1185-1188.
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Ion Production and Transport in Atmospheric Pressure Ion Source Mass Spectrometers

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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. Three well-known examples of the latter are Desorption Electrospray Ionization (DESI) , Direct Analysis in Real Time (DART), and the Low Temperature Plasma (LTP). 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 2010 - 2012: **Plasma source mass spectrometry.** We have completed two studies of matrix effects in ICP-based techniques. In the first, we have examined the effect that high concentrations of matrix species have on the plasma itself. Our results clearly indicate that one model of matrix effects involving argon metastable atoms that has been proposed in the literature is incorrect, and they strongly suggest that the matrix suppresses emission and ionization in the ICP by lowering the electron temperature in the plasma. Electron cooling appears to be driven by radiative losses from strongly-emitting matrix species.

In the second study we have imaged the cross section of a calcium ion beam at the entrance to the mass analyzer in a working commercial ICP-MS using planar laser-induced fluorescence. The images allowed us to directly monitor the effects of sample matrix on the formation and focusing of the ion beam. Somewhat unexpectedly, the addition of a high concentration of a heavy matrix element did not significantly degrade the focus of the beam, but it did shift the position of the beam far enough that the signal from the calcium test analyte dropped by an order of magnitude.

Our recent computational efforts have been focused on detailed reconciliation of results from the simulation with experimental measurements. In particular, we are using the model to explain mass-dependent radial spreads of analytes in the supersonic expansion in the first vacuum stage of the ICP-MS and to better understand observed dependence of shock formation at the tip of the skimmer cone on the shape of the cone.

Ambient ionization techniques. We have focused our efforts in this period on understanding the fundamental operating mechanism of a dielectric barrier discharge used as an ambient desorption-ionization (ADI) source. We have traced the evolution of key reactive species using a combination of laser-induced fluorescence and time-resolved emission measurements, with particular attention to helium metastable atoms, thought by many to be the key starting point for the chain of reactions that leads to analyte ionization. Our measurements demonstrate that the helium metastable atoms can play a central role under some conditions. However, a judicious choice of support gas can result in alternative ionization mechanisms that can be significantly more effective than those active in pure helium. In the mixtures the helium metastables are almost completely quenched. The effects of 1% hydrogen on the spectroscopic properties of our He ADI source are illustrated in fig. 1. Emission from excited helium atoms is suppressed by the addition of hydrogen, but is still clearly evident 15 mm downstream from the tip of the discharge capillary. In contrast, fluorescence from helium metastable atoms is almost completely quenched. Despite the low density of helium metastable atoms in the mixed-gas discharge, the ion signal for a limited number of test analytes can be an order of magnitude higher than it is in the pure helium plasma.

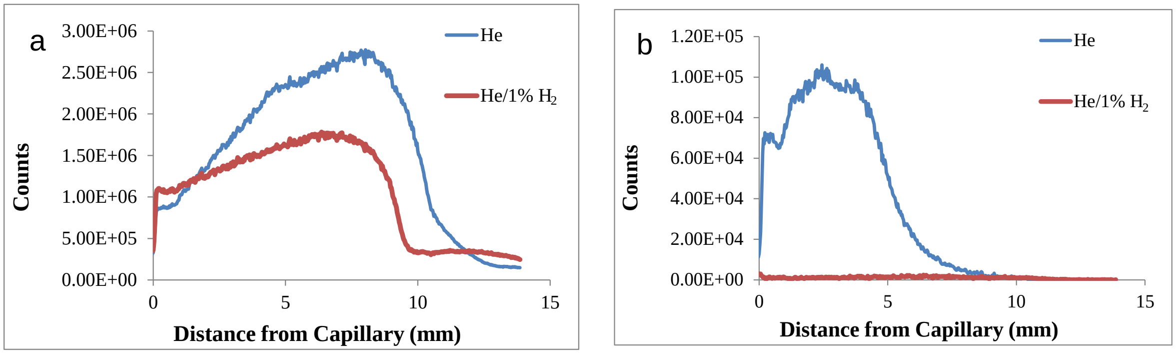

Fig. 1 Effect of the addition of 1% H_2 to helium support gas on the spectroscopic characteristics of a He ADI source. (a) Emission at 588 nm and (b) Helium metastable fluorescence.

Science objectives for 2012-2014

- Identify and quantify key reactive species in a variety of helium plasma-based ADI sources, and use the results to identify key commonalities and differences among the purportedly novel sources that have been described in the literature.
- Using the experimental data described above, develop a detailed model of helium plasmas as they are used for ADI mass spectrometry.
- Continue exploration of mixed-gas plasmas as ADI sources, addressing issues of economy, sensitivity, selectivity, and portability.
- Conclude work on ion transmission in the ICP-MS vacuum interface.

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3. Nicholas Taylor and Paul B. Farnsworth, "Experimental characterization of the effect of skimmer cone design on shock formation and ion transmission efficiency in the vacuum interface of an inductively coupled plasma mass spectrometer," *Spectrochimica Acta Part B* (2012), doi:10.1016/j.sab.2012.02.003

Session 4 – Membranes and Hydrogen

Interfacial Solvation under Aggressive Conditions

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

Significant achievements in 2010-2012: 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 380K up to 500bar with picosecond time resolution.
2) Determined the effects of terminal residue ($-CH_3$ vs. $-CF_3$) and CO_2 fluid density on the rotational reorientation dynamics of 'short' BODIPY 494/514 propylsilane monolayers.
3) Determined the effects of *n*-alkane chain length, surface loading, and CO_2 fluid density on the rotational reorientation dynamics of BODIPY 494/514 within $_n$-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)".

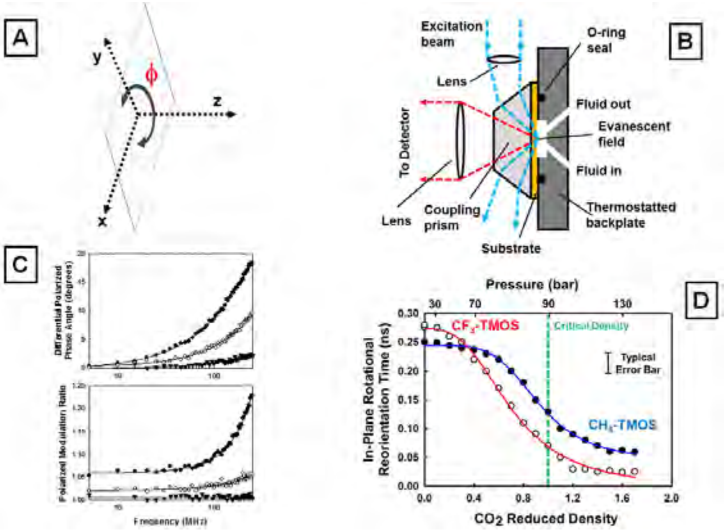

Figure 1. (A) Surface coordinate system for in-plane reporter (BODIPY 494/503) motion. (B) HP-TIRF system schematic (top down view). (C) Typical in-plane multifrequency differential polarized phase and polarized modulation amplitude ratio data (points) and fit (lines) for BODIPY 494/503 attached to a $CF_3(CH_2)_2$-TMOS surface in contact with $scCO_2$ at 313K at 10 (●), 70 (❍), and 250 bar (❑). λ_{ex} = 488 nm, λ_{em} = 520 nm, and $r_{0,\phi} = 0.48 \pm 0.03$ ($\chi^2 < 1.12$). Recovered density-dependent BODIPY 494/503 in-plane rotational reorientation times at $CH_3(CH_2)_2$-TMOS and $CF_3(CH_2)_2$-TMOS surfaces in contact with $scCO_2$ at 313 K.

Science objectives for 2010-2012:

- 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.

References to work supported by this project 2010-2012:

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8) M.J. Dabney and F.V. Bright, "Interfacial Solvation within *n*-Alkane Monolayers in Contact with Supercritical CO_2," in preparation.
9) M.J. Dabney and F.V. Bright, "Interfacial Solvation within *n*-Alkane Monolayers in Contact with Cosolvent Modified Supercritical CO_2," in preparation.
10) M.J. Dabney and F.V. Bright, "Interfacial Solvation within Crosslinked *n*-Alkane Monolayers in Contact with Pure and Cosolvent Modified Supercritical CO_2," in preparation.
11) M.J. Dabney and F.V. Bright, "Site Selective Interfacial Solvation within *n*-Alkane Monolayers in Contact with Pure and Cosolvent Modified Supercritical CO_2," in preparation.
12) M.J. Dabney and F.V. Bright, "Site Selective Interfacial Solvation within Crosslinked *n*-Alkane Monolayers in Contact with Pure and Cosolvent Modified Supercritical CO_2," in preparation.

Hyper-Thin Membranes For Hydrogen Purification

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Overall research goals: The objectives of this research are (i) to learn how to synthesize Langmuir-Blodgett (LB) films and polyelectrolyte multilayers (PEMs) having minimal film defects, and (ii) to use such knowledge to design "hyper-thin" (<100 nm) permeation-selective membranes that are capable of separating H_2 from CO_2.

Significant achievements in 2010-2012:

Minimizing Defects in Polymeric Langmuir-Blodgett Monolayers and Bilayers. Polymeric surfactants **1** and **2** were found to form stable LB monolayers at the air water interface (Fig. 1). Injection of poly(acrylic acid) (PAA) beneath the surface of these films led to a substantial increase in their cohesiveness (i.e., "gluing"), as evidenced by a significant increase in their surface viscosity. Examination of these monolayers by atomic force microscopy, after being transferred to silylated silicon wafers showed that PAA promotes the formation of intact film. In contrast, transfer of unglued monolayers resulted in substantial defect formation. Comparison of the barrier properties of single glued and unglued LB bilayers formed in the presence, and in the absence of PAA, confirmed that PAA minimizes defect formation within these ultrathin assemblies

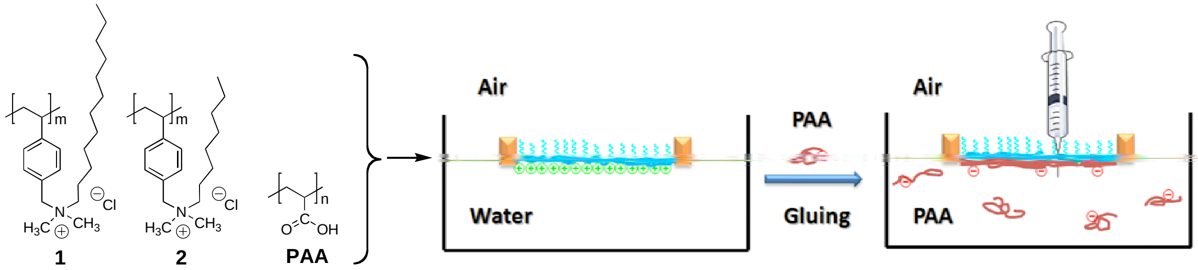


Figure 1. Polymers used to form glued and unglued LB monolayers and bilayers.

An Ionic Linker Strategy for the Synthesis of Poly(ethylene glycol)-based Polyelectrolytes. Poly(ethylene oxide) has been converted into a polyelectrolyte, **3**, using an ionic linker strategy. This polyelectrolyte has been used in combination with poly(allylamine hydrochloride) (PAH) to form polyelectrolyte multilayers (PEMs) (Fig. 2). Resulting 7 nm-thick films were found to exhibit modest He/CO_2 reverse size-selectivity (i.e., 0.75), where permeation the larger CO_2 molecule was favored over He. These same films were also exhibited exceptional CO_2/N_2 selectivity (>280).

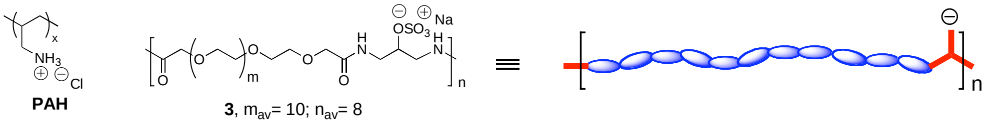
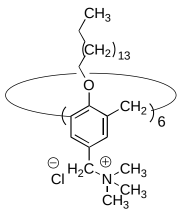


Figure 2. An ionic linker stratgey for the synthesis poly(ethylene glycol)-based polyelectrolytes.

Single Langmuir-Blodgett (LB) bilayers having exceptional H_2/CO_2 permeation selectivities. Single LB bilayers that were made from calix[6]arene **4**, which were ionically crosslinked (i.e., glued together) with PAA, exhibited exceptional H_2/CO_2 permeation selectivity as judged from an upper-bound plot (Figure 3). Comparison of the barrier properties of these glued bilayers with analogs that were made using poly(4-styrenesulfonate) (PSS) served as the gluing agent strongly suggests that the ionic crosslinking an self-healing processes contribute to the high permeation selectivity of the PAA-glued bilayers. In a broader context, these findings suggest that the combination of ionic crosslinking and hydrophobic interactions may prove important in fabricating high-quality, hyper-thin films having minimal defects.



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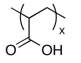

PAA

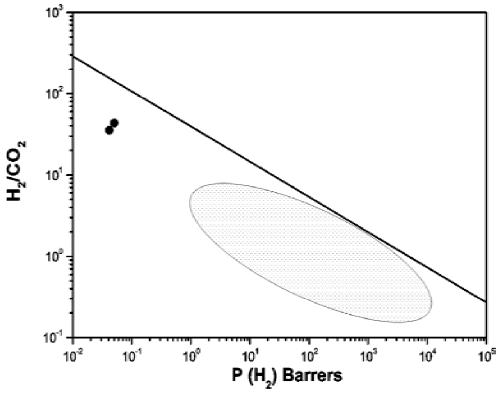

Figure 3. LB bilayers of **1** that have been glued together with PAA (total thickness of 6 nm) exhibit exceptional H_2/CO_2 permeation selectivity (●) as evidenced from an upper-bound plot.

<u>Science objectives for 2012-2014:</u>

- To probe the influence of structural matching of polyelectrolytes on the formation of defects in polyelectrolyte multilayers (PEMs).
- To examine the feasibility of reverse H_2/CO_2 permeation selectivity using poly(ethylene glycol)-based thin films.
- To test the feasibility of creating "anchor layers" on hydrophobic supports via self-assembly for the deposition of layer-by-layer thin films.

<u>References to work supported by this project 2010-2012:</u>

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Nanoporous Membranes for Hydrogen Production: Experimental Studies and Molecular Simulations

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Overall research goals: In this project, we study SiC nanoporous membranes, which show the potential to overcome some of the difficulties other inorganic membranes face, particularly under conditions typically encountered in reactive separations for H_2 production, and in fuel-cell applications. In particular, we systematically investigate and further develop the technique of pre-ceramic polymer pyrolysis to produce nanoporous SiC membranes and films, which are both cost-efficient and industrially viable. The main focus of our project is on trying to understand the formation process of the membranes, namely, how the initial structure of the polymeric precursor and the pyrolysis conditions impact the final membrane characteristics. Our efforts involve extensive experimentation of the membrane formation process, as well as modelling of the pyrolysis process itself by molecular dynamics simulations, since the understanding must be at the molecular level. The new science that is being developed impacts not only the fabrication of SiC membranes, but also the general field of inorganic membranes including, for example, carbon molecular-sieve and mixed-matrix membranes. A key outcome of our effort will be able to prepare a membrane with certain "optimal" properties (e.g., permeance, separation factor, and surface characteristics) by being able to determine in a systematic way the type of polymeric precursor one needs to use, and the preparation method and procedure that one must utilize.

Significant achievements in 2009-2011: Highly permeable macroporous SiC supports have been prepared. A novel dip-coating technique has been developed, that involves the modification of the slip-casting step using SiC nanofibers and nanotubes, which provides a more effective means for preventing infiltration in the underlying macroporous structure during both the slip-casting and the subsequent thin film deposition steps. A templating technique has been developed for the preparation of high surface area SiC materials with highly-interconnected pore structures.

A reactive force field, ReaxFF, which allows for accurate description of bond breaking and bond formation to examine the pyrolysis of HPCS polymer has been developed. ReaxFF simulations were performed with a massively-parallel MD code, enabling us to carry out multi-million atom reactive MD simulations of chemical processes. The obtained gaseous products from our MD simulations are in very good qualitative agreement with the experimental results as is the structure of the resulting ceramic. The key objective of the effort is to be able to design the SiC nanoporous membranes more optimally based on a more detailed understanding of the pyrolysis process of the polymeric precursor leading to membrane fabrication.

A pore network model has also been developed to study the evolution of the pore space of a nanoporous SiC membrane during its fabrication by (CVI/CVD) techniques. Good agreement was found between the simulation results and the experimental data. Thus, the model may be used for determining the optimal conditions under which a membrane may achieve a given value of permselectivity. The network model was also utilized to interpret the results of flow permporometry (FPP) that has been used widely for determining the pore size distribution (PSD) of a broad class of porous materials, and in our studies of the high-flux macroporous SiC supports. MD simulations were employed in order to examine the adsorption and diffusion of N_2, H_2, CO_2, CH_4, and n-C_4H_{10} in silicon carbide nanotubes (SiCNT's). The simulations indicated the strong effect of the nanotubes' chirality and curvature on the pressure-dependence of the adsorption isotherms and the self-diffusivities. Detailed comparison was made between the results and those for the CNT's, and the adsorption capacity of the SiCNTs for hydrogen is higher than the CNTs' under the conditions that we have studied.

Science objectives for 2011-2012:

- Continue our efforts on the preparation of high-temperature, steam-resistant, hydrogen-permselective membranes. Systematically investigate and further develop the technique of pre-ceramic polymer pyrolysis to produce nanoporous SiC membranes and films, which are both cost-efficient and industrially viable
- Continue the development of the ReaxFF. Validate the model by computing, in addition to entropy and the radial distribution function, the XRD spectra, and the melting point, and by comparing them with the experimental data. Simulate polymer pyrolysis inside a SiC pore, in order to understand nanopore formation during supported SiC membrane preparation. Compare computed and measured separation factors for binary gas mixtures.
- Continue efforts to prepare highly porous top SiC films with interconnected porosity, *via* templating techniques using inorganic as well as organic sacrificial templates.

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Computer Simulation of Proton Transport in Fuel Cell Membranes

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Overall research goals: The research objectives of this project are to study the solvation and transport of hydrated protons in proton exchange membranes (PEMs) such as Nafion^{TM}, using a novel multi-state reactive molecular dynamics (MD) approach, combined with a multiscale simulation methodology to characterize proton transport in complex polymer morphologies at mesoscopic scales.

Significant achievements in 2010-2012: The self-consistent iterative multi-state empirical valence bond (SCI-MS-EVB) approach allows for the reactive molecular dynamics (MD) simulation of Grotthuss proton hopping and excess charge delocalization in aqueous environments, including highly acidic systems. This reactive MD approach has been used to investigate the details of proton solvation and transport in hydrated Nafion. In the most recent work, by decomposing the motion of the hydrated protons into hopping and vehicular components, it was confirmed these two distinct processes do in fact have a substantial degree of anti-correlation. This behavior is especially evident in the vicinity of the sulfonate groups, where the excess hydrated protons tend, at times, to hop away from the sulfonate anion, but vehicularly diffuse back, or vice versa. Also, while experimental results had previously suggested that Grotthuss hopping is unimportant at low hydration levels, our study showed that it is still an important transport process, but is masked by the anti-correlated vehicular transport.

The effect of local polymer morphology on proton solvation and transport in hydrated Nafion was also investigated for the first time with large scale SCI-MS-EVB simulations. Three of the most significant morphological models of Nafion, the lamellar model, the cylinder model and the cluster-channel model, were studied. These three models exhibit distinct proton transport (PT) patterns, which result in different proton diffusion rates. In both the lamellar and cylinder models, the interaction between hydrated protons and the sulfonate groups were shown to be the key factor in determining the PT behavior. For the more widely accepted cluster-channel model, the geometrical shape was also found to play an important role in influencing the PT behavior. The proton solvation structural change as a function of the distance between protons and sulfonate groups was also analyzed. It was found that the increase of water cylinder radius or water layer height leads to the presence of more hydrated protons around the sulfonate groups, while for the cluster model an increase of water sphere radius leads to the presence of less protons around the sulfonate groups. Furthermore, for the lamellar and cylinder models, the hydrated protons around the sulfonate groups consist of more Zundel-like $H_5O_2^+$ structures when the hydration level decreases, which is also influenced by the distinct morphological structure of Nafion.

The development of a mesoscale model to simulate PT in PEMs on length and time scales that can effectively bridge the gulf between detailed atomistic MD simulations and experimentally relevant PEM systems was also completed. This method used aggressive coarse-graining to characterize the structural morphology of the PEM, while Smoothed Particle Hydrodynamics (SPH) was extended in a novel multiscale fashion to simulate mesoscopic proton transport within the resulting coarse-grained PEM structures. Good agreement was found with experimental results, paving the way for further implementation of the model with a multiscale bridging to the atomistic-scale SCI-MS-EVB results, as well as the use of the overall multiscale approach (cf. Fig. 1) to inform experimental synthesis and charaterization of PEM materials.

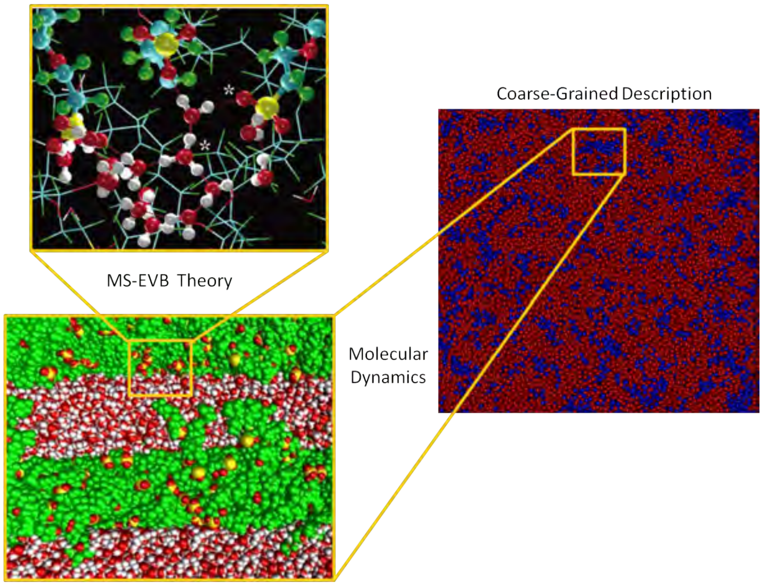

Figure 1. Representations of the different length scales used in the multiscale modeling of Proton Exchange Membranes. SCI-MS-EVB simulations are used to explore and quantify proton transport at the molecular scale. Such atomistic simulations are also used to examine structural features of the membrane and their effect on proton transport. Information from these simulations is then bridged to larger scale, coarse-grained simulations in a multiscale fashion in order to access experimentally relevant length and time scales.

Science objectives for 2012-2014:

- With the development and implementation of the mesoscopic coarse-grained/SPH method, further improvements of this method will be developed. This work will involve more detailed connections to the reactive MD SCI-MS-EVB simulations performed previously, especially the variation of proton diffusivity with the local region in the membrane pore. Determining the effect of the motion of the polymer backbone during the SPH simulations, which describe mesoscopic PT within the membrane, will also be an important task.
- In order to determine the origin of improved proton conductivities in PEM materials, such as the Hyflon^{TM} and 3M membranes, SCI-MS-EVB simulations will be carried out for these systems. Comparison of the results from these studies with the Nafion^{TM} results can serve to inform the synthesis of improved membrane materials.
- The SCI-MS-EVB method has shown its utility in shedding light on unexpected phenomena in PEM systems. Further improvement of the implementation of this method will be necessary to explore larger length scales and longer time scales in a computationally efficient manner. Improvements to the method include advanced parallelization techniques, more efficient methods to compute the expensive electrostatic calculations, and improved identification of the important bonding states in this multi-state reactive MD.

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Session 5 – Chemical Imaging

New Opportunities of Surface Nonlinear Vibrational Spectroscopy in Spectral, Structural and Dynamic Interactions at the Interfaces for Separation and Analysis

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For most heterogeneous chemical processes, from traditional solvent extraction, ion exchange and chromatographic analysis, to catalysis, microbial enzymatic reactions and mineralogical transformation in carbon sequestration, surface and interface reactions play the deciding role. In order to understand, improve, control and effectively utilize these processes, it is essential to be able to characterize the identity, conformation and structure of the interfacial molecular complexes, and to understand their molecular level interactions with the bulks phases in a quantitative manner. These apply to all interfaces such as solid-gas, solid-liquid, liquid-liquid, gas-liquid and bio-membranes.

Surface nonlinear spectroscopy techniques, such as second harmonic generation (SHG) and sum-frequency generation vibrational/electronic spectroscopy (SFG-VS/ES), pioneered by Ron Shen, Ken Eisenthal, etc. in the recent two dozen years, have shown the ability to measure such interfacial molecular species selectively against the bulk. The past decade or so has witnessed the convergence of the development of the laser technology and instrumentation for effective SHG and SFG-VS/ES, and the development of the quantitative measurement and analysis of the SHG and SFG-VS/ES for exploring the details of the structure, interaction and dynamics of molecular interfaces. Work from our group and others has successfully demonstrated that these non-linear techniques can be used to make detailed quantitative studies on interfacial properties such as symmetry, orientation and number density of molecules, molecular structure and interactions, and dielectric properties with sub-monolayer sensitivity. Our main research goal at PNNL is to develop and adapt SHG, and SFG-VS/ES techniques to the broad areas of separation and analysis, catalysis, and bio-geo-mineral transformation.

There are two major obstacles need to be overcome before SFG and SHG can be applied to probe and understand the detailed spectral, structural and dynamic interactions at interfaces, where the conformation, structure and chemical changes of the molecules and molecular complexes are usually controlled by small energy differences. One is how to accurate the SFG spectra; and the other is how to quantitatively analyze the spectra for detailed molecular level understandings.

In the past decade we have understood that by employing the strong polarization dependence in the SFG spectroscopy, detailed spectral assignment and orientation analysis of interfacial molecular groups can be achieved, leading to identification of unique surface species and to understanding of their interactions. Applying these concept and analysis, we have successfully studied the spectral, structure and interaction details of Gibbs layers and Langmuir monolayers at various liquid interfaces.

Recently, with the support of the Environmental Molecular Science Laboratory (EMSL) capability development project, we have developed a suite of SHG, SFG, SVG-VS capabilities, including the first sub-wavenumber high resolution broadband SFG-VS (HR-BB-SFG-VS) spectrometer. This HR-BB-SFG-VS spectrometer realizes broadband SFG spectral detection with spectrograph and CCD cameras, by synchronizing a 100 picosecond visible laser that ensures sub-wavenumber spectral resolution with a 40 femtosecond broadband infrared laser that provides broad spectral bandwidth and time resolution. With the Pacific Northwest National Laboratory (PNNL) LDRD project on molecular structure and interaction at aqueous, non-aqueous liquid interfaces and catalytic solid surfaces, we have shown that the accurate lineshape analysis from the high resolution SFG spectra measured under different polarization combinations can provide unique spectroscopic phase information that led to unprecedented spectral resolution and determination of the molecular conformation of surface molecules.

Such spectral and lineshape details make it possible to study the structural and conformational inhomogeneity driven by small energy differences near the interfacial region. Particularly, the spectral resolution and lineshape details also provide detail information on the coherent dynamics of such interfacial interactions. These developments provide quantitative spectroscopic analytical tool and new opportunities for characterize the molecular complexes and their interactions at various interfaces.

Here we would like to report how these synergetic developments can be employed to resolve inhomogeneous interactions at various liquid and solid interfaces. Examples on recent direct measurement of surface enrichment of heavy ion-ligand complexes are to be discussed.

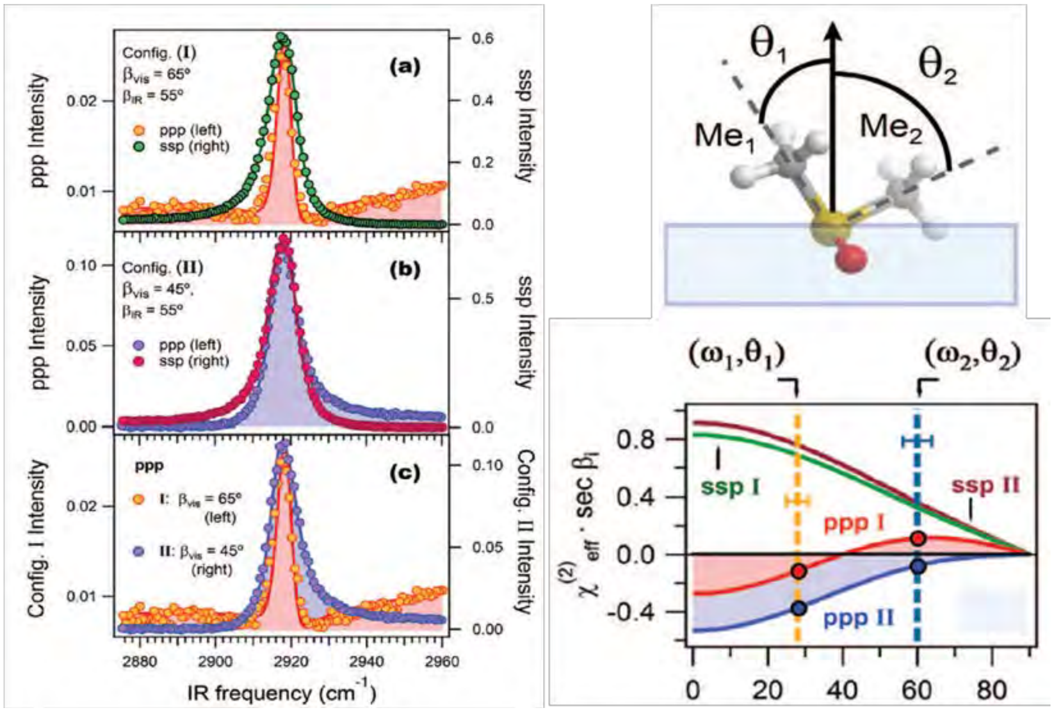

Figure 1. Spectral resolution and polarization/lineshape analysis in HR-BB-SFG-VS enables determination of the spectroscopic phases of closely overlapping spectral features with 2.8cm^{-1} splitting in the apparently single peak, allowing the determination of the distinctive orientation of the two methyl groups at the air/DMSO interface. (L. Velarde, X. Y. Zhang, Z. Lu, A. G. Joly, Z. M. Wang, and H. F. Wang, *J. Chem. Phys.*, 135, 241102, 2011.)

Chemical Microscopy of Conjugated Organic Nanomaterials

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Overall research goals: Our primary research goal is to elucidate connections between molecular architecture and morphology with optoelectronic function in nanostructured semiconductors. We use a suite of single-molecule imaging tools combined with scanning probe microscopies to investigate charge and energy transport processes in conjugated organic semiconductors and inorganic quantum dots.

Significant achievements in 2010-2012: Conjugated polymers and inorganic quantum dots (and nanostructured hybrids of both) represent important classes of nanomaterials under intense investigation for high-efficiency light-emitting and photovoltaic applications. Quantum dots, for example, are highly desirable as sensitizers in solar-cell applications, yet relatively little direct spectroscopic information exists on charge-attachment. Over the past two years, we have developed a combination of wavelength, polarization, and scanning probe (electric-force) imaging techniques to investigate electron attachment to quantum dots coupled to conjugated organic ligands, and semiconducting substrates (e.g. Indium Tin Oxide). The idea is that (single) charge attachment to quantum dots is manifested by a large negative (> 50 meV) Stark modification of the recombination energy, accompanied by a large induced *linear* polarization in emission. We observe interesting differences in Stark-modified luminescence of individual charged quantum dots in a large excess charge limit (≈4 – 6 electrons), and 1-2 electron charging on illuminated Indium Tin Oxide.

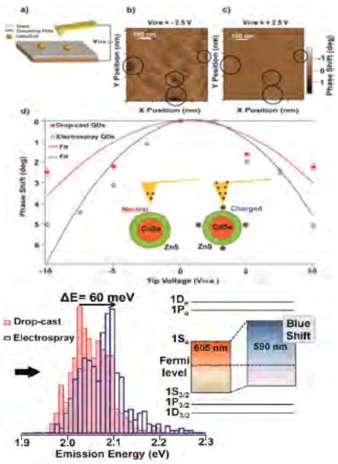

Figure 1. EFM (top) and distribution of recombination energies (bottom) for electrosprayed QDs showing a net *blue* shift of ≈ 60 meV. (*Nano Letters* **10**, 4425 (2010))

The second part of our research effort focuses on understanding the nature of polymer chain packing under the influence of 2- and 3-dimensional nanoconfinement. We have developed new chemical imaging probes designed to correlate exciton dynamics with polymer chain packing: (1) A variant of time-tagged/time-resolved photon counting which introduces a polarization 'tag' for each detected photon. This enables us to follow polarization contrast on a sub-nanosecond timescale (limited ultimately by time-to-digital resolution). (2) Near-field *absorption* probes that exploit difference in absorption properties of aggregated (crystalline) vs. amorphous polymer domains thus providing a sensitive local probe of crystalline structure in thin films, nanoparticles, or 2D nanofibers. The photoluminescence spectra of these species show interesting multiple vibronic replicas suggestive of distinct structural components with different electronic coupling.

Objectives for 2012-2014:

- Near-field absorption spectroscopy of polymer nanoparticles and nanofibers. Our proof of concept measurements have shown how NSOM probes can detect *absorption* in isolated polymer nanostructure. We will implement white-light (near-field) excitation combined with spectral analysis of the scattered light to directly measure the single nanostructure absorption spectrum.

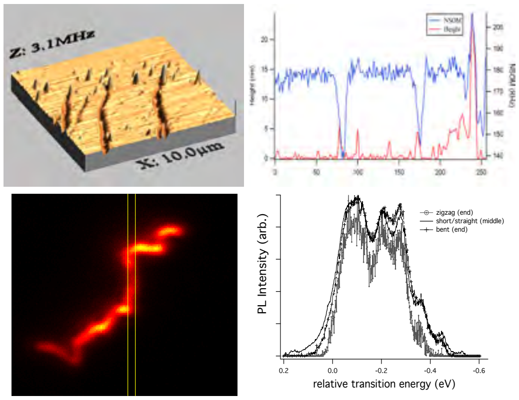

Figure 2. Top left/right: NSOM absorption image of P3HT Nanofibers, and corresponding surface height and scattering attenuation section, Bottom Left/Right: Wide-field PL image and PL spectra of single P3HT nanofiber showing multiple vibronic progressions.

- Correlation of polymer thin-film, and nanofiber photoluminescence spectra with high-resolution x-ray diffraction. In collaboration with Tom Russell's group, we will correlate the vibronic information from optical Pl measurements with structural information obtained in XRD experiments.

- Single-molecule studies of electronic coupling in synthetic multi-chromophoric model systems of potential use in OLED or organic photovoltaic applications. We will collaborate with Lahti and co-workers to study electronic interactions in covalently linked chromophores (oligo phenylene vinylenes, perylene derivatives, and fluorenones) with tunable linkers to enable different folded morphologies.

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Imaging of Conformational Changes

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Overall research goals: The combination of a scanning differential barrier-height imaging (DBHI)[1] system with tip-enhanced Raman spectroscopy (TERS)[2] will provide correlated maps of Raman band intensities for specifically designed single molecules undergoing or having undergone electric-field induced conformational change. This project includes the tailored synthesis of target molecules with built-in moities for TERS and DBHI detectable conformational change such that they function as surface-mounted molecular rotors.

Significant Achievements in 2010 - 2012: A procedure for covalent stabilization of self-assembled polygons and polyhedra has been developed (Fig. 1).[3] It allow a two-step synthesis of structures that are as complex as transition-metal-directed self-assembly of ligand-carrying rods into thermodynamically most stable entities under equilibrium conditions permits, yet are sturdy and chromatographable. The procedure is now being used for the synthesis of very complicated rotors for TERS examination.

The detection of conformational change such as rotator orientation by TERS requires the presence of a chromophore in the rotator. We have chosen a carbostyril derivative for a close examination of the polarization directions of electronic and vibrational transitions.[4] As a model system, we have prepared and characterized LB monolayers containing azimuthal rotor molecules carrying this carbostyril chromophore in the rotator.[5]

A molecular dynamics simulation of molecular rotors driven by a rotating electric field or by a flow of gas provided insight into the nature of friction in molecular machines.[6]

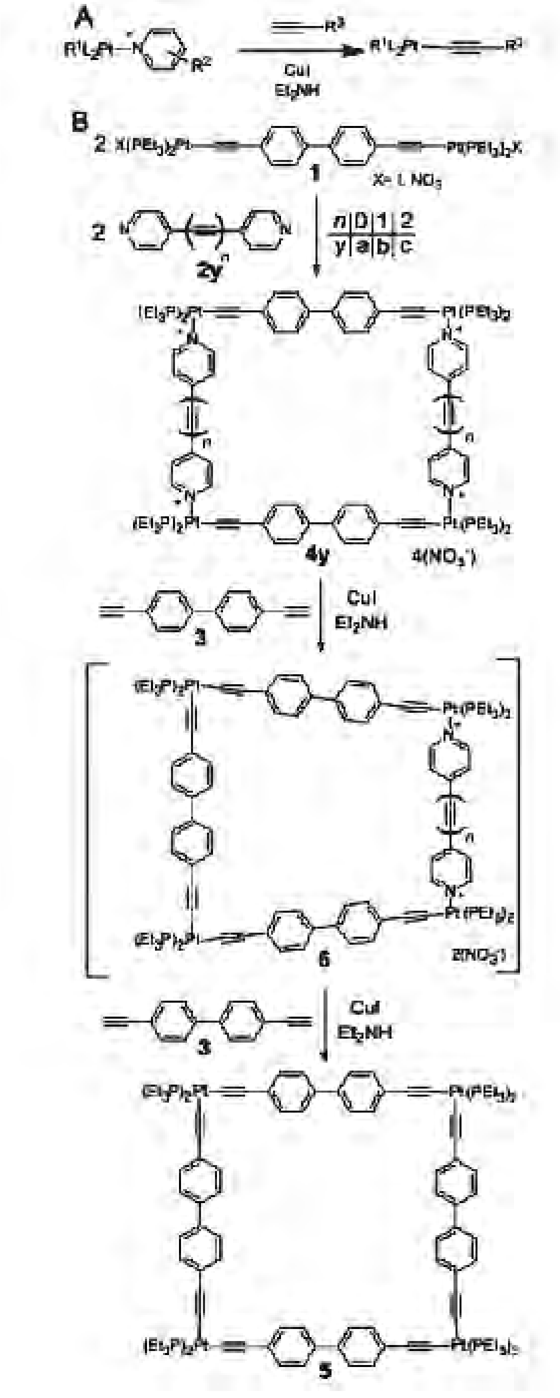

Figure 1 Synthesis of a covalently bonded square from a self-assembled precursor.

TERS capability was added to or DBHI STM system and the first Raman spectra of a self-assembled dense monolayer of a surface-mounted rotor (Fig. 2) attached to a Au surface by Hg atoms was obtained (Fig. 3). The DBHI of this rotor was measured and demonstrated that the DBHI signal did not "blink" with time as did similar rotors attached by R= $SCH_2CH_2SCH_3$.[1] Blinking is attributed to rotor blocking by the long thiol chains which are now absent.

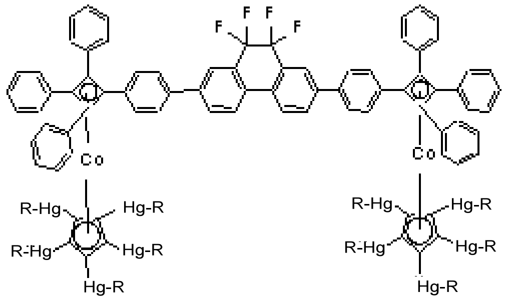

Figure 2. Dipolar altitudinal rotor designed for mounting on gold, R =CF_3CO_2.

Science Objectives for 1012-2014:

- Synthesis of a surface-mounted rotor with a rotor chormophore and Raman-active side groups that will permit the detection of conformational rotation by TERS.
- The extension of the range of the TERS instrument to the near UV with suitable excitation of surface plasmons on Co, Rh or Al STM stips.
- The mapping of conformational motion in surface-mounted rotors by simultaneous DBHI/TERS detection.

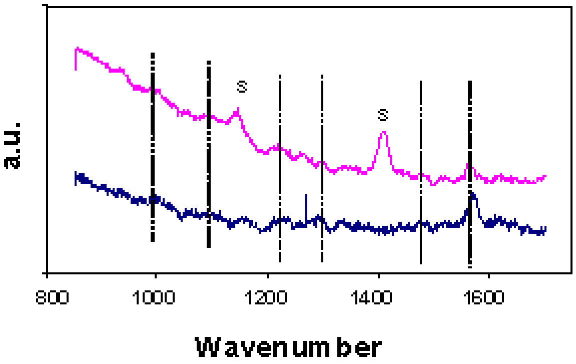

Figure 3. *(Top)* Raman spectrum of rotor (Fig. 2) in CH_2Cl_2. The letter *s* designates a solvent peak. *(Bottom)* TERS for the a SAM of the same rotor.

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Chemical Analysis of Nanodomains

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Overall research goals: The FWP's research goals are: (1) to develop sub-diffraction spatial resolution imaging techniques for the chemical characterization of nanodomains and (2) to design novel microscopy techniques to elucidate interactions and reactions at the liquid/solid interface. The systems we develop are stimulated emission depletion lifetime microscopy (STED), sub-diffraction stimulated Raman gain imaging, 3D stochastic optical reconstruction microscopy (3D STORM), differential interference contrast (DIC) microscopy and total internal reflection (TIR) fluorescence and Raman microscopy. Ultimately, the developed methods and instruments are applicable to diverse systems of interest to the DOE mission where the compositions and dynamics need to be measured on the nanoscale using non-invasive techniques, particularly for analyses in complex, heterogeneous environments.

Significant achievements in 2010-2012: A STED imaging system based on a pulsed, continuum laser, vortex phase plate and an inverted optical microscope with a piezoelectric stage has been developed for fluorescence intensity and lifetime imaging. The system was used to measure lifetimes in polymer bead films and biopolymer films with heterogeneous domains.

We described DIC polarization anisotropy for tracking rotational dynamics of gold nanorod (AuNR) probes. DIC polarization anisotropy enabled us to precisely determine the real-time orientation of the AuNR during the dynamic processes.

The TIR Raman signal at prism and prism/metal interfaces has been measured using near infrared excitation wavelengths and was modeled for different homogenous interfacial layers. Raman spectroscopy has been used to non-invasively and rapidly characterize plant biopolymer compositions and their enzymatic conversion to new species.

Science objectives for 2012-2014:

- STED lifetime imaging will be used to measure block co-polymer films with lateral heterogeneous domains that are smaller than the diffraction limit of light. Different blocks of the polymer will be fluorescently labeled, and the properties of the domains will be measured. Fluorescence lifetimes in spatial scales smaller than the diffraction limit of light will be measured for the first time using far-field optical microscopy and will reveal information about nanoscale environments.
- We will demonstrate that the SPORT technique combined with statistical analyses is able to identify three unique, fundamental rotational modes – in-plane rotation, out-of-plane tilting, and 3D wandering. We will measure the nanorod's rotational direction by combining the DIC polarization anisotropy measurement with DIC image pattern recognition to visualize clockwise or anti-clockwise rotation of nano-objects. We will introduce a precise 3D localization method of spherical gold nanoparticle probes and novel "non-blinking" quantum dots.
- TIR Raman spectroscopy will be developed at different metal and dielectric interfaces as a reproducible, well-modeled signal enhancement mechanism for measuring interfacial Raman scatter in three coordinates of spatial orientation. The technique will be used to measure the interactions of small molecules at chromatography-relevant interfaces. TIR Raman imaging will also be applied for axial profiling measurements of heterogeneous polymer multilayer films at metal and dielectric interfaces.

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Session 6 – Membrane Separations

Fundamental Structure/Property Studies of Thermally Rearranged Polymers for Use as Gas Separation Membranes

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Overall research goals: The overarching goal of this fundamental, experimental research program is to systematically synthesize, characterize, and develop a fundamental understanding of thermally rearranged polymers to rationally tailor a novel class of polymeric membrane materials with the chemical resistance and separation properties required for gas separation applications.

Significant achievements in 2010-2012: The synthesis and characterization of polyimides and their corresponding TR polymers is underway. Permeation measurements for a series of gases have shown that both polymer structure and synthesis route affect gas transport and plasticization behavior. As shown in Figure 1A, the incremental chemical transformation of a polyimide (labeled HAB-6FDA-C) to its corresponding TR polymer results in an over 20-fold increase in CO_2 permeability. Correspondingly, Figure 1B shows the concomitant change in CO_2/CH_4 selectivity. Surprisingly, a maxima was observed for CO_2/CH_4 selectivity in Figure 1B, and we hypothesize that these changes in properties relate to a beneficial distribution of free volume. Future work will focus on determining the free volume and free volume distribution of these materials through positron annihilation lifetime spectroscopy (PALS).

Figure 1 also shows a comparison for permeability and selectivity of HAB-6FDA as a function of synthesis route. An ester acid precursor (EA) was used for the HAB-6FDA-EA sample, and a chemically imidized precursor (C) was used for the HAB-6FDA-C sample. Samples prepared via EA differ from those prepared by C in that they have either hydroxyl or acetate functionality *ortho*-position to the aromatic diamine in the polyimide, respectively. These differences mean that CO_2 is evolved from thermal rearrangement of polyimides synthesized from EA, and acetic acid and CO_2 are evolved from thermal rearrangement of polyimides synthesized from C. The structural differences of these leaving groups results in vastly different transport properties.

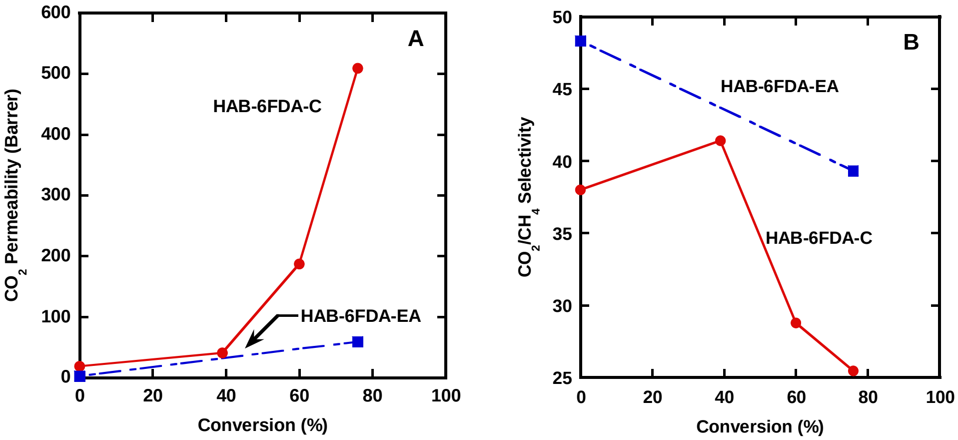

Figure 1. (A) CO_2 permeability versus conversion and (B) CO_2/CH_4 selectivity versus conversion (at 35°C and Δp = 3.1 atm) for HAB-6FDA-C and HAB-6FDA-EA.

Synthesis route also appears to influence the onset of plasticization in TR polymer films. Plasticization is the swelling of a polymer in the presence of highly condensable gases, an effect that increases the permeability of all components and decreases selectivity. Plasticization is typically determined by the so-called plasticization pressure, which is the pressure at which an increase in permeability occurs during a permeation experiment. For propylene, at 35°C TR polymers prepared via C showed a plasticization pressure of less than 2 bar, whereas TR polymers synthesized via EA showed a plasticization pressure near 4.5 bar. A third synthesis route, known as solid state imidization, was also investigated and showed a plasticization pressure of less than 1 bar.

For both ethylene/ethane and propylene/propane separation, TR polymers derived from HAB-6FDA operate with some of the highest combinations of permeability and selectivity of known polymers.

Science objectives for 2012-2014:

- Compile a database of precursor and TR polymer chemical and transport properties for polymers with the same chemical backbone but prepared via different synthesis routes.
- Test a series of precursor polyimide materials of systematically varied chemical structure and their corresponding TR polymers and compile a database of their chemical and transport property characteristics.
- Compare transport properties for TR polymers synthesized with varying *ortho*-position functional groups and further clarify the influence of synthesis route on TR polymer structure and properties.
- Compile an array of pure- and mixed-gas olefin and paraffin permeability, selectivity, and plasticization data for polyimide precursors and TR polymer films.
- Determine enthalpies of sorption and activation energies of diffusion for a series of TR polymers and for partially converted TR polymers.
- Compile a fundamental database of physical aging data of thin TR polymer films.

References to work supported by this project 2010-2012

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Synthesis and Analysis of Membrane Materials with High Permeabilities, Permselectivities and Potential for Economical Large Scale Energy-Intensive Separations

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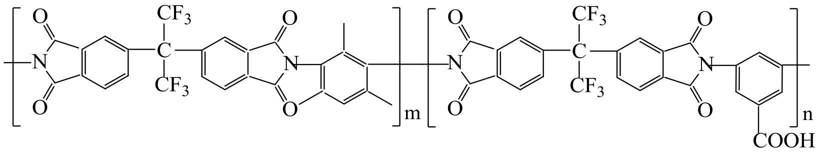
Overall research goals: I seek to develop a fundamental framework to guide the systematic discovery of advanced membrane materials based on polyimides and pyrolyzed polyimide carbon molecular sieve appropriate for important large scale energy intensive separations.

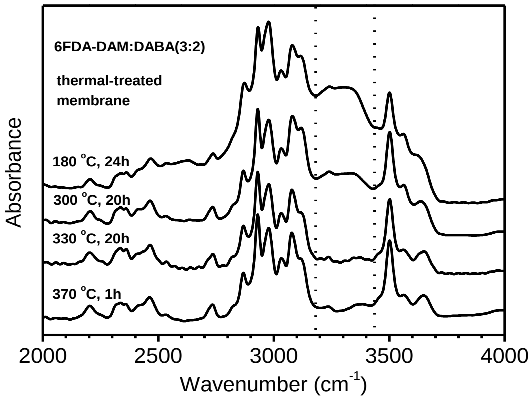
Significant achievements in 2010-2012:

We have identified a new technique, decarboxylation-induced crosslinking of polyimides, to stabilize membranes for use in aggressive feed streams. Our work shows this technique to be broadly applicable to an array of polyimides with glass transition temperatures ranging from 315-395 C, based on systematically varied monomers. The structure of a particularly attractive member of this family, 6FDA-DAM:DABA (3:2) is shown below where m =3 & n=2:

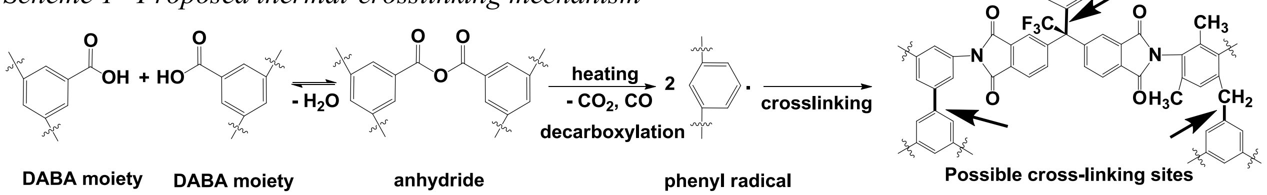


Precursor membranes were thermally treated under the conditions in Fig. 1, and tested for solubility in the aggressive solvent N-methylpyrrolidone. Membranes thermally treated at 330 °C for 1 h partially dissolved, indicating only partially cross-linkage; however, membranes treated at 330 °C for 10 h merely swelled in hot NMP. Membranes thermally treated at 350 °C or 370 °C for 1h, or at 330 °C for 20 h were insoluble even in hot NMP at 100°C for 1 week. These results indicate that decarboxylation-induced cross-linking of 6FDA-DAM:DABA (3:2) membrane can be performed at a temperature much below its T_g (387 °C), consistent with FTIR spectroscopy. The results in Fig. 1 show that the broad weak absorption at 3200-3500 cm^{-1}, attributed to –OH vibration of carboxylic acid groups in the DABA moiety, becomes weaker with increasing thermal treatment and finally disappears in the membranes annealed at 330 °C for 20 h or at 370 °C for 1 h. The proposed mechanism of this decarboxylation-induced thermal cross-linking is illustrated in Scheme 1, with likely cross-linking bonds noted with arrows.

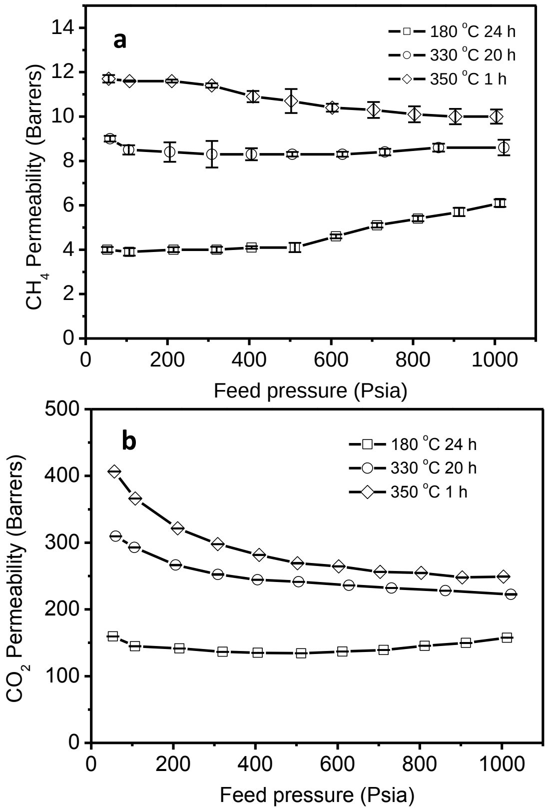
Fig. 1 *FTIR spectroscopy of the polyimide Thermally-treated under different conditions*



Scheme 1 Proposed thermal-crosslinking mechanism



Wide-angle X-ray scattering patterns of thermally treated samples verified that all were amorphous. And average interchain distances (*d*-spacing) values were calculated using Bragg's law ($d=\lambda/2\sin\theta$) for the maximum 2θ values of the broad peaks. Although *d*-spacing do not indicate true interchain distance, the *d*-spacing are indicators of the amount of room available for penetrating small molecules to diffuse through these membranes. After annealing and removal of trace solvent at 180 °C, the membrane showed a decreased *d*-spacing of 5.63 Å, indicating an increasing chain packing density. Thermal treatment of the membrane at or above 330 °C showed an increased *d*-spacing of 6.18 Å (330 °C), 6.43 Å (350 °C), and 6.55 Å (370 °C), indicated that average interchain distance increases due to the decarboxylation-induced cross-linking, which introduced packing disruptions in the matrix.



The permeation measurements for mixed gas of 50:50 CO_2/CH_4 feed mixture were conducted to subject the membranes to a highly aggressive condition. The figure to the right shows permeabilites of a mixed gas of 50:50 CO_2/CH_4 for typical membranes. The cross-linked membrane has a much higher CO_2 permeability than the un-crosslinked one, which was annealed at 180 °C. The CO_2 permeability of cross-linked membranes decreased monotonically with the increasing of feed pressure, while the un-crosslinked membrane shows an upturn in CO_2 permeability beyond the feed pressure of 500 psia, indicating that the membrane is plasticized. The plasticization in the un-crosslinked membrane is also indicated by the CH_4 which shows plasticization for feed pressures beyond 500 psia reflected by the upswing in CH_4 permeability. Both penetrants show higher permeabilities in the cross-linked membrane versus the uncrosslinked case, and the permeability increased with the increase of thermal treatment temperature. The cross-linked membranes did not show instability even up to the CO_2 partial pressure of 500 psia, or a feed pressure of 1000 psia.

Science objectives for 2012-2014:

- Extend the crosslinked polymer platform noted above to define and explain effects on carbon molecular sieve material permeability, sorption and diffusivity coefficients caused by *systematic variations in* ***precursor polyimide structures*** under a well-controlled standardized pyrolysis protocol
- For selected precursor structures identified in the above screening study, define and explain carbon properties created under *systematically varied differences in* ***pyrolysis protocol and atmosphere*** relative to a standardized control protocol and atmosphere.

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Towards Separations of Stable Isotopic Ions in Homogeneous, Highly Charged Nanopores

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Overall research goals: The first aim of this work is to develop fine control over the charge and diameter of nanopores in membranes. Subsequently, we will separate monovalent ions using streaming-potential induced selectivity during pressure-driven transport. Finally, we aim to optimize pore size, surface charge, concentration polarization, and flow rate for efficient separation of isotopes. One objective that spans all areas of the project is the development of models that will help us to both understand and optimize the separations. Professor Yaroshchuk is working with us in this area.

Significant achievements in 2010-2012: To create highly charged nanopores, we adsorbed multilayer polyelectrolyte films within the 30 nm-diameter pores of track-etched membranes (Figure 1a). Based on the decrease in flow rate after adsorption of a poly(styrene sulfonate)/protonated poly(allylamine) (PSS/PAH) film, the pore diameter decreases to around 14 nm after polyelectrolyte deposition. Most importantly, the polyelectrolyte creates a highly charged nanopore that affords selective ion transport at low ionic strength. Figure 2 shows the rejections of K^+ and Mg^{2+} during flow of a $KCl/MgCl_2$ solution through the membrane. At low ionic strength the pores reject >98% of the Mg^{2+} but only partly reject K^+. Evidently, the double layer in the highly charged pores effectively excludes the multivalent Mg^{2+}. As the ionic strength of the feed solution increases, the double-layer becomes more compact and ion rejection decreases. In the future, we aim to use the streaming potential created by flow through these membranes to control transport.

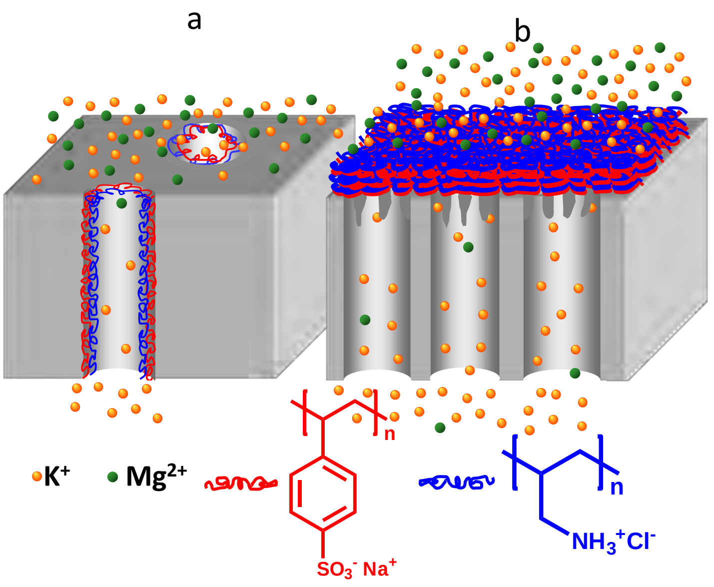

Figure 1. Schematic drawing of (a) a track-etched membrane with pores coated with a PSS/PAH film and (b) a porous alumina membrane with a $(PSS/PAH)_n$ film on its surface. The membranes show high K^+/Mg^{2+} selectivity.

We also examined transport through multilayer polyelectrolyte films that coat the top of membrane pores without filling them (Figure 1b). Remarkably, the K^+/Mg^{2+} selectivity in diffusion dialysis is >1000. The Mg^{2+} diffusive flux through the membranes is below the analysis detection limit. However, under pressure-driven flow, the Mg^{2+} rejection is typically between 95 and 98% (2-5% passage). This suggests either convective coupling of water and Mg^{2+} transport, or that the thin membrane skin's permeability changes under applied pressure. Measurements of membrane potentials under a concentration gradient across the membrane show that the polyelectrolyte membranes are generally anion selective, even with 1:1 salts such as KCl. This property could prove useful in creating depletion regions in microfluidic devices. The anionic permselectivity also leads to some negative rejections when filtering mixed-salt solutions. For example when filtering solutions containing KCl in an excess of $MgCl_2$, the concentration of K^+ in the permeate is twice that in the feed. The selective permeation of Cl^- relative to Mg^{2+} creates a large streaming potential that enhances the K^+ transport.

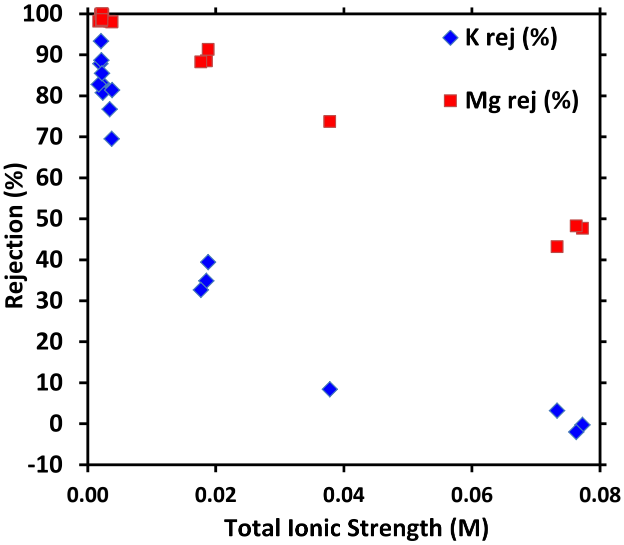

Figure 2. Cation rejections as a function of feed solution ionic strength during pressure-driven filtration through a track-etched membrane that contains 30 nm pores coated with a PSS/PAH film.

Science objectives for 2012-2014:

- Investigations of monovalent-ion transport to determine if streaming potentials can lead to extremely high rejections of more mobile monovalent ions. Electrical migration fluxes will oppose convective transport in track-etched membranes to give high rejections of mobile ions.
- Examination of ion-transport through polyelectrolyte films that bind metal ions to see whether hopping transport can occur between binding sites, and whether the introduction of charged ions within the polyelectrolyte film leads to higher selectivities.
- Studies of transport with applied electrical potentials will show whether electrodialysis and diffusion dialysis exhibit similar selectivities and if an applied potential can perform the same function as streaming potentials for separating ions.

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

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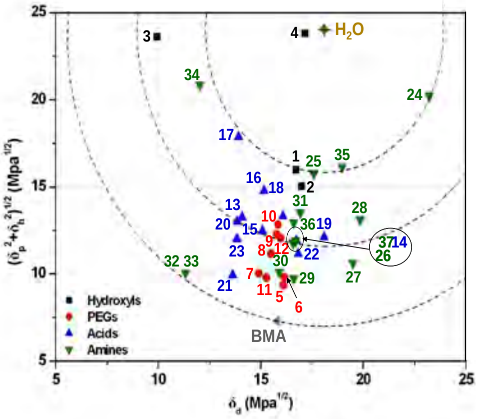
Overall research goals: The research objectives are (i) to study the application and mechanism of *atmospheric pressure plasma-induced graft polymerization (APP)* on poly(ether sulfone) (PES) membranes; (ii) to test, screen and select the best performing (i.e. with respect to protein fouling, protein sieving and membrane permeability) vinyl monomers from a large library of commercially available monomers using high throughput methods; (iii) to expand the monomer library using hypermodern combinatorial chemistry methods; and (iv) to investigate the mechanisms of protein-resistance using Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D).

Significant achievements in 2010-2012: We have developed a predictive tool for choosing grafted optimal surface chemistries to identify anti-fouling monomers for ultrafiltration [1]. It is based on solubility parameters. We have also demonstrated that our new irradiation method, APP, is superior to the widely used UV photo-graft-induced-polymerization. We have identified a series of novel antifouling monomers such as glycosyloxyethyl methacrylate, poly(ethylene glycol) methyl ether methacrylate, di(ethylene glycol) ethyl ether acrylate and [2-(Methacryloyloxy) ethyl]dimethyl-(3-sulfopropyl) ammonium hydroxide. Different solvents were used to optimize grafting and fouling resistance of poly(ethylene glycol) [2]. Also, we have synthesized, and are now testing in filtration-mode, a series of previously unreported amide monomers using combinatorial chemistry techniques. Five classes of 44 monomers were tested with APP. Most reduced BSA fouling while a few exhibited superior properties (listed above).

Fig. 1. HSP approach for determining the water affinity of monomers.



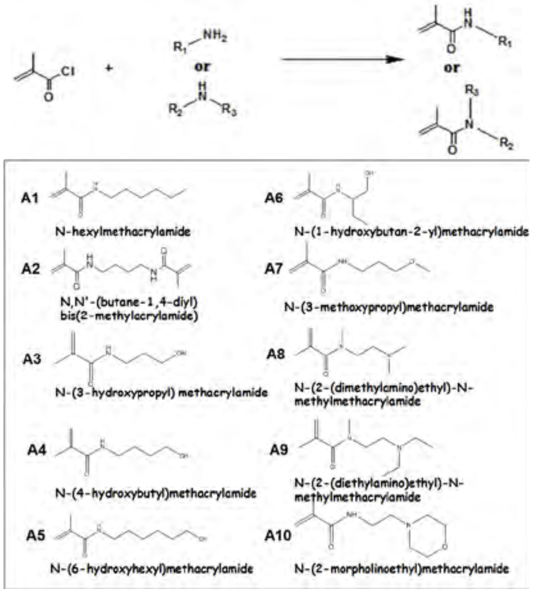
Here we focus on two aspects of the research:

1. Structure-property relationships for understanding protein-resistance [1]: We first estimate the Hansen solubility parameters (HSP) with the group contribution method (dispersion, δ_d, polar, δ_p, and hydrogen bonding, δ_h) for a series of monomers (#s 1-37 and butyl methacrylate, BMA). These are then plotted as δ_d versus $(\delta_p^2+\delta_h^2)^{1/2}$, for each monomer in **Fig. 1**. All the monomers lie between the water and BMA coordinates. The dotted lines are a measure of the radial distance from water, and the shorter this distance the higher is their solubility in water. Hydroxyl monomer points (#s 1-4) lie close to the water coordinate due to their very high values of δ_h and gave very low $\Re$ values. Although polyethylene glycols exhibit low $\Re$ values they do not lie close to water in **Fig. 1**. Molecular simulation and experimental work indicates that a flexible helical conformation of PEG or OEG can hold a tight hydration layer for good protein-resistance [3,4].

2. Combinatorial chemistry for improved protein resistance with HTP-APP: We have synthesized twelve novel amide vinyl monomers using combinatorial chemistry (**Fig.2**). These new types of the amide monomers have functional groups of alkyl (A1), methylacrylamide (A2), hydroxyl (A3-A6), ethylene glycol (A7), tertiary amine (A8, A9) and morpholinoethyl (A10). We are currently testing their anti-fouling properties, and our preliminary results are consistent with the Whitesides group's research

[5] that surface without hydrogen-donor exhibits much lower protein adsorption than that with hydrogen-donor and also consistent with our previous research [6,7]. Related published papers [8-11].

Fig.2. The reaction (above) and chemical structure (below) of the novel synthesized amide monomers.



Science objectives for 2012-2014:

- *Combinatorial chemistry* will be used to prepare an expanded library of vinyl monomers for APP-grafting of PES UF membranes and then graft screen and test the best performing monomers in filtration-mode.
- *The mechanism of grafting and the reasons for success of certain "winner" monomers* will be pursued using QCM-D, pulse NMR and molecular modeling.

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Poster Session 2

Molecular Aspects of Transport in Thin Films of Controlled Architecture

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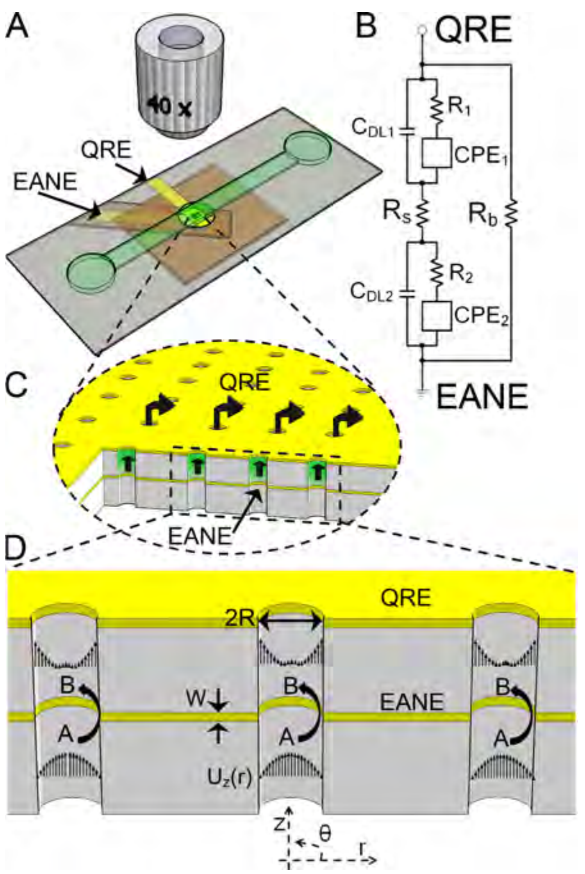
Overall research goals: Understanding and control of molecular transport in nanoscale structures is a problem of considerable continuing interest that is critical to numerous energy-related technologies, including problems in energy storage, membrane separations, and environmental remediation. The ultimate 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.



Schematic diagram showing the macroscopic layout of an NCAM-EANE. (B) Circuit diagram corresponding to electron transfer at the QRE and EANE; (C) Schematic cross-section showing relative locations of the QRE, EANE and nanochannels; (D) Magnified view of the EANE depicting locations of an arbitrary reaction A→B at the EANE, with flow profiles and geometric parameters. Drawings not to scale.

Significant achievements in 2010-2012: A key current objective is to study electrochemical reactions in the confined geometries of model nanocapillaries, where heterogeneous electron transfer reactions are directed to occur at a specific nanoscale location. Coupling enhanced molecular transport to electron transfer reactions in nanoscale structures offers a route to high efficiency electrochemical conversions. To this end cylindrical nanoelectrodes were fabricated on the interior pore volume of a nanocapillary array membrane (NCAM) to create an array of ~1000 embedded annular nanoband electrodes (EANEs). The membrane is positioned between two axially separated microchannels to form an integrated micro/nanofluidic architecture in which transport and electron transfer reactions are tightly coupled. Since the middle Au electrode is embedded within dielectric layers, electrochemical reactivity is permitted only at the nanoband region at the center of the nanochannel, resulting in enhanced mass transport. The NCAM-EANE structure represents a potentially powerful construct for electrochemical processing, and it has been studied both experimentally and by detailed simulations. The EANE array was first characterized by studying the behavior of the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ redox couple, which exhibits steady state currents enhanced by >10x over a comparable structure without convective transport. Dimensional analysis has been used to parameterize the electrode width, nanopore diameter, and electrochemical overpotential in a format applicable to various reagents, and the results indicate that under conditions of low Pe flow the

EANE-NCAM structure significantly outperforms a comparable microband/microchannel structure at high overpotential.

In other experiments, solvent electrolysis was coupled to nanochannels for the generation of reactive H_2. The production of hydrogen-rich liquid volumes within nanofluidic structures, without bubble nucleation or nanochannel occlusion, was explored both experimentally and by modeling. Devices comprised of multiple horizontal nanochannels intersecting planar working and quasi-reference electrodes were constructed and used to study the effects of confinement and reduced working volume on the electrochemical reduction of H_2O to H_2 and OH^-. Local dissolved H_2 concentrations were correlated to partial pressures through Henry's Law and values as large as 8.3 atm were obtained at the most negative potential steps. The downstream availability of electrolytically produced H_2 in nanochannels was evaluated in terms of its possible use as a downstream reducing reagent. The results obtained indicate that H_2 can easily reach saturation concentrations at modest overpotentials.

Science objectives for 2012-2014:

- Development of *in situ* hydrogenation catalysts for microchannel conversion of oxyanions to reduced forms with significantly altered toxicity. Initial experiments are focusing on binary Pd-based catalysts and the reduction of ClO_4^- toDevelop Cl^-.
- Development of an *in situ* potentiometric detector for Cl^- to place downstream of the catalytic hydrogenation nanoreactor. Current design utilizes Ag/AgCl-based potentiometry and initial constructs have show adequate stability.
- Extension of the *in situ* nanochannel electrolysis method to O_2 generation and downstream catalytic oxidation.
- Completion of initial fluorescence correlation spectroscopy studies of the transport behavior of green fluorescent protein in the presence of surface-bound crowding agents.

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Molecular-Level Investigation of Diffusion Behaviors within Cylindrical Nanoscale Pores

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Overall research goals: The goal of this project is to develop a quantitative understanding of molecular mass transport within solution-filled nanoporous media at the molecular level. Single-molecule and ensemble mass transport behavior will be measured within identical cylindrical nanopores having well-defined diameters and surface properties. Ensemble and single molecule data will be directly linked to clarify key molecular-level mechanisms determining the rate and selectivity of mass transport within nanopores. A comprehensive understanding will be obtained and will aid in the engineering of nanoporous media optimized for energy-relevant applications such as in chemical separations and power sources. This 3-year project aims to (1) establish simple methods to prepare capillary-incorporated monoliths comprising well-aligned cylindrical nanopores (2-35 nm in diameter) fabricated from cylinder-forming block copolymers (CFBCP) and surfactant-templated mesoporous silica (STMS) and (2) measure ensemble and single-molecule diffusion within them under the influence of electrostatic and steric interactions.

Significant achievements in 2010-2012:

1. Development of a new orthogonal regression analysis method for quantifying nanopore orientation and order by single molecule tracking (SMT). We have developed a new method for quantitative assessment of nanopore alignment using SMT data. Trajectory segments of fluorescent molecules are fit to lines using orthogonal regression methods. The orientations of the fitted lines provide a quantitative measure of orientational order within μm-scale and larger sample regions. Further statistical analysis also permits us to distinguish between 1D and 2D trajectories. This method has revealed the presence of multiple differently-oriented, but very well-ordered domains in a spin-coated STMS films.

2. Shear-flow-induced microscopic alignment of nanostructures in capillary-incorporated STMS monoliths. We successfully fabricated flow-aligned STMS monoliths of very high nanopore orientational order within microfluidic channels. The nanopore organization, which was assessed by SMT and small-angle X-ray scattering, was found to depend on sol aging time prior to monolith preparation. Aging times ≥ 20 hours produced disordered materials, due to gelation of the silica sol.

3. Millimeter-range solvent-induced alignment of cylindrical domains in CFBCP films. Using SMT, we have discovered that directional penetration and evaporation of 1,4-dioxane induces long-range (millimeter-scale) alignment of cylindrical domains in polystyrene-poly(ethylene oxide) diblock copolymer (PS-*b*-PEO) films. PEO domain orientation and order were assessed by SMT of fluorescent dyes that partition into the PEO domains. 1,4-Dioxane-annealed films mainly showed 1D trajectories aligned along the direction of solvent penetration over millimeter length scales, demonstrating long-range alignment of the PEO domains. In contrast, toluene- and benzene-annealed PS-*b*-PEO films produced 2D trajectories, consistent with previously-reported short-range (≤ 1 μm) alignment.

4. Relationships between diffusion coefficients (D) obtained by SMT and fluorescence correlation spectroscopy (FCS). We employed SMT and FCS to measure D for fluorescent molecules within flow-aligned cylindrical micelles of a nonionic surfactant (F127). The probes preferentially partition into the hydrophobic regions of the micelles, exhibiting 1D diffusion, and revealing the micelle orientation. SMT data revealed only relatively slow 1D dye motion, consistent with diffusion through the high viscosity hydrophobic cores of the F127 micelles, while FCS data depicted two distinct diffusion modes, one corresponding to the slow diffusion observed by SMT and a second reflecting much faster (i.e., 20-fold larger *D*) motions that were not observed by SMT.

5. Characterization of the surface and ensemble mass transport properties of CFBCP-derived nanoporous monoliths. Using ensemble techniques we have clarified the surface chemistry of cylindrical nanopores derived from polystyrene-poly(methylmethacrylate) diblock copolymers (PS-*b*-PMMA); demonstrated solvent-induced control of effective nanopore diameter, as revealed by electrochemical impedance spectroscopy; and investigated hindered diffusion of cytochrome c within these nanopores by electrochemical methods and finite element computer simulations. In addition, we assessed the functional characteristics of microcapillary-incorporated PS-*b*-PMMA-derived nanoporous monoliths by conductance and flux measurements. The observations of surface conductance and permselective transport indicated the presence of nanopores penetrating through the monoliths. However, these measurements and FE-SEM images showed the presence of cracks at the monolith-capillary interface due to monolith shrinkage induced by PS crosslinking during UV irradiation (254 nm) used for PMMA domain removal.

Science objectives for 2012-2014:

- Prepare substrate-supported STMS and CFBCP-derived monoliths containing aligned nanopores using microchannel-based approaches.
- Characterize ensemble and single-molecule diffusion within nanopores under different solution conditions (pH, supporting electrolyte concentrations, types of fluorescent molecules).
- Measure ensemble flux and single-molecule diffusion data for nanopores having different pore diameters.
- Develop new fluorescence techniques to obtain more reliable molecular diffusion data.

References to work supported by this project 2010-2012:

A total of 12 manuscripts acknowledging DOE support have been published, submitted or are currently in preparation. Those most directly related to the project goals are listed below.

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Laser-Material Interactions (Ablation) for Chemical Analysis

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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. Our endeavor is to utilize this knowledge to increase spatial resolution down to namometer dimensions and sensitivity to attogram detection.

Significant achievements in 2010-2012: The research effort has emphasized understanding the laser induced plasma and how it influences sensitivity of analysis when the laser beam is focused to nanometer spatial and depth scales. Our emphasis is on the detection of optical emission from these laser plasmas and how plasma properties affect spectral line shape and intensity, background broadband electron emission and population of states. We achieved spatial (27nm) and depth resolution (1.5nm) by laser ablation. However, we are currently not able to measure optical emission. The questions are whether optical emission exists on this scale – is there enough mass and are there enough collisions that lead to optical emission. Emission is through electron ion recombination processes. To address the emission question, we work at slight larger resolution where we can measure emission and study the laser plasma properties. We also address how to enhance the plasma emission by using secondary excitation sources, including a second laser pulse into the primary laser-induced plasma or micro-plasma secondary excitation. Figure 1 shows how temperature and electron density change with seeding a first pulse plasma with a second laser pulse.

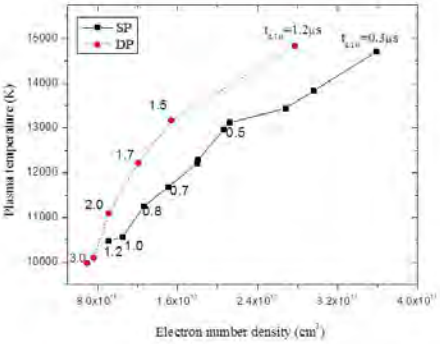

Fig. 1. Time evolution of the plasma temperature vs. electron number density of Mg II lines at $\Delta t_{\text{laser}} = 1$ μs in single-pulse (black solid line) and double-pulse excitation (red dotted line) on an Al alloy sample.

We also study the use of double-pulse LIBS for increasing the signal intensity and sensitivity of laser-ablation based chemical analysis. Our results show that the orthogonal double-pulse configuration can increase the sensitivity by ~120 times as compared to a single-fs laser pulse. In addition we find that although the spectral emission lifetime for the single pulse is less than 20 ns, the second pulse enhances the signal hundreds of nanoseconds later, indicating that a significant number of non-radiative species (neutrals and/or particles) exist in these small-lengthscale plasmas long after the fs-laser pulse is over.

A significant capability of ultrafast pulse ablation optical emission is the ability to achieve nanometer depth resolution. Figure 2 shows record results for 7nm depth resolution measurement of several elements in the SEI (surface electrolyte interphase) layer of a Li-ion battery half-cell. Nanometer depth resolution cannot be achieved using nanosecond pulsed lasers due to a large hear affected zone. The 7nm resolution is a breakthrough for allowing researchers in the Li-ion battery community of DOE to study and understand electrode interface chemistry.

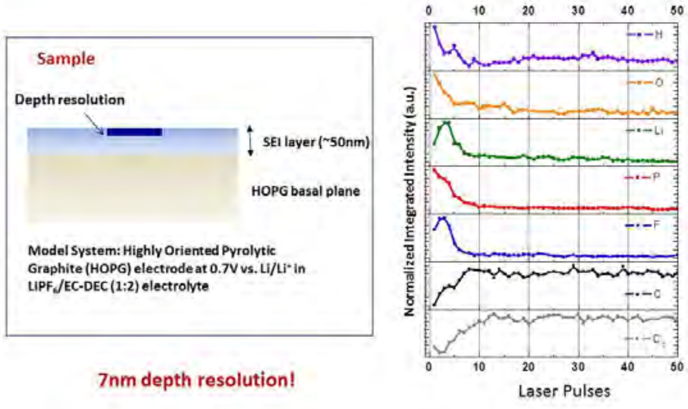

Figure 2: 7nm depth resolution laser ablation sampling into the SEI layer of a Li-ion battery halp-cell using femtosecond laser and measuring optical emission in the laser induced plasma.

Science objectives for 2012-2014:

- 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)
- Study near-field excitation (ablation) using near-field detection using a unique capability at LBNL – a new dual head near field optical microscope configuration.

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Nanophotonic and atmospheric pressure ion production in imaging mass spectrometry

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Overall research goals: The goals of this research are to develop ultrasensitive laser ionization platforms for mass spectrometry, based on nanophotonic interactions, e.g., silicon nanopost arrays (NAPA); to enhance the ion yield in atmospheric pressure ionization techniques, e.g., in laser ablation electrospray ionization (LAESI), and to demonstrate their efficacy for tissue imaging and in the direct analysis of microorganisms.

Significant achievements in 2010-2012: During the reporting period, we introduced and characterized the highly efficient NAPA photonic ion sources. Their ion yields exhibit strong polarization dependence, resonances at certain post aspect ratios and fluence dependent energy deposition. Using p-polarized radiation high ion yields are achieved, whereas s-polarized laser pulses produce few or no ions. The optimized NAPA chips possess ultralow limits of detection, e.g., 800 zeptomoles (800×10^{-21} moles) for the verapamil test compound. The detected ion intensities are proportional to the amount of deposited analytes, exhibiting an up to four orders of magnitude dynamic range. This enables the direct metabolic analysis of small populations of microorganisms. The analysis of ~80 yeast cells resulted in the identification of 109 of the 584 known yeast metabolites, i.e., 19% of the yeast metabolome.

The LAESI ion source was utilized in radically new mass spectrometric imaging experiments. By analyzing individual cells in the region of interest in plant tissue, we were able to create chemical images using single cells as pixels. This novel approach enables the in situ investigation of metabolite distributions and transport processes in live tissue. For the mass spectrometric analysis and imaging of non-polar compounds, we introduced the laser ablation atmospheric pressure photoionization (LAAPPI) method based on VUV radiation. The application of LAESI was demonstrated in the direct analysis of phycobilisomal antenna proteins and metabolites in cyanobacteria. During the reporting period, Protea Biosciences, Inc., licensed the LAESI ion source from GW and produced a commercial version. This year, the LAESI tissue and cell analysis technology and the corresponding commercial product were selected as one of the "Top 10 Innovations in 2011" by the British life sciences magazine, The Scientist.

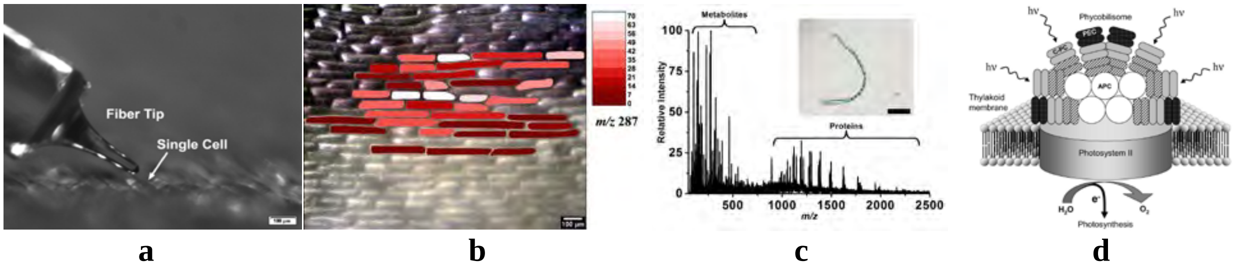

Figure 1. Mass spectrometric imaging and analysis of live tissues and cells performed by LAESI ionization. (a) Targeting individual cells by the mid-IR laser is achieved using an etched optical fiber tip. b) Cell-by-cell analysis of a plant tissue at the interface of two epidermal cell phenotypes (purple and transparent) indicates higher cyanidin pigment concentrations in the purple region. c) LAESI mass spectrum of *Anabaena* sp. PCC7120 cyanobacteria reveals the composition of the antenna protein complex in d) the phycobilisome protein assembly.

Science objectives for 2012-2014:

- Metabolic analysis of yeast in small cell populations will be extended down to single cell level. We will explore if the effect of oxidative and thermal stress can be followed by laser ionization on NAPA and mass spectrometry.
- The LAESI experiments on cyanobacteria will be extended to see if changing light conditions alter the protein composition of the light harvesting antennae. Metabolic changes will also be explored by LAESI mass spectrometry.
- The combination of LAESI ionization, ion mobility separation and mass spectrometry will be developed to improve the coverage of the metabolome in direct tissue and cell analysis experiments.

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Nanoparticle Imaging, Assembly, and Chemistry

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Overall research goals: The research objectives are to provide an understanding for control of nanoparticle chemistry by imaging individual nanoparticles with chemical contrast and nano-scale spatial resolution. Our approach is linear, nonlinear optical, and time-resolved spectroscopy as a means to probe important nanoparticles and their interfaces.

Significant achievements in 2010-2012: We have assembled a microscope that captures tip-enhanced second harmonic generation images at 100-nm spatial resolution in registration with atomic force microscope images for physical topography. We have studied the degradation of 100 nm diameter ZnO nanowires (NWs) by contact with carbon dioxide and water vapor. Controlling this detrimental chemical process is important for ZnO semiconductor applications. Our study was conducted on single NWs to avoid ensemble averaging effects to ascertain if particular changes were unique to specific wire locations. The resulting images reveal that the degradation is complex, with a variety of different product morphologies represented. We have identified different locations along the NW where the chemical conversion produced different structural effects.

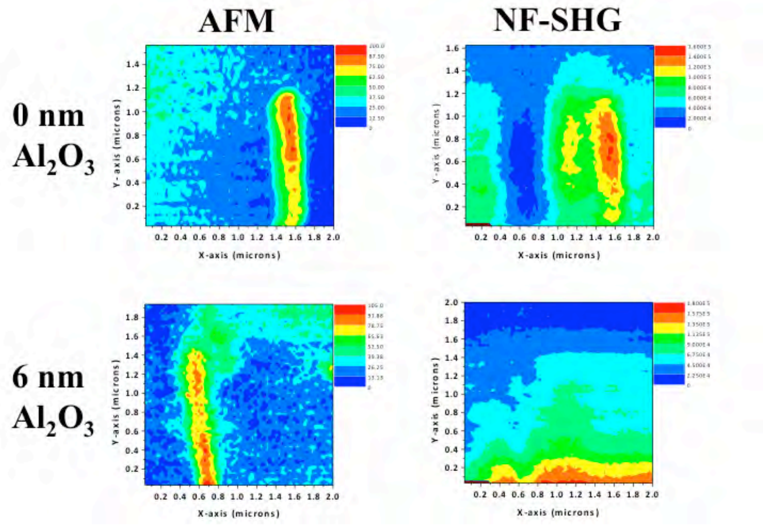

Figure 1. Comparison of AFM and tip-enhanced near-field (NF) SHG images for fresh 0-nm and 6-nm alumina-coated 100-nm ZnO nanowires.

We coated some NWs with about 3-5 nm of amorphous alumina to serve as a potential protective layer; for these NWs the corrosion process was less pronounced and resulted in less dramatic morphological changes, but degradation still proceeded over a several day exposure to carbon dioxide. As seen in Figure 1, a 6-nm coating was sufficient to null the near-field effect due to tip standoff from the ZnO. Understanding NW chemical changes is important for successful use of ZnO based nano-devices for optoelectronic applications, for example in solar energy harvesting cells; methods to mitigate degradation of the high surface area ZnO material must be found to permit long term device stability.

Through a user proposal we have had access to a focused ion beam instrument at the CNMS, where we have successfully modified our scanning probe tips in an attempt to increase the sensitivity of tip-enhanced SHG microscopy. We have developed the protocol to ion mill gold from the probe to leave only the bottom 200 micrometers of the tip coated. This should increase the enhancement effect because the tip plasmon resonance will be more aligned with the excitation wavelength. We are currently beginning to test the modified tips.

Gold nanorods have been imaged and their plasmon spectra analyzed. These nanoparticles have found important applications as image markers due to their bright plasmon scattering, the spectrum of which can be tuned by synthetically altering their diameter and length. It is important to understand the structures nanorod clusters adopt upon assembly and the associated spectral alterations. Typical nanorods are a few tens of nanometers in diameter and up to 100 nm in length. We have investigated 10 x 28 nm gold nanorods, from single particles to rafts with up to about ten rods to ascertain the spectral changes that result from particle assembly. Particles were drop cast on microscope coverslips from dilute suspensions. The samples were then subjected to atomic force microscopy (AFM) to differentiate single nanorods from clusters of rods. The nanorods were then laser-excited on an inverted fluorescence microscope. For a cluster of rods, the emission was broadened and red shifted relative to a single nanorod. Both the longitudinal and transverse plasmon resonances red shift by as much as 100 nm and the relative intensity ratio changes. Through analysis of several clusters and modeling of the spectra, we hope to derive structures of how the nanorods assemble.

Science objectives for 2012-2014:

- Extend nonlinear optical imaging to third harmonic generation (THG) and sum frequency generation (SFG) to encompass a greater number of sample types and permit surface vibrational analysis of nanoparticles.
- Interpret structures of purposefully and self-assembled nanoparticles through modeling of their plasmonic scattering spectra, with a goal of demonstrating directed excitation energy flow.
- Demonstrate femtosecond transient absorption for single nanoparticles. In combination with structural characterization, we hope to understand how the size, shape, defects and/or impurities of nanostructures affect their electronic excited-sate dynamics.

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Analytical Spectroscopy Methods for Liquid/Solid Interfaces

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Overall research goals: Liquid/solid interfaces play a key role in numerous aspects of energy-related chemistry. 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 spectroscopic imaging methods for investigating molecular structure, transport, and reactions at liquid/solid interfaces that govern these applications. Specifically, we are developing fluorescence and Raman microscopy methods capable of *in situ* characterization of sub-monolayer interfacial populations, to the limit of imaging the behavior of individual molecules.

Significant achievements in 2010-2012: Fluorescence microscopy has been adapted to *quantify* surface populations at the single-molecule level and to study transport of molecules at surfaces. Image analysis methods have been developed to locate molecules, correlate their locations across multiple images, and characterize their diffusion behavior. An algorithm to identify single molecules by finding connected pixel intensities that fit the instrument point-spread function allows thresholds to be set close to the noise level and lowers both false-positive and false-negative events. This method has been applied to identifying and quantifying single-molecules and to measuring interfacial molecular transport in trajectories of single-molecules diffusing in thin films of a temperature-responsive polymer and within the interior of porous particles. It has been also been used to quantify the accumulation of polyelectrolytes in the electrical double layer (see figure).

Confocal Raman microscopy has been developed for examining the interior composition of individual porous particles. This method was applied to investigate ion-pair interactions responsible for retention of charged solutions in reversed-phase liquid chromatographic support particles. This experiment has also been adapted to *in situ* detection of solid-phase extraction into single particles, enabling rapid, ultra-trace level detection in extremely small volume samples. Changes in interfacial molecular populations and chemical structure in response to applied potentials have been characterized by surface-enhanced Raman scattering (SERS). Potentials applied to SERS-active electrode surfaces were used to manipulate the structure and properties of the interface. Changes in structure are apparent in the vibrational spectra of surface-bound species and include potential-dependent proton-transfer reactions and the kinetics of monolayer self assembly.

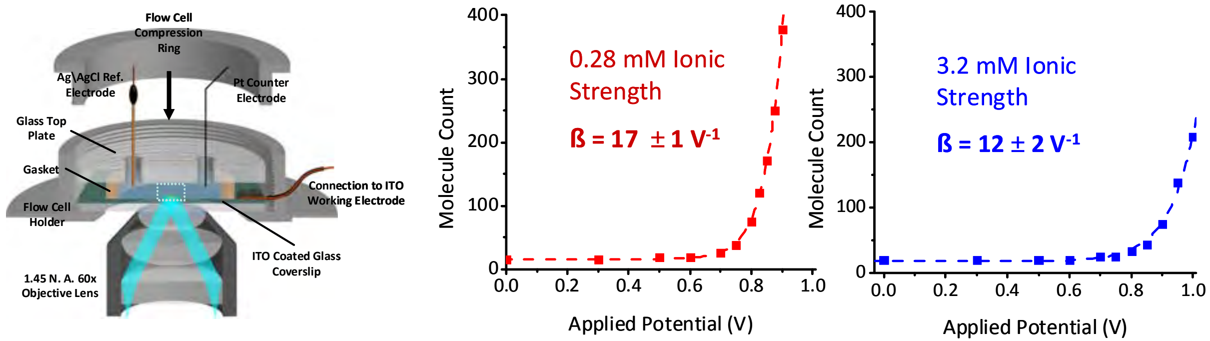

Figure 1 (Left) Single-molecule spectroelectrochemistry for imaging individual polyelectrolyte molecules in the double-layer. (Center and Right) Interfacial accumulation of DNA molecules versus applied potential, fit to a Poisson-Boltzmann model, showing the sensitivity of the exponential term, $\beta = (z_{eff}\, e/ kT)$, to ion strength and Debye length.

Science objectives for 2012-2014:

- Confocal-Raman microscopy will be applied to single-particle, solid-phase extraction, where the Raman spectra of only a few million molecules, concentrated into a femtoliter particle, can be readily detected. The time dependence of accumulation will be measured to provide information about the kinetics of transport of molecules within porous particles.
- Surface-enhanced Raman spectroscopy will be used to monitor surfactant accumulation and ion pairing at hydrophobic surfaces under potential control, in order to determine the role of electrostatic interactions in the accumulation of the surfactant monolayer. Ion-pair chemistry will also be harnessed for enhanced selectivity of electrochemical reduction of nitroaromatics. Shell-isolated nanoparticle-enhanced Raman scattering will be employed to monitor reaction steps in the surface-modification of dielectric materials.
- A new approach to measuring fast interfacial diffusion of molecules on surfaces is being developed and tested. Fluorescence imaging correlation spectroscopy can measure surface diffusion when transport rates exceed the ability of single-molecule imaging to track molecular motion. The method employs a fast framing CCD camera and can thereby map diffusion on inhomogeneous surfaces, where the size and location of a test area are controlled electronically.
- Single-molecule imaging will be being applied to measure complimentary-strand DNA binding kinetics. Using a high-density ssDNA capture surface, single fluorescently labeled complimentary strands will be imaged as they bind. From single-molecule counting and residence-time measurements, the rates of binding and unbinding and their sensitivities to ionic strength will be determined, providing estimates of electrostatic barriers to DNA association and dissociation.

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Mapping Non-covalent Surface Functionality using Single Molecule Probes

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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 resonance energy transfer (RET). 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 RET to probe the local molecular environment, and to identify and measure reaction rates at individual immobilized catalytic sites.

Significant achievements in 2010-2012: A new chemical imaging technique was developed, MAPT (Mapping using Accumulated Probe Trajectories) [1]. In MAPT, a time series of images is obtained using single-molecule TIFRM, and image processing is used to determine the locations of all the individual molecules adsorbed to the surface. By tracking these locations through a time series, physical properties of probe/surface interactions (adsorption rates, local diffusion, desorption probability and surface coverage) are determined. By distributing these events to locations on the surface, characteristic values are determined as a function of position. **Figure 1** shows MAPT images of photo-patterned trimethylsilane on fused silica. MAPT analysis is intrinsically super-resolution and we have demonstrated resolution of ~100 nm in our initial results. MAPT can be used on any surface and provides absolute and quantitative values of physical interaction properties that can be connected to specific surface chemistries.

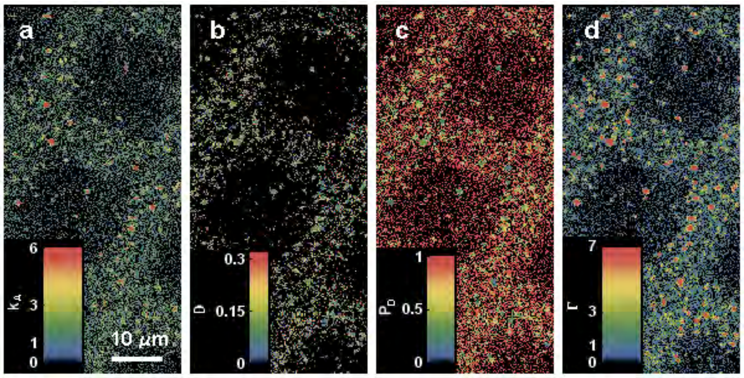

Figure 1: MAPT images of a photopatterned trimethylsilane surface using multiple modes of contrast. (**a**) adsorption rate (10^{13} $\mu m^{-2}s^{-1}M^{-1}$) (**b**) average diffusion coefficient ($\mu m^2/s$) (**c**) desorption probability per 400 ms and (**d**) surface coverage/occupancy (10^{13} $\mu m^{-2}s^{-1}M^{-1}$).

MAPT provides a unique opportunity to directly connect local surface chemistry with dynamic molecular behavior on heterogeneous surfaces. The capability led to new understandings of: "crawling" vs "flying" modes of molecular surface diffusion [2], anomalously long surface residence times and anisotropic protein diffusion on crystalline regions of nanostructured melt-drawn polyethylene [3], and aggregation of proteins at the oil-water interface [4].

In other work, we developed a variant of single-molecule tracking based on dynamic single-molecule resonance energy transfer (i.e RET a.k.a. FRET), that permits us to make direct connections between the conformation (e.g. end-to-end distance) of individual molecules and their dynamic behavior at nanometer and micron length scales [5]. Additionally, by applying methods that allowed the observation of $>10^5$ molecular trajectories, we were able to identify direct correlations between rare extended molecular conformations and important dynamic events such rapid surface mobility, conformational fluctuations, and desorption.

The advances required for MAPT were significant. In previous realizations of single-molecule trajectory analysis, the number of trajectories analyzed was limited to only $\sim 10^2$ molecules. The methods developed for MAPT, however, permit routine analysis of 10^4–10^6 trajectories [6], providing new opportunities to study heterogeneous molecular populations. Similar advances were made with respect to temporal resolution, spatial resolution, and the quantitative analysis of multiple populations and molecular trajectories [7].

Studies are currently under way to characterize the adsorption rate, desorption rate, and molecular mobility of hydrophobic probe molecules on a homologous series of surfaces that exhibit subtle differences in hydrophobicity. In other experiments, we are developing probes that are sensitive to local surface charge. Finally, we are using single molecule RET to map active catalytic sites for copper-catalyzed alkyne-azide click chemistry. We have successfully made real-time observations of this surface-catalyzed bimolecular addition reaction, and are currently optimizing this system to obtain statistically-significant reaction rate information on a site-by-site basis.

Science objectives for 2012-2014:

- Methods that provide quantitative information about the kinetics and energetics of adsorbate/reactant adsorption, desorption, and interfacial mobility. This will allow us to design and prepare probe molecules whose dynamic behavior and spectral response are sensitive to surface hydrophobicity, hydrogen-bonding, electrical charge, and aromatic π-stacking.
- Quantitative surface imaging methods with sub-diffraction spatial resolution and high temporal resolution that are able to recognize and distinguish chemical functionality while simultaneously obtaining quantitative local dynamic and spectral information about molecules of interest.
- Quantitative single-molecule RET imaging methods that enable dynamic tracking of both reactants and products in the vicinity of individual reactive sites that catalyze addition, dissociation, and fluorogenic reactions.

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Mass Spectrometric Imaging of Plant Metabolites

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Overall research goals: The scientific goal of our research is to understand plant metabolic biology at the single cell level and eventually subcellular and suborganelle levels. We develop mass spectrometric (MS) imaging techniques to map metabolite distributions within plant tissues, and among individual plant cells. Such information will provide unprecedented details about the distribution of metabolites from cell to cell, cooperative and antagonistic effects among the metabolites, and environmental influences on metabolism. These details will ultimately lead to a predictive understanding of the mechanisms that multicellular organisms use to regulate metabolic processes.

Significant achievements in 2010-2012: Multiplex mass spectrometric imaging technology has been developed to reduce the data acquisition time while obtaining diverse chemical information in a single experiment. This methodology allows high mass resolution MS imaging, high-spatial resolution MS imaging, and a few MS/MS and MSn imaging at the same. We successfully applied this technique to obtain asymmetric distribution of structural isomers of flavonoids.

MS imaging technique has been successfully adapted as a high-resolution tool for functional genomics. Flavonoid imaging of the Arabidopsis flower showed an asymmetric distribution of kaempferol and/or its glycosides on the distal region of petals and quercetin, isohamnetin, and/or their glycosides on the proximal region of petals. In contrast, a homogeneous distribution of kaepferol and/or its glycosides is observed in the mutant (tt7), suggesting asymmetric gene expression.

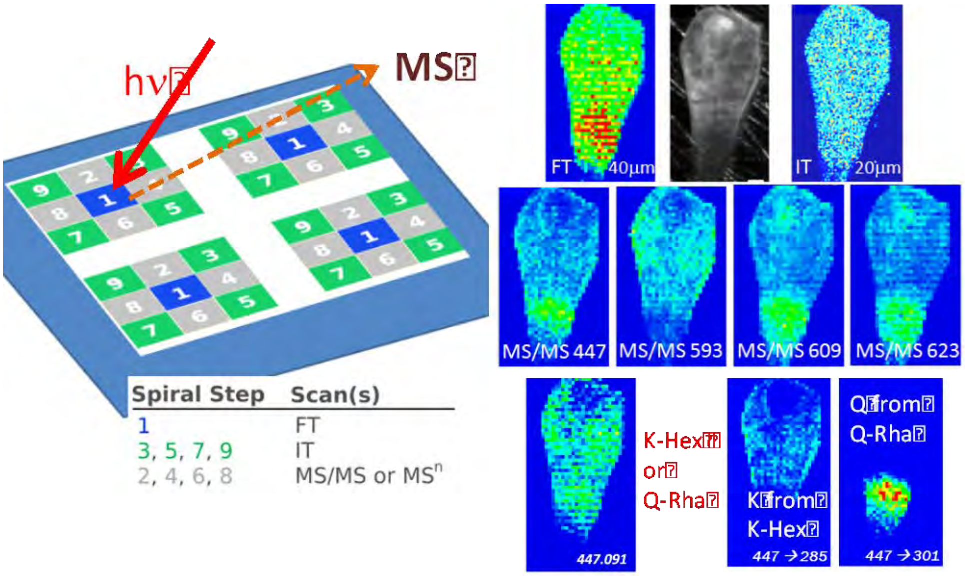

Figure 1. Illustration of Multiplex MS Imaging. (Left) A set of nine MALDI-MS spectral acquisitions for each raster position: Orbitrap MS (FT; #1), 4x ion trap MS (IT; #3, 5, 7, 9) and 4x MS/MS (#2, 4, 6, 8). (Top Right) Various imaging information obtained from an Arabidopsis petal: high-mass resolution FT image, high spatial resolution IT image (20 µm), 4x MS/MS imaging. (Bottom Right) Asymmetric distribution of flavonoid structural isomers (keampferol-hexose (K-Hex) and quercetin-rhamnose (Q-Rha)) distinguished by MS/MS imaging.

MS imaging of cryosections of cotton embryos revealed a distinct, heterogeneous distribution of molecular species of triacylglycerols (TAG) and phosphatidylcholines (PC), the major storage and membrane lipid classes in cotton embryos. Other lipids were imaged, including phosphatidylethanolamines, phosphatidic acids, sterols, and gossypol, indicating the broad range of metabolites and applications for this chemical visualization approach. Comprehensive lipidomics images generated by MALDI-MSI report accurate, relative amounts of lipid species in plant tissues and reveal previously unseen differences in spatial distributions providing for a new level of understanding in cellular biochemistry. For example, TAG species with palmitic and linoleic acids (c.f., TAG 50:2 (PLL) or TAG 52:4 (LLL)) have a higher abundance in cotyledon than in the embryonic axis. The similar distribution in PC (c.f., PC 34:2 (PL) or PC 36:4 (LL)) supports the synthesis of TAG via membrane lipids as an intermediate.

Science objectives for 2012-2014:

- New instrumentation is being developed to achieve high spatial resolution down to 5-μm or lower.
- New matrixes will be developed to improve sensitivity at the cellular/subcellular level, including new classes of ionic liquids.
- Metabolite trafficking will be studied in single cell and/or subcellular level, particularly in C4 photosynthesis and lipid trafficking.
- Ionization and transmission efficiency will be improved in AP MALDI imaging using post-ionization and specialized sampling device.

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DC to Daylight:
Local Spectroscopies for Subnanometer Spatial Resolution Chemical Imaging

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Overall research goals: The research objectives are to develop broadly applicable local, imaging spectroscopies based on the scanning tunneling microscope (STM) for the microwave, infrared, visible, and near-ultraviolet ranges. All of these measurements give insight into molecular/assembly function that are beyond the typical purview of scanning probe microscopies.

Significant achievements in 2010-2012: We have made significant headway in identifying amino acids in oligopeptides using local polarizability. Multiple bonds exhibit enhanced polarizability, which is measured locally with the ACSTM. Additional signal comes from molecule-substrate and molecule-molecule contact. Coupling experimental results to calculations enables determination of the orientations of side groups.

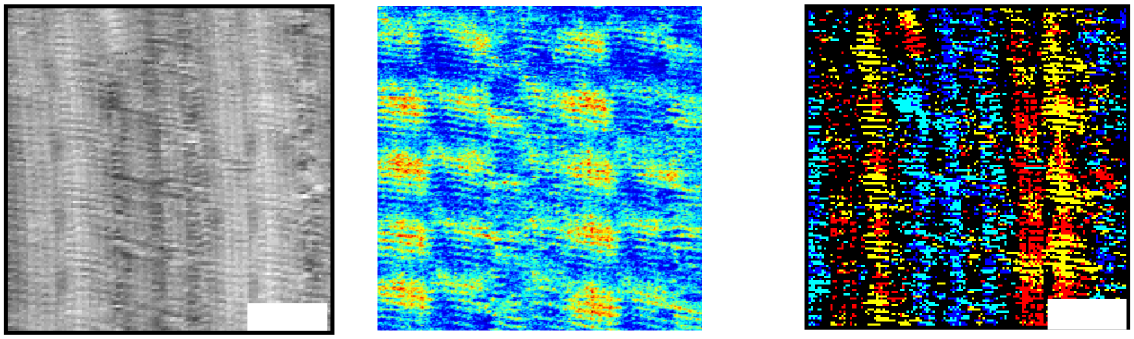

Figure 1. (Left) Topographic STM and (middle) simultaneously recorded polarizability map of the decapeptide FFFFFHHHHH on graphite. (Right) Merged image. Scale bar = 5 nm. From these images and modelling, the structure of the lamellae formed and the orientations of the side groups of the amino acids are determined.

After demonstrating regioselective photoreactions of pairs of molecules inserted in self-assembled monolayers, we have succeeded in measuring the intrinsic photoconductances of molecular dyad and triads that are designed for organic photovoltaics. We have established collaborations with leading groups in this field and are expanding these collaborations further, as no comparable capabilities exist elsewhere.

We have developed special nanohole array substrates to enhance local and far-field spectra. Our first publication on this work, featuring tracking of the photoisomerization of isolated azobenzene molecules, appeared in *Nano Letters* in 2011, with two other manuscripts now ready to submit on other systems.

Science objectives for 2012-2013:

- Apply our unique photon scanning tunneling microscope to measure local/molecular photoconductivity and optical spectra to molecules and materials for photovoltaics.
- Continue to 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, based on the successful UV-visible STM design.

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Session 7 – MS Analysis Science

Chemistry and Microphysics of Small Particles

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Overall research goals: The overall goal is to achieve fundamental understanding of the processes that control formation, chemical and physical properties, and transformations of small particles, in particular particles composed of complex organics and aspherical particles.

Significant achievements in 2010-2012: This project proceeded along four parallel pathways. (1) Gaining a fundamental understanding of particle physicochemical properties to guide development of improved multidimensional particle characterization and achieve dynamic chemical imaging of individual particles with nanometer resolution; (2) Study of the chemistry and microphysics of size-selected complex organic particles; (3) Investigation of the effect of particle shape on particle dynamics in different flow regimes and its physicochemical properties; and (4) Development and application of novel data analysis and visualization approaches.

The results of our studies of chemistry and microphysics of size-selected complex organic particles challenge prevalent assumptions that these particles are liquid droplets at equilibrium with the gas phase. Utilizing our recently developed shape characterization and “depth-profiling” approaches, we characterized with an unprecedented level of detail the shape, phase, and morphology of organic particles composed of liquid hydrophobic organic core coated with the α-pinene oxidation products and of particles with the reverse morphology. We showed that these mixed particles are layered and demonstrated that both morphologies are stable, indicating that particles composed of thousands of α-pinene oxidation products, cannot be in the liquid phase - a conclusion of great import for the way these particles must be treated in models. In a separate study, we showed that even a submonolayer of the organic coating condensed on wet sodium nitrate cores inhibits water evaporation and the amount of water retained increases with the organic coating thickness.

Recently we conducted the first room temperature, evaporation kinetics measurements of size-selected complex organic particles for more than 24 hours. We showed that these particles evaporate orders of magnitude slower than predicted by current models, indicating that these particles are not at thermodynamic equilibrium with the gas phase, as models assume. Furthermore, we demonstrated that when vapors of hydrophobic organics are present during particle formation, they become adsorbed and trapped inside the highly viscous particles, reducing evaporation rates. In the same study, we also examined the effect of aging and found that aging of mixed particles further reduces evaporation rate, and nearly stops it.

Our most recent study of α-pinene oxidation by ozone and NO_3 radicals also shows that contrary to expectations, the observed particle formation and growth are inconsistent with equilibrium partitioning between the gas phase and a liquid particle phase and can only be explained by irreversible, kinetically determined uptake of the organic nitrates on particles surfaces.

We continued to investigate the properties of particles with multifaceted shapes and morphologies and their relation to particle aerodynamic properties, and developed a new approach that offer, for the first time, the opportunity to identify the presence of particles with different shapes, separate them based on their shapes, and characterize their chemical and physical properties. It provides, for the first time, the ability to measure simultaneously, in-situ, and in real-time particle dynamic shape factors in the transition and in free-molecular regimes over the entire range of particle shapes present in the aerosol sample. For example, it makes it possible to identify, separate, and separately characterize, cubic particles with rounded and sharp edges.

Science objectives for 2012-2014:

- Continue to investigate the formation, properties and transformations of complex organic particles, with particular focus on particle phase, morphology, evaporation kinetics, and rates of heterogeneous chemistry.
- Apply newly developed method to separate particles based on their shape to quantify the effect of particle shape on particle dynamics in different flow regimes and physicochemical properties.
- Continue development and application of novel approaches for multidimensional data classification, visualization and analysis. Implement the parallel coordinates interface to quantify the relationships between the particle properties and other observables.

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Fundamental Studies of the Inductively Coupled Plasma and Glow Discharge

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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 2010-2012: *Characterized the spatial dependences of matrix interferences in axial-viewing Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES):* Previously, we reported on the spatial dependence of matrix interferences in radial-viewing ICP-AES and developed a universal method to flag the presence of matrix interferences. In this reporting period, the research was extended to axial-viewing ICP, which is known to yield better detection limits but worse matrix interferences. The most significant findings are: (1) different categories of matrix interferences along the cross-sectional emission profile of axial-viewing ICP-AES were characterized; (2) As in radial viewing, the spatial (i.e., cross-sectional) emission profile is effective for flagging interferences in axial-viewing ICP–AES; (3) the performance and operating conditions for flagging matrix interferences in the two ICP-observation modes were compared; (4) most (but not all) ionic emission lines yield matrix-interference free cross-over points in axial-viewing mode, and (5) similar spatially dependent matrix-interference behavior was observed in axial-viewing ICP-AES when an organic solvent (isopropanol) was used. It now appears that spatial emission profiles in ICP-AES (regardless of observation mode and the solvent) could lead to future expert systems for ICP–AES.

Characterized the temporal change in plasma characteristics during single droplet injection into an ICP: There is recent growing interest in introducing single aerosol droplets into the ICP for the analysis of individual entities (e.g., engineering nanoparticles and biological cells). The analysis of individual particles will provide new information (e.g., distribution of particle sizes and stoichiometry) that cannot be achieved by simple bulk analysis. Analyzing individual particles by ICP is challenging because of the strong dependence of signals on desolvation, vaporization and atomization processes caused by local cooling of the plasma by these physical events, and the lack of calibration standards. In this reporting period, we coupled a commercial monodisperse droplet generator with an ICP, and found that even a single droplet introduction is sufficient to perturb the plasma size (i.e., the so-called thermal pinch effect). Second, hydrogen (from dissociation of water) was found to diffuse throughout the load coil region of the plasma. Third, a droplet cools the plasma locally but the liberated hydrogen enhances the thermal conductivity of the plasma. As a result, excitation efficiency in the plasma, as indicated by an argon emission line, declines downstream from a vaporizing droplet but rises upstream. Fourth, changes in plasma impedance and RF coupling efficiency were also found during droplet introduction.

Elucidation of Species and Reaction Mechanisms Responsible for Analyte Desorption/Ionization in Plasma-based Ambient Ionization Sources: Plasma sources operated at atmospheric pressure, such as corona and glow discharges, have been used for over 30 years for molecular analyses through soft, chemical-ionization pathways. Recently, several plasma-based sources have been developed to perform direct desorption/ionization of analytes from complex matrices, resulting in a field termed Ambient Desorption/Ionization Mass Spectrometry (ADI-MS). These ionization sources often yield high desorption/ionization efficiencies and simple mass spectra, typically consisting of only the molecular ion or its protonated counterpart. Though numerous applications of these plasma-based sources have been explored, little work has been performed to fundamentally characterize and compare the discharges themselves and the different ionization pathways they utilize. Recently, we optically and mass-spectrometrically characterized two plasma-based ADI-MS sources: the flowing atmospheric-pressure afterglow (FAPA) and the low-temperature plasma (LTP) probe. Fundamental plasma parameters such as rotational temperature and electron number density were found to be substantially different between the two discharges. This finding was expected, as FAPA and LTP utilize vastly different discharges: a direct-current glow discharge and an alternating-current dielectric-barrier discharge, respectively. However, mass spectra obtained with both ionization sources for a variety of analytes were found to contain comparable fragments and reactive species, implying that the ionization pathways are quite similar. While many polar analytes produce spectra consisting only of protonated molecular ions, other analytes, such as polycyclic aromatic hydrocarbons and ionic liquids, yield spectra containing unexpected adduct and/or fragment ions as well as odd-electron species. These mass spectra were found to contrast with those obtained with a similar, commercial ionization source, Direct Analysis in Real Time (DART). This difference was attributed to a direct analyte-plasma interaction that occurs with FAPA and LTP analyses. These fundamental studies were used to improve the design of both ionization sources. Specifically, the FAPA was changed from a pin-to-plate configuration to a pin-to-capillary geometry, which reduced unwanted adduct formation as well as chemical background, yielding detection limits improved by at least two orders. The LTP source and its supporting electronics were redesigned into a small, handheld device for trigger-based, "point and shoot" sampling/ionization. When this source was coupled with a miniature mass spectrometer, the result was a truly portable, yet robust, instrument that is ideal for *in situ* analyses of a wide range of small molecules in their native environment with little or no sample pretreatment.

Science objectives for 2010-2012:

- Continue characterizing excitation and ionization processes and interference effects in the ICP, in both radial and axial viewing modes and with both aqueous and organic solvents.
- Examine thoroughly the mutual (droplet-plasma) influence that occurs when individual droplets of sample solution are introduced into an ICP
- Devise indicators, correction methodologies, and expert systems for interferences in ICPs.
- Continue characterization of FAPA and LTP sources. 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

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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, e.g., in ejection of streams of small charged drops from pointed tips of raindrops in thunderclouds, and technology, e.g., in electrospray mass spectrometry or electric field-driven solvent extraction. More recently, EHD cone-jetting has emerged as a powerful technique for direct printing of solar cells, micro- and nano-particle production, and microencapsulation for controlled release. In many of the afore-mentioned situations, of equal importance to the processes by which one drop disintegrates to form several drops are those by which (a) two drops come together and coalesce and (b) two drops are coupled to form a double droplet system (DDS) or a capillary switch (CS). The main objective of this research program is to advance through simulation, theory, and experiment the breakup, coalescence, and oscillatory dynamics of single and pairs of charged as well as uncharged drops.

Significant achievements in 2010-2012: One 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/nanoscopic jets that emanate from the conical tip structures. In this research, computation, theory, and experiment are being used in concert to investigate EHD tip streaming from liquid drops and films of finite conductivity. A main accomplishment of this work has been the demonstration by careful simulations that EHD tip streaming does not occur if the liquid is perfectly conducting or perfectly insulating, as had been assumed in almost all previous studies. Another major accomplishment has been the successful performance of the first set of simulations in which it has been possible to calculate not only the emitted tip streaming jets but also the drops that are shed from their tips. Through such calculations, we have been able to determine theoretically the sizes and charges carried by the emitted electrospray drops. We have already shown that contrary to conventional wisdom, there are multiple scaling laws governing drop size and charge. Two current challenges being tackled include the following. (1) First, as the conductivity of the liquid increases, the sizes of the emitted drops decrease. (2) Second, if the parent drops bear net charge, the emitted jets are longer than those in situations in which the parent drops are uncharged. Both of these issues exacerbate the multi-scale nature of the problem being tackled. Moreover, drop size and charge appear to follow different scaling laws when the parent drop is uncharged and when it is.

An important scientific question is the relationship between tip streaming in EHD and tip streaming in other physical problems. We had already investigated this relationship earlier in the case of dripping-jetting transitions when two liquids flow out of two concentric nozzles. We have recently discovered and have started studying a yet closer analog to EHD tip streaming than a two-liquid co-flow. This closer analog is referred to as the transition from selective withdrawal (SW) to viscous entrainment (VE). As in EHD tip streaming, the SW to VE transition is also replete with multiple scaling laws. We have already discovered that some of the heretofore theoretically predicted scaling laws may in fact be suspect.

Drop coalescence is central to diverse processes involving dispersions of drops in industrial and scientific realms. During coalescence, two drops first touch and then merge as the liquid neck connecting them grows from initially microscopic scales to a size comparable to the drop diameters (Fig. 1.). The curvature of the interface is infinite at the point where the drops first make contact, and the flows that ensue as the two drops coalesce are intimately coupled to this singularity in the dynamics. Conventionally, this process has been thought to have just two dynamical regimes: a viscous and an inertial regime with a crossover region between them. We have used experiments and simulations to reveal that a third regime, one that describes the initial dynamics of coalescence for all drop viscosities, has been missed. An argument based on force balance has led to the construction of a new coalescence phase diagram [1].

It is now well known that a pendant or a sessile drop that is subjected to an electric field elongates in the field direction and ultimately becomes unstable at a turning point in field strength. Upon loss of stability, an EHD tip streaming jet is emitted from the conical tips of such drops. What happens, however, if a pendant drop is connected to a sessile drop through a cylindrical hole in a plate from which a pendant drop hangs and a sessile drop protrudes? Quite recently, we have successfully began a systematic study of the equilibrium shapes and stability of such electrified double droplet systems (DDSs) or capillary switches (CSs) and the oscillatory responses of uncharged DDSs [2,3]. We are now poised to study the dynamics of electrified DDSs, including EHD tip streaming from their tips and how they may be used as liquid grabbers in applications in microfluidics and analytical chemistry.

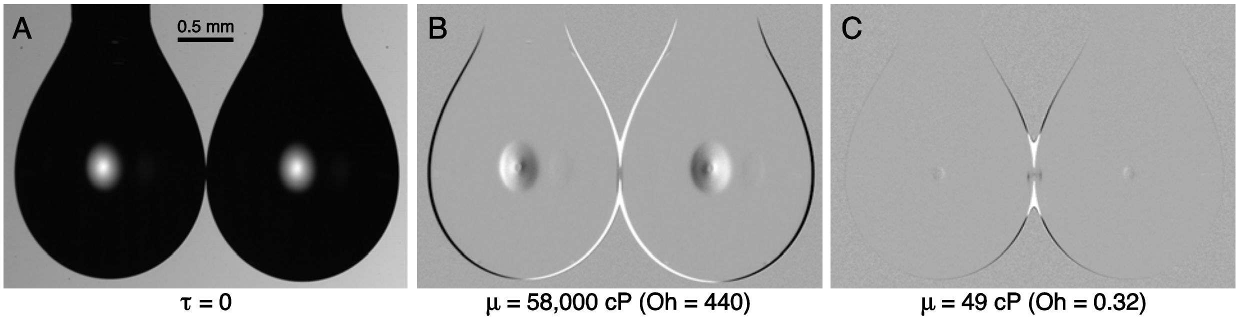

Figure 1. Coalescence of silicone oil drops with viscosities μ = 58,000 cP (Oh = 440) and 49 cP (Oh = 0.32). (A) Two pendant drops at the instant they contact, $\tau = 0$. (The two bright spots are from back-lighting.) We subtract an image taken after the neck has grown to a size $r_{min} = 0.25A$ from the one at $\tau = 0$ for (B), μ = 58,000 cP and (C), 49 cP. Here, A is the drop radius and Oh is the Ohnesorge number (ratio of viscous to inertial force). (From [1].)

Science objectives for 2012-2014:

- Elucidate differences in the physics of EHD tip streaming from uncharged drops subjected to an external electric field and charged drops bearing net charge.
- Analyze drop coalescence in another liquid and in the presence of an electric field.
- Investigate how electric fields can be used to activate and oscillate DDSs as liquid grabbers and adaptive liquid lenses.

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Session 8 – Surface Chemistry and Properties

Energetics of Nanomaterials

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Overall research goals: The objective of this research is to develop understanding and predictive systematics for the thermodynamic properties of nanomaterials and their anhydrous and hydrated surfaces and to apply such knowledge to systems of importance in energy technology.

Significant achievements in 2010-2012:

- Our major discovery has been the identification of strong size-induced shifts in oxidation-reduction potentials for transition metal oxides, suggesting a new thermodynamic landscape for the transition metal oxides and their hydrated layers at the nanoscale.
- We have advanced the development and understanding of our new metal oxide synthetic technique based on the solvent deficient mixing of metal salts with NH_4HCO_3. We have been able to produce a wide range of alumina and titania catalyst supports with varying pore structures and temperature stabilities as well as Fischer-Tropsch catalysts.
- We have continued studies of the behavior of water on various surfaces using INS techniques in combination with heat capacity measurements. Systems of interest include titania, SnO_2 (rutile), cobalt oxides, alumina and various iron oxides. INS spectra not only allow us to evaluate the heat capacity and vibrational entropy of the water confined on the surface of these nanoparticle systems, but also to determine the magnetic behavior of the Co- and Fe-oxides at low temperature.
- One of our major accomplishments was completing a detailed thermodynamic study of the TiO_2-SnO_2 system at the nanoscale. We have shown that SnO_2 (rutile) has a smaller surface energy and less exothermic integral enthalpy of adsorption of H_2O than TiO_2 (rutile) and other oxides. This may explain the superior behavior of SnO_2 as a gas sensor for organics in a humid atmosphere.
- We are completing thermodynamic studies of the CoO-ZnO-O_2 system at bulk and nanoscales, confirming large shifts in solid solubility in wurtzite and rocksalt $Co_xZn_{1-x}O$ phases and in the formation of the Co_3O_4-$ZnCo_2O_4$ spinel phases at the nanoscale.

Science objectives for 2012-2014:

- Can one find systematic trends in surface energy as a function of structure, composition, and oxidation state and use these to develop a useful and practical set of thermochemical parameters for nanomaterials to enable calculation of stability fields and redox equilibria at the nanoscale?
- What are the nanoscale controls on the synthesis, structure, and function of iron-based multi-component FT catalysts?
- How do surface and interfacial energies control the synthesis, porosity, and properties of alumina and titania based nanocermaics?

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Surface Chemistry Issues in the Development of Nonsulfide Flotation Technology

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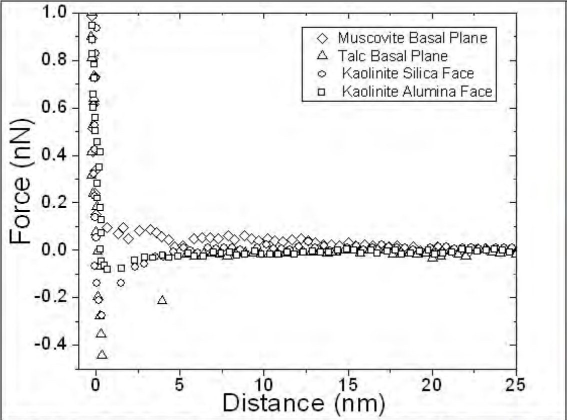
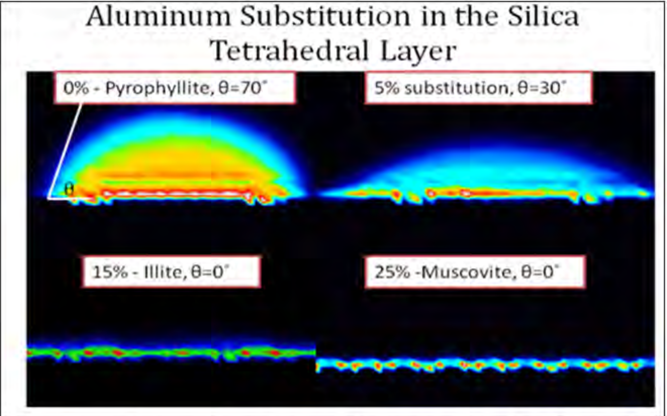
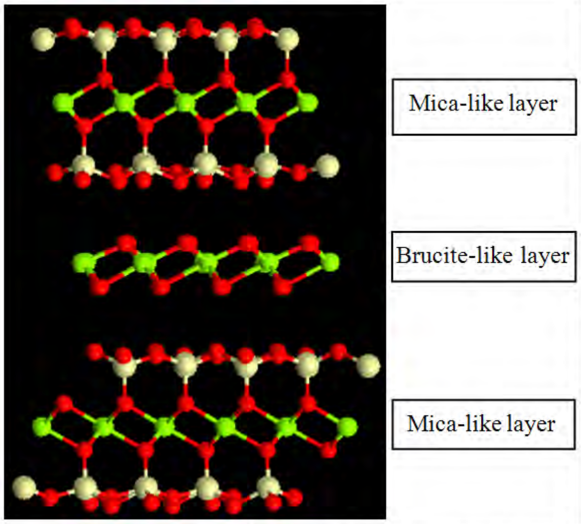
Overall research goals: The primary goal of this research program is to provide a basis for improved flotation separation efficiency in nonsulfide mineral systems by establishing the fundamental features of collector (surfactant) adsorption reactions associated with the hydrophobic surface state and developing appropriate surface chemistry control strategies.

Significant achievements in 2010-2012: Advanced surface chemistry research to support the development of nonsulfide flotation technology 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 at the surfaces of layered silicate minerals, soluble salt minerals, and semi-soluble salt minerals, including rare earth minerals.

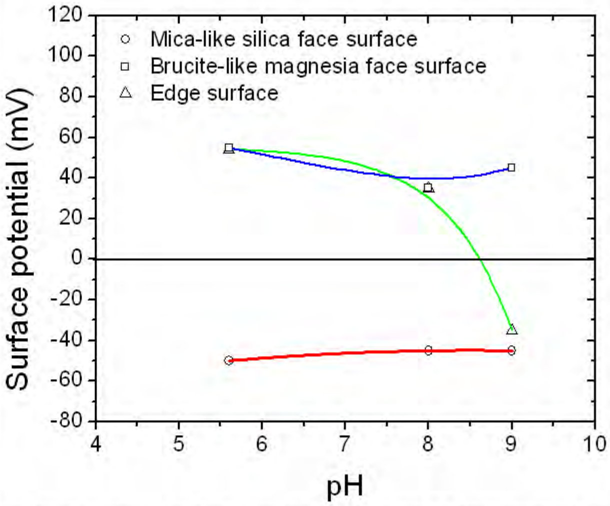
Research on the surface chemistry of layered silicate minerals continues, particularly focusing on the hydrophobicity of anisotropic surfaces and charging of the same. An AFM-based technique has been developed to describe the wettability of the two basal planes of kaolinite ($Al_2Si_2O_5(OH)_5$) particles with an average size of 500 nm. Interaction forces have been measured between a hydrophobic diamond-like-carbon (DLC) tip and the kaolinite surfaces as well as hydrophilic muscovite and hydrophobic talc surfaces at pH 4 which is the isoelectric point of the DLC tip. The results reveal that the kaolinite silica face has a moderate degree of hydrophobicty due to its low polarity and inability to hydrogen bond with water molecules. These results help to explain the behavior of kaolinite in flotation separations. In contrast, the kaolinite alumina face is hydrophilic, as it is terminated with a layer of hydroxyl groups which do hydrogen bond with water molecules. It is expected that the isomorphous lattice substitution is the primary explanation for charging at the silica tetrahedral surface of phyllosilicates and that such substitution significantly influences the surface hydrophobicity. In this regard, the effect of isomorphous substitution on the water contact angle has been investigated using the method of molecular dynamics simulation. It has been found that the water contact angle sharply decreases with even a small level of substitution in the silica tetrahedral layer.

	
AFM interaction forces measured between a hydrophobic tip and muscovite, talc and kaolinite silica face surfaces in 1mM KCl solution at pH 4.2.	The effect of isomorphous lattice substitution (0%, 5%, 15% and 25%) on the water contact angle studied using the two-dimensional water density analysis based on the MDS results.

In previous research, anisotropic surface charging of kaolinite was reported. Currently, the research has been extended to chlorite which is another type of layered silicate showing significant anisotropic surface properties. Chlorite is a 2:1 layered silicate with a general chemical formula of $(Mg_5Al)(AlSi_3)O_{10}(OH)_8$. Each repeating unit of chlorite has one magnesium hydroxide layer, known as the brucite-like layer and two mica-like layers. Cleavage occurs between the mica-like basal plane and the brucite-like basal plane creating a silica face surface and a magnesia face surface as well as an edge surface. By measuring the surface forces between a silicon nitride tip and the each of the three chlorite surfaces, the anisotropic surface charging characteristics of chlorite have been established. It has been noted that in the normal pH range, the chlorite mica-like basal plane surface is negatively charged, whereas the brucite-like basal plane surface is positively charged. The chlorite edge surface is pH-dependent with an IEP around pH 8.5.



Crystalline structure of chlorite, Green: magnesium; White: silicon; Red: oxygen.



Surface potentials for chlorite surfaces as a function of pH as determined by AFM

<u>Science Objectives for 2012-2014:</u> Future research is planned to understand and improve flotation separation efficiency using AFM, SFVS, MDS, as well as other traditional surface chemistry tools.

- Research will continue in the area of layered silicate minerals and be extended to examine the nature of surfactant/polymer adsorption at the different surfaces of these anisotropic particles and under what conditions the hydrophobic surface state is established.
- Research will continue to describe the interfacial chemistry of soluble salt flotation systems and develop fundamental understanding for the use of improved collectors for the complex carnallite and polyhalite resources in order to separate and recover potash values.
- Flotation chemistry studies with semi-soluble salt minerals are in progress to determine the interfacial water structure and collector adsorption state for fluorite and the rare earth fluoro carbonate mineral, bastnasite.
- The organization of collector (surfactant) molecules at mineral surfaces before and after bubble attachment will continue to be examined by SFVS.

<u>References to work supported by this project (2012-2014):</u> Selected recent publications include,

- V. Gupta, M.A. Hampton, J.R. Stokes, A.V. Nguyen, and J.D. Miller, “Particle Interactions in Kaolinite Suspensions and Corresponding Aggregate Structures,” J. Coll. Inter. Sci. 359 (1), 95-103 (2011).
- X. Yin and J.D. Miller, “Wettability of Kaolinite Basal Planes Based on Surface force Measurements Using Atomic Force Microscopy,” Min. Metall. Process., Special Industrial Minerals Issue, 29(1), 13-19 (2012).

In addition to 16 journal/proceedings publications, 16 presentations were made between 2010 and 2012.

Abstracts Not Presented

Ultrasonic Distillation, Thermal Diffusion and Photoacoustics

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Overall research goals: The research objectives for this project are to investigate ultrasonic distillation, especially with regard to a reported high efficiency for separation of ethanol and water, to investigate both theoretically and experimentally the Ludwig-Soret effect for a binary mixture in a linear temperature field, and to study the generation of a transient photoacoustic wave that is predicted by theory to exist whenever short pulse laser radiation is used to generate ultrasound.

Significant achievements in 2010-2012: Ultrasonic distillation refers to the separation of components of a mixture by an ultrasonic fountain that produces distillate in the form of mist and vapor. The distillate has a different composition from that in the remaining solution. We have carried out experiments to investigate ultrasonic distillation using three different analytical methods for determining the composition of the distillate. The results from ultrasonic distillation were compared with conventional sparging which refers to bubbling a gas through a mixture. The experiments carried out here contradict the reported perfect separation of ethanol from water and, as well, show that sparging is more efficient than ultrasonic distillation over a range of mole fractions of ethanol in water.

The Ludwig-Soret effect (also known as thermal diffusion) refers to the separation of mixtures in a thermal gradient. We have introduced a new experimental method for recording the Ludwig-Soret effect where a confocal microscope views a cell that is heated on one side and cooled on the other. Our method follows the entire concentration profile in space and time and determines thermal diffusion parameters by recording either the distribution in time, or the final distribution of components of a mixture in space. Using the Hopf-Cole transformation, we have found an exact solution to the nonlinear partial differential equation that describes the Ludwig-Soret effect. As the solution includes ordinary mass diffusion as well as thermal diffusion, data in experiments can be fitted to the solution to give Soret parameters such as the thermal diffusion factor.

Work has been carried out on solution to the problem of the photoacoustic effect in a structure whose compressibility or density varies sinusoidally in space. The photoacoustic effect in this case reduces to an inhomogeneous Mathieu equation which has received little attention in the mathematics literature. We give a general solution for arbitrary excitation of a periodic structure based on the use of new eigenfunction and orthogonality relations for the integer order Mathieu functions. We show that the solutions possess the space equivalent of subharmonic frequency generation, a property not previously investigated in periodic structures. The solution shows, as well, a qualitatively new feature of the photoacoustic effect, namely, that acoustic waves can be generated when the optical source is independent of the space coordinate. The manuscript notes that photoacoustic effect can be generated as easily within band gaps as outside of them. In addition we give a solution for the photoacoustic pressure for a source confined in space based on new traveling wave Mathieu functions. The paper gives the Floquet forms of these new functions inside and outside band gaps. Results of the calculations show a new "confinement" of photoacoustic waves in space when the waves are generated within band gaps, and an amplitude enhancement of the wave amplitudes at the edges of the gaps—irrespective of whether the excitation is within or outside the gaps. We have also extended our results to thermal waves in structures where the thermal diffusivity or specific heat capacity vary sinusoidally in space. The temperature in this case is described in terms of a complex Mathieu equation, which has seen no treatment in the literature. We show that solutions for the temperature can be obtained using our series expansion method.

In addition, we have carried out exploratory work on combining a grating with phase contrast X-ray imaging which we have shown to be sensitive to the granularity of particles, and which has the possibility of becoming an analytical method for determination of particulate properties using X-ray images. We have obtained data for several sized particle distributions and have formulated a theory for how the method works.

Science objectives for 2012-2014:

- The current thrust of the research is towards showing experimental evidence for the existence of fast transients on photoacoustic waveforms predicted by theory. The generation of sound through the conventional mechanism for producing the photoacoustic effect takes place through light absorption and heat deposition. The photoacoustic effect is governed by two differential equations where pressure and temperature are coupled. It has been shown that this coupling results in a wave equation for the pressure that includes a source term dependent on the space gradient of the temperature. Solutions to the wave equation show that the rapid diffusion of heat causes a fast pressure transient that has not as yet been reported, and which is fundamental to the understanding of the mechanism for producing the photoacoustic effect.

References to work supported by this project 2010-2012:

1. "The photoacoustic effect in a periodically modulated structure" Gerald J. Diebold, *Journal of Physics*, **214,** 012101 (2010)

2. "Comparison of ultrasonic distillation to sparging of liquid mixtures", Hye Yun Jung, Han Jung Park, Joseph M. Calo, and Gerald J. Diebold *Analytical Chemistry* **82**, 10090-4 (2010)

3. "Dynamics of thermal diffusion in a linear temperature field", Vitalyi Gusev, Binbin Wu, and Gerald J. Diebold *J. Appl. Phys*. 110, 044908 (2011)

4. "Ludwig-Soret Effect in a linear temperature field: Theory and experiments for steady state distributions", Hye Yun Jung, Vitalyi Gusev, Hyoungsu Baek, Yaqi Wang and Gerald J. Diebold, *Phys. Lett. A* **375**, 1917-1920 (2011)

5. Photothermal waves in a periodically modulated structure", Binbin Wu and Gerald J. Diebold, *Appl. Phys. B: Lasers and Optics* **105**, 619-622 (2011)

6. "Effects of exothermic chemical reaction on the photoacoustic effect from particulate suspensions", Han Jung Park, Binbin Wu, and Gerald J. Diebold, *J. Chem. Phys*. **134**, 124513 (2011)

7. "X-ray spatial harmonic imaging of phase objects", Yanan Liu, Brian Ahr, Alexander Linkin, Gerald Diebold, and Christoph Rose-Petruck, *Opt. Lett* **36**, 2209-2211 (2011)

8. "Photoacoustic effect in a sinusoidally modulated structure", Binbin Wu and Gerald J. Diebold, *Appl. Phys. Lett*. (in press)

9. "X-ray spatial frequency heterodyne imaging", Binbin Wu, Yanan Liu, Christoph Rose-Petruck, and Gerald J. Diebold, *Appl. Phys. Lett.* **100**, 061110/1-4 (2012)

Charge Transfer, Transport, and Reactivity in Complex Molecular Environments

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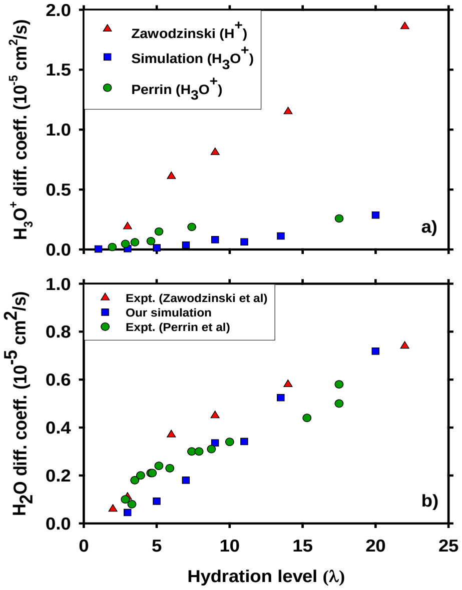
Overall research goals: The main research objective of this theory program is to apply modern theoretical and computational methods to advance our fundamental understanding of proton transfer, charge transport, and reactivity in complex molecular materials and environments relevant to energy technologies.

Significant achievements in 2010-2012: We achieved significant progress in the fundamental understanding needed for the design of membrane materials and disseminated these findings in highly-cited journal articles. Our earlier worked validated our molecular dynamics (MD) simulation strategy through excellent agreement between experiment and modeling of the water and hydronium vehicular diffusion and many other properties for models of Nafion (see Fig.1) even though Grotthuss diffusion is not captured by the model. We also applied percolation theory (see Fig. 2) to the characterization of the water network under varying hydration conditions and its percolation of a persistent network that facilitates proton conductivity. We examined a number of polymeric materials of experimental interest in the fuel cell community, such as Nafion-like polymers with altered acidic groups, from a sulfonic imide acid to an aromatic imide acid, and to phosphonic and phosphinic acids, as well as the non-perfluorinated phenylated sulfonated poly ether ether ketone ketone (Ph-SPEEKK). All Nafion-like materials were found to exhibit essentially similar vehicular proton conductivity as Nafion in accord with experimental data. Percolation theory showed that these polymers exhibit similar persistent water network as well, with a marked difference for Ph-SPEEKK that requires a much higher hydration level for percolation and proton conductivity.

Fig. 1 Diffusion coefficients of a) H_3O^+ ions and b) H_2O molecules



Simulations of Hyflon, a short-side chain (SSC) version of Nafion but with the same backbone, also showed similar vehicular proton conductivity. Our comparative study of short side chain and Nafion membranes show that a) the hydrophobic-hydrophilic separation in the two membranes is surprisingly similar; b) at all hydration levels, the longer side chain of Nafion is bent and is equivalent to a short side chain (see Fig. 3); and c) vehicular proton transport occurs mainly between SO_3^- groups. We have also characterized the morphology and the transport of water, methanol and hydronium in Ph-SPEEKK and Nafion membranes at 360 K for a range of hydration levels using MD simulations. In Ph-SPEEKK, the average pore diameter is smaller, the sulfonate groups are more closely packed, the H_3O^+ ions are more strongly bound to SO_3^- groups, and the methanol crossover is reduced relative to the corresponding properties in Nafion. This work demonstrates the potential of aromatic membranes as low-cost challengers to Nafion for direct methanol fuel cell applications.

Science objectives for 2012:

- We will continue and complete our *ab initio* molecular dynamics (AIMD) simulations of proton transport in models of Nafion and Hyflon membranes at elevated temperature. We will decompose proton hopping into vehicular and structural components and will benchmark our results against AIMD results for proton hopping in bulk water. AIMD simulations for about 1 ns are needed to examine the validity of recent empirical valence bond simulations in the literature that show an excessively high vehicular diffusion coefficient for the hydrated proton.

- We will continue to characterize the nanostructure, water clustering, vehicular proton transport, and methanol diffusion in novel membranes that will be evaluated as alternatives to Nafion for direct methanol fuel cells operating close to 100 ºC.
- We will perform AIMD simulations of the ionic liquid diethyl methyl amine and triflic acid to study proton transfer barriers as a function of selected reaction coordinates, such as the distance between proton donor and acceptor.

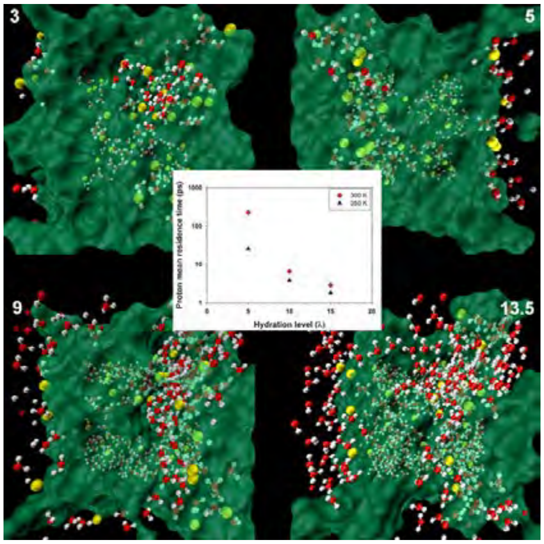


Fig. 2 Percolation and proton conductivity in Nafion for the hydration levels shown (3, 5, 9 and 13.5).

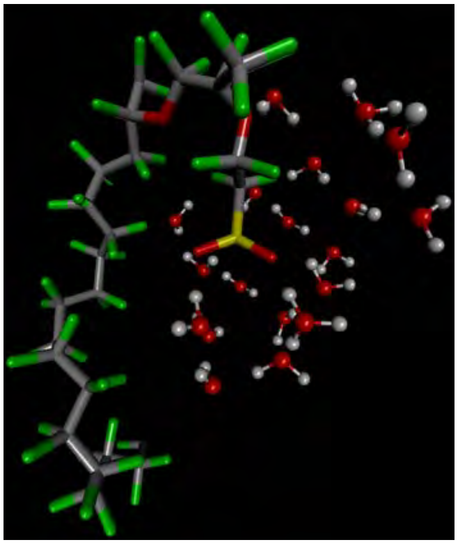


Fig. 3. The side chain of Nafion is bent, which makes it equivalent to a short side chain.

<u>References to work supported by this project 2010-2012:</u>

1. R. Devanathan, A. Venkatnathan, R. J. Rousseau, M. Dupuis, T. Frigato, W. Gu, and V. H. Helms, “Atomistic Simulation of Water Percolation and Proton Hopping in Nafion Fuel Cell Membrane,” Journal of Physical Chemistry B **114**, 13681-13690 (2010). **Cover article**.
2. R. Devanathan, “Proton Exchange Membranes for Fuel Cells,” In Energy Production and Storage - Inorganic Chemical Strategies for a Warming World (Ed. Robert H. Crabtree) pp 89-100. ISBN: 978-0-470-74986-9, Wiley, (2010).
3. T. M. Chang, L. X. Dang, R. Devanathan, and M. Dupuis, “Structure and Dynamics of N,N-Diethyl-N-Methylammonium Triflate Ionic Liquid, Neat and with Water, from Molecular Dynamics Simulations,” Journal of Physical Chemistry A **114**, 12764-12774 (2010).
4. R. D. Lins, R. Devanathan, and M. Dupuis, “Modeling the Nanophase Structural Dynamics of Phenylated Sulfonated Poly Ether Ether Ketone Ketone (Ph-SPEEKK) Membranes as a Function of Hydration,” Journal of Physical Chemistry B **115**, 1817-1824 (2011).
5. N. Idupulapati, R. Devanathan, and M. Dupuis, “Atomistic Simulation of Perfluoro Phosphonic And Phosphinic Acid Membranes and Comparisons to Nafion,” Journal of Physical Chemistry B **115**, 2959-2969 (2011).
6. N. Idupulapati, R. Devanathan, and M. Dupuis, “Molecular Structure and Transport Dynamics in Perfluoro Sulfonyl Imide Membranes,” Journal of Physics: Condensed Matter **23**, 234106 (2011).
7. J. K. Clark, II, S. J. Paddison, M. Eikerling, M. Dupuis, and T. A. Zawodzinski, Jr., “A Comparative Ab Initio Study of the Primary Hydration and Proton Dissociation of Various Imide and Sulfonic Acid Ionomers,” Journal of Physical Chemistry A **116 (7),** 1801–1813 (2012).

Analysis of Hydrocarbons and Lipids in Microalgae by Two-Dimensional HPLC

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Overall research goals: The research objectives are to identify a maximum number of the metabolites involved in the synthesis of hydrocarbons and lipids by *Botryococcus Braunii*, a microalga the dry weight of which contains 40 to 50% of saturated hydrocarbons related to triterpenes, to investigate the main parameters affecting its rate of growth and the composition of its products, and to elucidate unravel the important chemical pathways of these reactions. 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 2010-2012: We made cultures of the *Botryococcus Braunii* unicellular alga under a variety of different environmental conditions, extracted the non-polar components of their dry mass, and investigated a number of different combinations of HPLC separations in order to develop an effective two-dimensional liquid chromatography process [1,2]. The project consists in applying to the separation and identification of the metabolites of microalgae, particularly those involved in the synthesis of hydrocarbons and lipids, the same analytical method as used earlier for the separation of protein digests. For this purpose, we need to develop several techniques, including (1) a method of production of sufficient amounts of the selected microalga; (2) an analytical procedure for the recovery of cells from the filtrates of culture solutions, for the lyzing these cells, and for the extraction of the non-polar compounds from the lyzates; (3) an analytical procedure for the separation of these extracted compounds by two-dimensional chromatography (2D-LC); (4) suitable methods for the detection, identification, and quantitation of these chemicals.

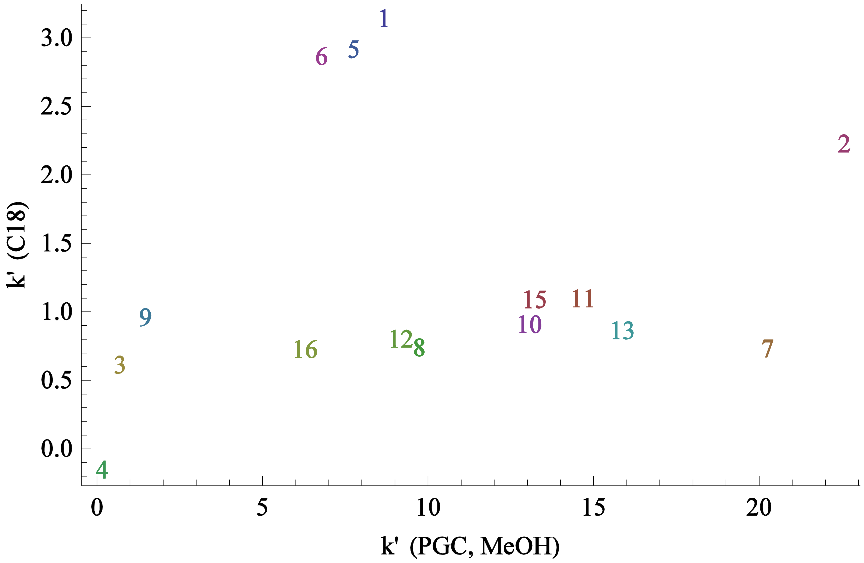

Figure 1. Plot of the retention factors of compounds eluted from one column versus their retention factors on the second column. Compounds 1, 2, 3, 5, 6, 9 are hydrocarbons. The other ones are polar compounds.

Although significant progresses were made toward the solution of these sets of problems, the coordination of their solutions has just begun. (1) We selected *Botryococcus Braunii* because it has 30 to 40% of its weight in hydrocarbons, mostly the branched or cyclic alkenes botryococcenes that have 27 to 36 carbon atoms and 5 to 6 double bonds [2]. (2) We learned how to cultivate algae

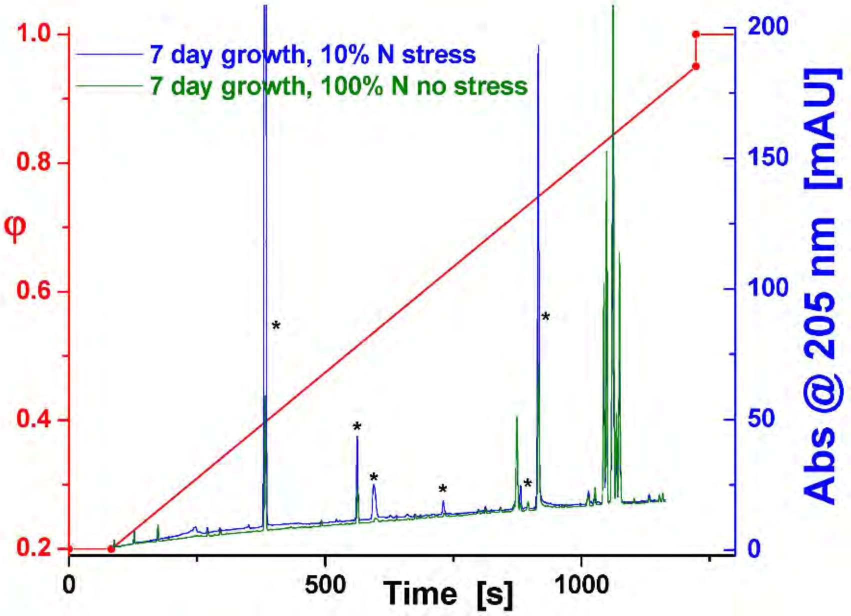

Figure 2. Chromatograms of the extracts from cultures in solutions of different concentrations in nitrogen fertilizer (KNO_3).

colonies, selected the culture medium and conditions. The rate of growth of the colonies is followed by measuring their fluorescence under UV irradiation. We found that these microalgae grow more slowly that we had anticipated. In spite of significant support by colleagues in the UT Department of Microbiology, we have so far been able to obtain only limited amounts of dry cell material [2]. The addition of trace elements enhances the production of algae; the lack of nitrogen inhibits it markedly and so does the use of acidic growth medium, but to moderate degree. Further work is continuing on the growth of algae under different conditions. (3) After a colony of alga has grown for seven days, it is centrifuged to separate algae and medium. The supernatant is removed; the cells are collected and lysed in a mixture of chloroform and methanol. The whole mixture is separated in a water and a chloroform solutions, the containing the hydrocarbons and other weakly polar compounds [2]. (4) We are developing and testing a comprehensive off-line 2D-LC procedure [2] for the qualitative and quantitative analysis of the lipids and related components extracted from these algae. The procedure involves the successive use of two reversed-phase separations. Several approaches are considered [3-5]. In the most attractive [3,4], the columns are packed with C_{18}–bonded silica particles and with carbon particles, both eluted with methanol. Another procedure involves supercritical fluid chromatography in the second dimension [5]. Detection is carried out by selective reaction monitoring (SRM) in mass spectrometry. The fractions eluting from the first column are successively analyzed on the second column. Sensitivity is limited by the large dilution due to the very principle of liquid chromatography, which explains why SRM must be used and why full-scan mass spectrometry detection cannot be used for identification purposes.

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3. P. G. Stevenson and G. Guiochon, “Retention divergence of terpenes on porous graphitized carbon black and C stationary phases,” J. Chromatogr. A, Submitted.
4. P. G. Stevenson, J. N. Fairchild, G. Guiochon, “Retention mechanism divergence for high performance liquid chromatography,” J. Chromatogr. A, **1218**, 1822-1827 (2011).
5. P. G. Stevenson, A. Tarafder, G. Guiochon, “Comprehensive two-dimensional chromatography with coupling of reversed phase high performance liquid chromatography and supercritical fluid chromatography,” J. Chromatogr. A, **1220**, 175-178 (2012).

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