2014 DOE Separations and Analysis Research Meeting

Marriot, Washingtonian Center
Gaithersburg, MD
April 27 - 29, 2014

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

Principal Investigators' Meeting

Marriot, Washingtonian Center
Gaithersburg, MD
April 27 - 29, 2014

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

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Cover Graphics:
The cover displays a sampling of journal cover artwork that Principle Investigators in the BES Separations and Analysis Research Program have published in association with journal papers supported by the Program. The geometrical arrangement of citations below parallels that on the preceding cover. Note that at the bottom of each citation one can find the page number in this book of the relevant abstract.

X. Zhu; P. C. Hillesheim; S. M. Mahurin; C. M. Wang; C. C. Tian; S. Brown; H. M. Luo; G. M. Veith; K. S. Han; E. W. Hagaman; H. L. Liu; S. Dai, "Efficient CO_2 Capture by Porous, Nitrogen-Doped Carbonaceous Adsorbents Derived from Task-Specific Ionic Liquids," ChemSusChem 5, 1912-1917 (2012).
See abstract page 47.

C.E. Wilmer, M. Leaf, C. Y. Lee, O.K. Farha, B.G. Hauser, J.T. Hupp, R.Q. Snurr, "Large-scale screening of hypothetical metal-organic frameworks," Nature Chem. 4, 83-89 (2012).
See abstracts pages 31, 61.

K.-H. Tran-Ba, J. J. Finley, D. A. Higgins, T. Ito "Single Molecule Tracking Studies of Millimeter-Scale Cylindrical Domain Alignment in Polystyrene–Poly(ethylene oxide) Diblock Copolymer Films Induced by Solvent Vapor Penetration", J. Phys. Chem. Lett. 3, 1968-1973 (2012).
See abstract page 41.

"Laser Ablation in Analytical Chemistry:" Russo, Richard E.; Mao, Xianglei; Gonzalez, Jhanis J.; et al. ANALYTICAL CHEMISTRY Volume: 85 Issue: 13 Pages: 6162-6177: 2013
See abstract page 3.

McDaniel, J. G.; Schmidt, J. R., "Physically-Motivated Force Fields from Symmetry-Adapted Perturbation Theory." J. Phys. Chem. A 2013, 117, 2053-2066.
See abstract page 13.

Y. B. Zheng, B. K. Pathem, J. N. Hohman, J. C. Thomas, M. H. Kim, and P. S. Weiss, "Photoresponsive Molecules in Well-Defined Nanoscale Environments," Advanced Materials 25, 302-312 (2013).
See abstract page 1.

Foreword

This abstract booklet provides a record of the U.S. Department of Energy biennial contractors' meeting in separations and analysis science. This year the meeting is co-chaired by Dr. De-en Jiang (Oak Ridge National Laboratory) and Professor Graham Cooks (Purdue University). This meeting is sponsored by the Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences and includes invited presentations from the Nanoporous Materials Genome Center and the Center for Gas Separations to Clean Energy Technologies. The latter is an Energy Frontier Research Center. Other related research funded in the BES Computational and Theoretical Chemistry Program is also represented.

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 De-en Jiang and Graham Cooks 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 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 R. Pederson

Agenda

2014 Separations and Analysis Research Meeting

Marriot, Washingtonian Center, Gaithersburg, MD, April 27 - 29, 2014
De-en Jiang, Graham Cooks, Meeting Co-chairs

Sunday, April 27 2012

10:00 a.m.–1:00 p.m. **Registration**

1:00 – 1:20 p.m. Welcome – Larry Rahn, Mark Pederson, De-en Jiang, Graham Cooks

Session 1 – Imaging Analysis – Alla Zelenyuk, Chair

1:20 – 1:45 Professor Paul S. Weiss – Subnanometer Spatial Resolution Chemical Imaging
1:45 – 2:10 Dr. Richard E. Russo – Laser Ablation Molecular Isotopic Spectroscopy (LAMIS)
2:10 – 2:35 Dr. Ning Fang – Chemical Analysis of Nanodomains: Optical Imaging Platforms for Visualizing Nanoparticles
2:35 – 3:00 Dr. Olga Ovchinnikova – Multimodal Chemical and Physical Imaging and Characterization of Surfaces using a Combined AFM-MS Platform

3:00 – 3:30 **Break**

Session 2 – Computation of Porous Materials – Joe Hupp, Chair

3:30 – 4:20 **Invited** – Professor Laura Gagliardi – The Nanoporous Materials Genome
4:20 – 4:45 Professor J. R. Schmidt – Transferable physically-motived force fields for nano-porous materials and beyond
4:45 – 5:10 Professor Francesco Paesani – Theoretical Studies of Spin-Crossover Metal-Organic Frameworks
5:10 – 5:35 Professor James Lewis – Light-Matter Interactions in Azo-Functional Porous Coordinated Polymers

5:35 – 6:00 **Break**

6:00 – 7:00 **Dinner**

Session 3 – Information from DOE

7:00 – 7:20 John Miller – DOE Update

Poster Session 1

7:20 – 9:30 p.m. Poster Session 1 – (no-host at bar)

P1-1 Professor Michael D. Barnes – Chemical Microscopy of Conjugated Nanomaterials
P1-3 Dr. Thomas Magnera – Imaging of Conformational Changes
P1-5 Dr. Alla Zelenyuk – Chemistry and Microphysics of Small Particles
P1-7 Dr. Vilmos Kertesz – Chemical Imaging with Mass Spectrometry Utilizing Liquid Extraction and Laser Ablation Liquid Capture-Based Surface Sampling/Ionization Strategies

Sunday April 27 (Cont’d)

P1-9	Professor Maciej Haranczyk – Knowledge-Guided Screening Tools for Identification of Porous Materials for CO_2 Separation
P1-11	Professor Jan D. Miller – Surface Chemistry Aspects of Bastnaesite ($Ce,LaFCO_3$) Flotation With Octyl Hydroxamate
P1-13	Professor Benny D. Freeman – Fundamental Structure/Property Studies of Gas Separation Membrane Polymers
P1-15	Professor Randall Snurr – Coordination-Chemistry-Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities: Modeling
P1-17	Professor Brian Woodfield – Energetics of Nanomaterials
P1-19	Professor Gregory A. Voth – Computer Simulation of Proton Transport in Fuel Cell Membranes
P1-21	Professor William Koros – Precisely Tunable High Performance Carbon Molecular Sieve Membranes for Energy Intensive Separations
P1-23	Dr. De-en Jiang – Understanding Porous Graphene and Ionic Liquids for Gas Separation by Simulation
P1-25	Dr. Shannon Mahurin – Fundamental Interactions in Porous Carbon and Ionic Liquids for Gas Separations

Monday April 28

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

Session 4 – Characterization of Separation Media – Randy Snurr, Chair

8:00 – 8:50	a.m.	**Invited** – Dr. Wendy Queen – Understanding the structure-derived function of porous adsorbents relevant to energetically favorable industrial gas separations
8:50 – 9:15		Professor Takashi Ito – Molecular-Level Investigation of Diffusion Behaviors within Cylindrical Nanoscale Pores
9:15 – 9:40		Professor Paul W. Bohn – Molecular Aspects of Transport in Thin Films of Controlled Architecture
9:40 – 10:05		Professor Richard M. Crooks – Separations and Analysis using Bipolar Electrodes
10:05 – 10:35		**Break**

Session 5 – Novel Membrane Separations – Benny Freeman, Chair

10:35 – 11:00	a.m.	Dr. Sheng Dai – Controlling Porosities and Functionalities in Novel Separation Media
11:00 – 11:25		Professor Rohit Karnik – Graphene Membranes with Tunable Nanometer-Scale Pores
11:25 – 11:50		Professor Ruilan Guo – Design, Synthesis and Characterization of Triptycene-Containing Macromolecules with Hierarchically Controlled Architectures as Functional Membrane Materials for Energy Applications
11:50 – 12:15		Professor Stephen E. Creager – Fluoropolymers, Electrolytes, Composites and Electrodes
12:15 – 1:00	p.m.	**Working Lunch**
1:00 – 4:00		**Interaction Time** - Put up posters for Poster Sessions

Monday April 28 (Cont'd)

Poster Session 2

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

P2-2	Dr. Emily Smith – Chemical Analysis of Nanodomains: Diffraction-limited and Subdiffraction Spatial Resolution Imaging
P2-4	Dr. Benjamin Doughty – Probing Materials and Interfaces with Nonlinear Optical Spectroscopy and Microscopy
P2-6	Professor Nicholas Winograd – Strong Field Molecular Photoionization in the mid-IR: Implications for submicron molecule-specific imaging with mass spectrometry
P2-8	Dr. Gary Van Berkel – Towards Nanoscale Multimodal Imaging by Combining Atomic Force Microscopy, Optical Spectroscopy and Atmospheric Pressure Surface Sampling/Ionization Mass spectrometry
P2-10	Professor Gary M. Hieftje – Fundamental Studies in Plasma Sources for Elemental and Molecular Analysis
P2-12	Professor Basil Nikolau – Mass Spectrometric Imaging of Plant Metabolites
P2-14	Dr. Grant E. Johnson – Investigating the Properties of Supported Metal Particles Prepared Using Soft Landing of Mass-Selected Ions
P2-16	Professor Joseph T. Hupp – Coordination-Chemistry–Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities
P2-18	Professor R. Graham Cooks – Preparation of Chemically Functionalized Surfaces through Ion Soft Landing and Ion/surface Reactions under Vacuum and in the Ambient Environment
P2-20	Dr. Andrew Stack – Aqueous Ion Solvation Structure and Ion Pairing: Integrated Neutron Diffraction and Molecular Dynamics
P2-22	Professor Georges Belfort – Development of Anti-Fouling Membranes via Combinatorial Chemistry and a Novel High Throughput System
P2-24	Professor Steven L. Regen – Hyperthin Membranes for Gas Separations
P2-26	Professor Merlin Bruening – Electrically Driven Ion Separations in Permeable Membranes

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

Tuesday April 29

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

Session 6 – MS Fundamentals and Imaging – Gary Van Berkel, Chair

8:00 – 8:25	Dr. Julia Laskin – Ion-Surface Interactions in Mass Spectrometry
8:25 – 8:50	Professor David H. Russell – Cryogenic Ion Mobility-Mass Spectrometry (IM-MS): Probing the Structure of Ionic Water Clusters and Hydrated Cluster Ions of Hydrophilic Molecules
8:50 – 9:15	Professor Scott A. McLuckey – The Dynamics and Thermodynamics of Gaseous Macro-ions
9:15 – 9:40	Dr. Young-Jin Lee – Mass Spectrometric Imaging of Plant Metabolites
9:40 – 10:05	Professor Akos Vertes – New Approaches for Metabolomics by Mass Spectrometry
10:05 – 10:30	**Break**

Tuesday April 29 (Cont’d)

Session 7 – Characterization and Analytical Methods – Mike Barnes, Chair

10:30	–	10:55	a.m.	Professor Daniel K. Schwartz – Mapping Surface Functionality and Reactivity Using Single Molecule Probes
10:55	–	11:20		Professor Joel Harris – Imaging of Interfacial Chemistry within Porous Particles
11:20	–	11:45		Dr. Yingzhong Ma – Ultrafast Electronic Excited-State Dynamics in Selected Nanostructures and Polymer Materials
11: 45	–	12:10		Professor Gerald J. Diebold – Optical Mass Spectrometer and Photoacoustics

12:10	–	1:10	p.m.	**Working Lunch**

Session 8 – Close-out Session – Dr. De-en Jiang, Prof. Graham Cooks, Chairs

1:10	–	3:00	p.m.	Presentation of program area summaries and discussion
3:00	–	3:15		Larry Rahn, Notes from Program Manager
3:15		4:00		Open Discussion and take down posters

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Session 2 – Computation of Porous Materials

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Session 7 – Characterization and Analytical Methods

Abstracts Not Presented

Subnanometer Spatial Resolution Chemical Imaging

Paul S. Weiss, Principal Investigator
California NanoSystems Institute (CNSI) and Departments of Chemistry & Biochemistry and Materials Science & Engineering, University of California, Los Angeles, Los Angeles, CA 90095
Email: psw@cnsi.ucla.edu; Web: www.nano.ucla.edu

Collaborators: Prof. Ken Houk, UCLA, Los Angeles, CA
Prof. Tony Huang, Penn State, University Park, PA
Prof. Alex Jen, University of Washington, Seattle, WA
Prof. Lasse Jensen, Penn State, University Park, PA
Dr. Hong Ma, University of Washington, Seattle, WA
Dr. Mogens Nielsen, Copenhagen University, Copenhagen, Denmark

Overall research goals: We develop submolecular-resolution spectroscopic imaging in the visible, near-visible, and vibrational infrared ranges. These scanning tunneling microscopes (STMs) are used for chemical imaging in order to measure structure, function, and spectroscopy simultaneously. By combining these measurements we will develop enabling tools to elucidate the nanoscale rules of function at the ultimate limits of miniaturization.

Significant achievements in 2012-2014: We have constructed two photon-coupled scanning tunneling microscopes (STMs), one for use in the visible (and near-visible) region and the other for use in the infrared (IR). These instruments are designed to measure: 1) optical spectra, photoconductivity, and photoreactions of single molecules and assemblies in well-defined environments, and 2) vibrational spectra of single and even parts of single molecules.

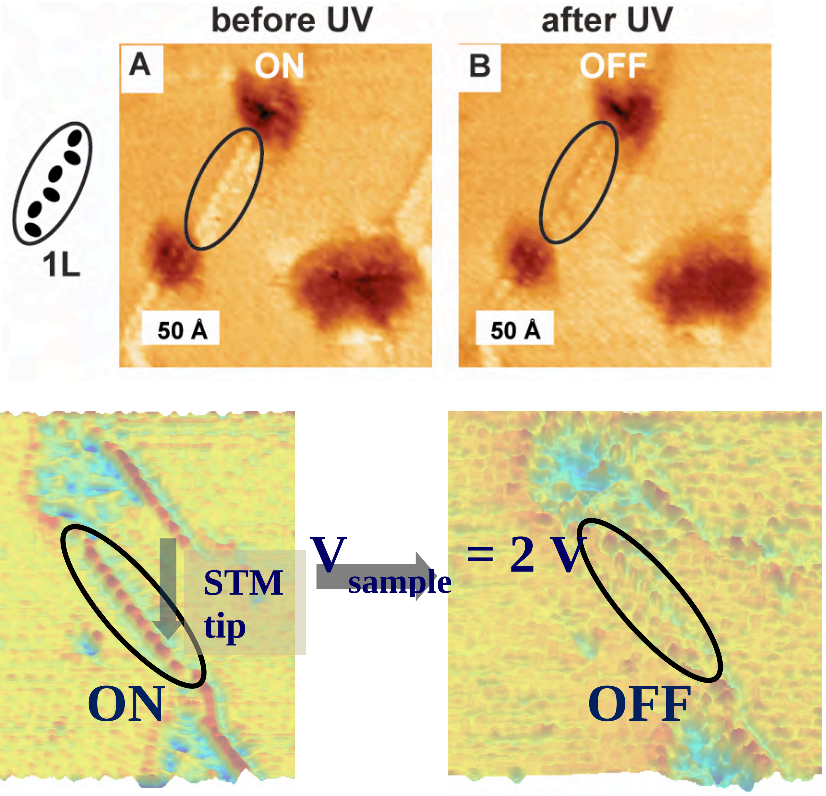


Figure 1. Cooperative motion of one-molecule-wide chains of azobenzene-functionalized molecules is induced by photoexcitation (top) and electrons from the STM probe tip (bottom).

We have developed nanohole array substrates in which the pitch of holes determines the resonant energy of the surface plasmons, giving us sufficient enhancements to measure the Raman spectra of a fraction of a percent of a monolayer chromophores and thus to follow their photoreaction/isomerization. The flatness of the substrate is sufficient that we can use the STM between the holes to confirm assembly and isolation conditions with molecular resolution.

We have induced (the first recorded) cooperative motion in precisely assembled one-molecule-wide lines of azobenzene-functionalized molecules. This motion has been induced both with ultraviolet (UV) photons in "broadcast" mode and locally with electrons of substantially lower energy, supplied by the STM probe tip (Figure 1).

Science objectives for 2014-2016:

- Develop the methodology to measure the photoconductance and excited state electronic spectra of individual molecules and assemblies in well-defined environments using the evansescently coupled UV-visible scanning tunneling microscope (STM).
- Determine if there are near-field antenna effects in the evanescently coupled UV-visible STM analogous to those found in apertureless near-field scanning optical microscopy.
- Use the photoconductance measurements to optimize molecular design within families of chromophore structures to optimize absorption and charge separation.
- Use plasmonic nanohole array substrates to in the UV-visible STM to enhance absorption and the measurements described above.
- Demonstrate infrared absorption spectroscopic imaging using the analogous IR STM.

References to work supported by this project 2012-2014:

1. S. Tarr and P. S. Weiss, "Very Small Horses: Visualizing Motion at the Nanoscale," Leonardo **45**, 439-445 (2012).
2. Y. B. Zheng, B. Kiraly, P. S. Weiss, and P. S. Weiss, "Molecular Plasmonics for Biology and Nanomedicine," Nanomedicine **7**, 751-770 (2012).
3. Y. B. Zheng, B. K. Pathem, J. N. Hohman, J. C. Thomas, M. H. Kim, and P. S. Weiss, "Photoresponsive Molecules in Well-Defined Nanoscale Environments," Advanced Materials **25**, 302-312 (2013).
4. S. A. Claridge, W.-S. Liao, J. C. Thomas, Y. Zhao, H. Cao, S. Cheunkar, A. C. Serino, A. M. Andrews, and P. S. Weiss, "From the Bottom Up: Dimensional Control and Characterization in Molecular Monolayers," Chemical Society Reviews **42**, 2725-2745 (2013).
5. B. K. Pathem, Y. B. Zheng, S. Morton, M. A. Petersen, C.-H. Chung, Y. Yang, L. Jensen, M. B. Nielsen, and P. S. Weiss, "Photoreaction of Matrix-Isolated Dihydroazulene-Functionalized Molecules on Au{111}," Nano Letters **13**, 337-343 (2013).

Laser Ablation Molecular Isotopic Spectroscopy (LAMIS)

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

Overall research goals: The goals of this research are to elucidate fundamental mechanisms underlying laser ablation processes as they relate to chemical analysis, with current emphasis on understanding molecular formation and emission in laser plasmas as a new technology for measuring isotope ratios at atmospheric pressure (mass spectrometry without a mass spectrometer).

Significant achievements in 2011-2013: This BES supported program is world recognized for research to understand and utilize laser ablation for rapid chemical imaging and analysis. Our effort addressed near-field ablation for nanometer scale spatial resolution, simultaneous use of laser plasma emission with mass spectrometry, and the discovery of a new technology for the measurement of isotopes in the laser plasma. During the laser ablation process, species within the plasma undergo chemical reactions with each other and with the ambient environment that result in the formation of molecules, especially oxides or nitrides. How these molecules are formed, including the role of pressure, temperature, and ion and electron number densities in the chemical reaction, remains an open question. Our research endeavours to understand and use molecular species emission in these laser plasmas as molecular emission provides significantly enhanced isotope splitting compared to atomic and ionic emission lines. The ability to measure large isotope shifts at atmospheric pressure opens capabilities for 'mass spectroscopy without a mass spectrometer.' The new technology has been named LAMIS for Laser Ablation Molecular Isotopic Spectroscopy. LAMIS won a 2012 R&D100 award and was voted as best paper of the year by Spectrochimica Acta. Russo received the 2013 Strock Award from the Society of Applied Spectroscopy based on the LAMIS.

We utilized LAMIS to study several isotopic systems; only one example for carbon is presented here. The temporal and spatial distribution of CN and C_2 from laser ablation of carbon isotopic samples is an ideal case to study laser plasma chemistry. Temporal and spatial resolved measurements of $^{12}C_2$, $^{12}C^{13}C$, and $^{13}C_2$ show that C_2 forms from recombination reactions in the plasma. The ratio of $^{12}C/^{13}C$ varies with time after the laser pulse and with distance above the sample; $^{12}C/^{13}C$ deviates from the nominal ratio at early times and closest to the sample surface. Figure 1 shows plasma emission for atomic and molecular carbon. The C_2 molecular band exhibits large isotopic splitting compared to the small shift for the atomic emission of ^{12}C and ^{13}C, which could not be resolved using the spectrometer with 0.02 nm (Figure 1).

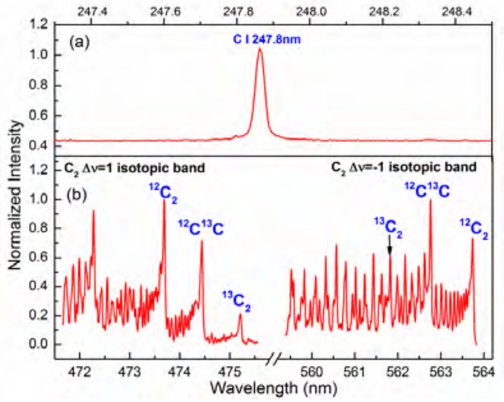


Figure 1. Emission spectra of (a) atomic carbon (b) molecular isotopic bands during laser ablation of carbon sample. Simultaneous measure of atomic and molecular spectra allows isotope ratio analysis and study of plasma chemistry.

Science objectives for 2014-2016:

- Develop understanding and utilization of molecular emission in atmospheric pressure laser plasmas for isotopic analysis
- Experimental and theoretical understanding of laser ablation to advance chemical imaging and analysis
- Extend laser-based chemical analysis to the nanoscale utilizing near-field laser optical principles.
- Study secondary excitation processes for mass removal < 10^8 atoms.

Selected references to work supported by this project 2011-2013:

1. Multiple emission line analysis for improved isotopic determination of uranium - a computer simulation study: Chan, George C-Y.; Mao, Xianglei; Choi, Inhee; et al. SPECTROCHIMICA ACTA PART B-ATOMIC SPECTROSCOPY Volume: 89 Pages: 40-49: 2013
2. Laser ablation molecular isotopic spectrometry of water for D-1(2)/H-1(1) ratio analysis: Sarkar, Arnab; Mao, Xianglei; Chan, George C. -Y.; et al. SPECTROCHIMICA ACTA PART B-ATOMIC SPECTROSCOPY Volume: 88 Pages: 46-53: 2013
3. Applications of laser-induced breakdown spectroscopy for geochemical and environmental analysis: A comprehensive review: Harmon, Russell S.; Russo, Richard E.; Hark, Richard R. SPECTROCHIMICA ACTA PART B-ATOMIC SPECTROSCOPY Volume: 87 Pages: 11-26: 2013
4. Laser Ablation in Analytical Chemistry: Russo, Richard E.; Mao, Xianglei; Gonzalez, Jhanis J.; et al. ANALYTICAL CHEMISTRY Volume: 85 Issue: 13 Pages: 6162-6177: 2013
5. Determination of Vanadium/Nickel Proportionality in the Asphaltene Fraction of Crude Oil Using Thin-Layer Chromatography with Femtosecond Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry: Chirinos, Jose; Oropeza, Dayana; Gonzalez, Jhanis; et al. ENERGY & FUELS Volume: 27 Issue: 5 Pages: 2431-2436: 2013
6. Carbon Isotope Separation and Molecular Formation in Laser-Induced Plasmas by Laser Ablation Molecular Isotopic Spectrometry: Dong, Meirong; Mao, Xianglei; Gonzalez, Jhanis J.; et al. ANALYTICAL CHEMISTRY Volume: 85 Issue: 5 Pages: 2899-2906: 2013
7. UV fs-ns double-pulse laser induced breakdown spectroscopy for high spatial resolution chemical analysis: Lu, Yuan; Zorba, Vassilia; Mao, Xianglei; et al. JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY Volume: 28 Issue: 5 Pages: 743-748: 2013
8. Femtosecond Versus Nanosecond Laser Pulse Duration for Laser Ablation Chemical Analysis: Russo, R. E.; Mao, Xianglei; Gonzalez, Jhanis L.; et al. SPECTROSCOPY Volume: 28 Pages: 24: 2013
9. Liquid sampling-atmospheric pressure glow discharge optical emission spectroscopy detection of laser ablation produced particles: A feasibility study: Quarles, C. Derrick, Jr.; Gonzalez, Jhanis; Choi, Inhee; et al. SPECTROCHIMICA ACTA PART B-ATOMIC SPECTROSCOPY Volume: 76 Pages: 190: 2012
10. Ultrafast laser induced breakdown spectroscopy of electrode/electrolyte interfaces: Zorba, Vassilia; Syzdek, Jaroslaw; Mao, Xianglei; et al. APPLIED PHYSICS LETTERS Volume: 100 Issue: 23 Article Number: 234101: 2012
11. Laser-nanostructure interactions for ion production: Stolee, Jessica A.; Walker, Bennett N.; Zorba, Vassilia; et al. PHYSICAL CHEMISTRY CHEMICAL PHYSICS Volume: 14 Pages: 8453-8471: 2012
12. Time-resolved LIBS of atomic and molecular carbon from coal in air, argon and helium: Dong, Meirong; Mao, Xianglei; Gonzalez, Jhanis J.; et al. JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY Volume: 27 Issue: 12 Pages: 2066-2075: 2012
13. Rapid bulk analysis using femtosecond laser ablation inductively coupled plasma time-of-flight mass spectrometry: Gonzalez, Jhanis J.; Oropeza, Dayana D.; Longerich, Henry; et al. JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY Volume: 27 Issue: 9 Pages: 1405-1412 : 2012
14. Femtosecond laser ablation particle introduction to a liquid sampling-atmospheric pressure glow discharge ionization source: Carado, Anthony J.; Quarles, C. Derrick, Jr.; Duffin, Andrew M.; et al. JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY Volume: 27 Issue: 3 Pages: 385-389: 2012
15. Laser Ablation Molecular Isotopic Spectrometry: Strontium and its isotopes: Mao, Xianglei; Bol'shakov, Alexander A.; Choi, Inhee; et al. SPECTROCHIMICA ACTA PART B-ATOMIC SPECTROSCOPY Volume: 66 Issue: 11-12 Pages: 767-775: NOV-DEC 2011
16. Laser Ablation Molecular Isotopic Spectrometry: Parameter influence on boron isotope measurements: Mao, Xianglei; Bol'shakov, Alexander A.; Perry, Dale L.; et al. SPECTROCHIMICA ACTA PART B-ATOMIC SPECTROSCOPY Volume: 66 Issue: 8 Pages: 604-609: AUG 2011
17. Ultrafast laser induced breakdown spectroscopy for high spatial resolution chemical analysis: Zorba, Vassilia; Mao, Xianglei; Russo, Richard E. SPECTROCHIMICA ACTA PART B-ATOMIC SPECTROSCOPY Volume: 66 Issue: 2 Pages: 189-192: FEB 2011
18. Laser Ablation Molecular Isotopic Spectrometry: Russo, Richard E.; Bol'shakov, Alexander A.; Mao, Xianglei; et al. SPECTROCHIMICA ACTA PART B-ATOMIC SPECTROSCOPY Volume: 66 Issue: 2 Pages: 99-104: 2011

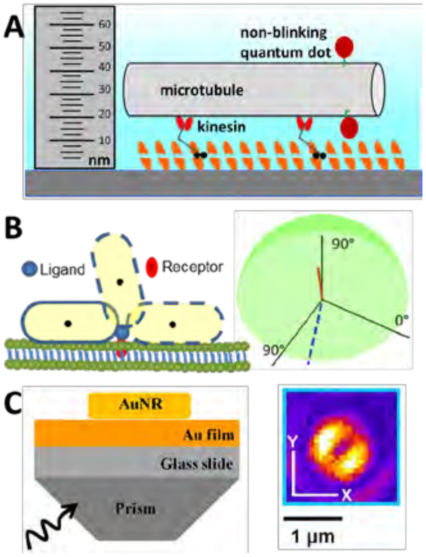
Chemical Analysis of Nanodomains: Optical Imaging Platforms for Visualizing Nanoparticles

Ning Fang
Jacob W. Petrich, Emily A. Smith
1605 Gilman Hall, The Ames Laboratory, Ames, IA 50011
Email: nfang@iastate.edu; Web: www.ameslab.gov/cbs/fwp/nanodomains

Collaborators: Dr. Javier Vela, The Ames Laboratory, Ames, IA

Overall research goals: The Chemical Analysis of Nanodomains team seeks to understand the basic principles that underlie energy-relevant events at solid-liquid interfaces including the development of new analytical approaches to improve the sensitivity, reliability, and productivity of analytical determinations. Our research emphasizes instrumentation, technique development and measurements highly relevant to address the Grand Challenge of mastering energy and information on the nanoscale to create new technologies with capabilities rivalling those of living things.

Significant achievements in 2012-2014: A fully automated total internal reflection fluorescence microscope (TIRFM) has been built and employed for high-precision tracking of non-blinking quantum dots (Fig. A). Stable signals from non-blinking quantum dots under the microscope allows for continuous super-localization of single probes with sub-10-nm precision in both lateral and axial directions at solid-liquid interfaces.



A dual-color total internal reflection scattering (TIRS) microscopy imaging system has been demonstrated for dynamic tracking of 3D orientation changes of single gold nanorods. This technique is capable of resolving the out-of-plane angle with a high angular resolution comparable to that for the in-plane angle to probe rotational dynamics of gold nanorods interacting with functional surfaces. In combination with superlocalization through point spread function (PSF) fitting, it becomes possible to resolve the conformations of surface-bound nanorods in unprecedented detail (Fig. B). Furthermore, we have demonstrated another TIRS-based method based on the far-field scattering patterns of in-focus gold nanorods supported on a dielectric gold film (Fig. C). The 3D orientation of AuNRs within a single frame can be extracted from the characteristic image patterns.

Science objectives for 2014-2016:

- Measurements of nanodomains in ionic liquids using sub-diffraction fluorescence correlation spectroscopy.
- Characterization of heterogeneous catalysis and chemical reactions within nanodomains using our suite of optical imaging techniques.
- Development of multi-layer anisotropic nanoparticle probes for high-speed high-resolution single particle orientation and rotational tracking.
- Understanding fundamental interactions on chromatographic surfaces by single particle orientation and rotational tracking.

Selected References to work supported by this project 2012-2014:

1. S. Budhi, C. Peeraphatdit, S. Pylypenko, V.H.T. Nguyen, E.A. Smith, B.G. Trewyn, “Enhanced Metal

Loading in SBA-15-type Catalysts Facilitated by Salt Addition: Synthesis, Characterization and Catalytic Epoxide Alcoholysis Activity of Molybdenum Incorporated Porous Silica" Applied Catalysis A: General, in press.

2. J.W. Ha, P.A. Ruberu, R. Han, B. Dong, J. Vela, N. Fang, "Super-resolution mapping of photogenerated electron and hole separation in single metal-semiconductor nanocatalysts " J. Am. Chem. Soc. 136, 1398-1408 (2014).
3. J.W. Ha, K.C. Chen,N. Fang, "Differential interference contrast microscopy imaging of micrometer-long plasmonic nanowires " Chemical Communications 49,11038-11040 (2013).
4. Y. Gu, J.E. Ha, A.E. Augspurger, K.C. Chen, S.B. Zhu, N. Fang "Single Particle Orientation and Rotational Tracking (SPORT) in biophysical studies" Nanoscale 5,10753-10764 (2013).
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Spatially Resolved Material Characterization at Interfaces

Gary J. Van Berkel, Principal Investigator
Vilmos Kertesz, Co-Principal Investigator
Yingzhong Ma, Co-Principal Investigator
Olga S. Ovchinnikova, Co-Principal Investigator
Robert W. Shaw, Co-Principal Investigator
Benjamin Doughty, Wigner Fellow
Su Liu, Postdoctoral Research Associate
Mathias Lorenz, Postdoctoral Research Associate
Tamin Tai, Postdoctoral Research Associate
Oak Ridge National Laboratory (ORNL), 1 Bethel Valley Road, Oak Ridge, TN 37831
Email: vanberkelgj@ornl.gov; Web: http://web.ornl.gov/sci/csd/

Overall research goals: The overarching goal of this program is to transcend the existing analytical capability for nanometer scale spatially resolved material characterization at interfaces under ambient conditions through a unique merger of advanced spectroscopic and ultrafast time-resolved imaging, scanning probe microscopy, and mass spectrometry. New techniques and tools to study and characterize a surface, particularly techniques capable of submicrometer spatial resolution with the ability to specifically detect or identify a wide range of elements, molecular compounds from small molecules to large macromolecules, and functional domains, over a variety of time scales, will advance the frontiers of analytical sciences and the DOE mission.

Significant achievements in 2012-2014: *Combined Atomic Force Microscopy (AFM) and Mass Spectrometry (MS) Imaging.* We have enabled and advanced the ability of ambient mass spectrometry, in combination with AFM and optical spectroscopic techniques to study and characterize, ultimately with submicrometer spatial resolution, molecular and elemental constituents of material interfaces under real world conditions. We successfully developed a hybrid atmospheric pressure AFM/MS imaging system utilizing nano-thermal analysis probes for thermal desorption surface sampling with subsequent atmospheric pressure chemical ionization and mass analysis. The ability to correlate topographic images of a surface with atomic force microscopy and a mass spectral chemical image of the same surface, utilizing the same probe without moving the sample from the system, was demonstrated. Co-registered mass spectral chemical images and atomic force microscopy topographical images were obtained from inked patterns on paper (Figure 1). Spatial resolution of the topography images based on pixel size (0.2 µm x 0.8 µm) was better than the resolution of the mass spectral images (2.5 µm x 2.0 µm), which were limited by current mass spectral data acquisition rate and system detection levels.

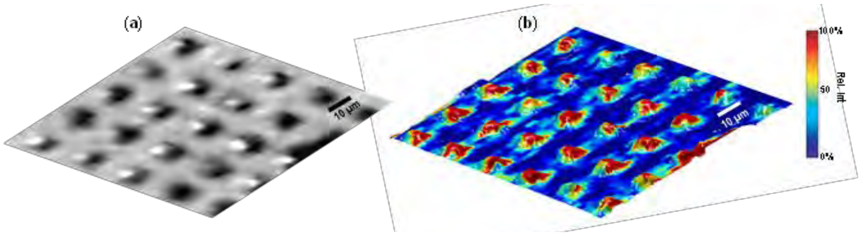

Figure 1. (a) Optical image of yellow ink stamped onto photo paper. (b) Corresponding AFM surface topography image overlaid with the interpolated mass spectral chemical image using the extracted ion current from major product ion of pigment yellow 74 present in the ink.

Multimodal Imaging Combining Laser Capture Microdissection and Mass Spectrometry. We developed a laser ablation (LA)/atmospheric pressure chemical ionization (APCI)-MS system that comprised a commercially available laser microdissection instrument for microscopic optical characterization of a surface as well as transmission geometry LA and a modestly modified ion source for secondary ionization of the ablated material. The set-up was successfully applied for multimodal imaging using the ability to co-register bright field, fluorescence and mass spectral chemical images (pixel size of about 4 µm x 8 µm, spatial resolution of 13 µm) on one platform.

High Spatial Resolution Liquid Extraction Based Surface Sampling/Ionization for Chemical Imaging. We recently advanced a controlled-resonance surface tapping-mode single capillary liquid junction extraction/electrospray ionization (ESI) emitter for mass spectrometry imaging. Under optimized conditions, a spatial resolution of approximately 35 µm was provided based on the ability to distinguish between features observed both in the optical and mass spectral chemical images. This resolution was comparable to the best resolution that has been reported for other types of atmospheric pressure liquid extraction-based surface sampling/ionization techniques used for mass spectrometry imaging. Present efforts aim to incorporate a feedback mechanism into this sampling system to both better control the sampling/ionization process and to gain additional information about the surface like topography. In addition, nanoscale liquid dispense and spray sampling probes are being designed and the fluid dynamics of the systems being modeled to enable a combined AFM/ liquid extraction/ESI emitter imaging system.

Nanohole patches for optical spectroscopy and MS. We have been investigating the use of surface plasmon-mediated enhanced light transmission through metallic nanohole arrays – Microscale Patch Nanohole Arrays (MPNA) - as a possible means for sub-diffraction limit, nanometer scale spatially resolved multimodal optical spectroscopy and mass spectrometry chemical imaging. Our plan has been to illuminate MPNAs to enhance optical spectrometric methods such as Raman spectrometry and to desorb material deposited on top of the nanohole array with submicron spatial resolution. Figure 2 shows an array of nanoholes (NHs) fabricated using focused ion beam (FIB) milling (NH diameter = 200 nm; NH period = 600 nm) and the corresponding optical transmission spectrum through the holes. We have yet to calibrate the absolute NH patch transmission coefficient for the data in Figure 2, but in the observed transmission zones (625 and 708 nm), the transmission is expected to be greater than 100%. We have also recorded plasmonic scattering spectra and enhanced Raman spectra for similar arrays of nanoholes. Creation of different array patterns is underway to optimize the patch transmission and the transmission zone wavelength for overlap with common laser wavelengths. The test patches will also be evaluated for plasmonic enhancement of Raman scattering, so as to enable a second mode of analysis beyond mass spectrometry. The ability of MPNAs for laser ablation of material from an area smaller than that of the micropatch was successfully tested using a thin-film of an ink containing rhodamine 6G coated directly on the surface and a 633 nm helium-neon laser. A desorption cross section profile showed a full width at half maximum (FWHM) ~850 nm diameter, which is smaller than the 2 µm MPNA diameter.

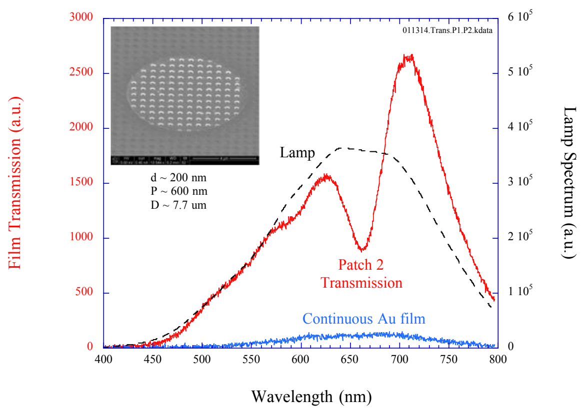

Figure 2. Optical transmission spectrum of a NH patch.

Time Resolved Spectroscopic Studies. To efficiently utilize solar energy, a better understanding of the elementary physical processes of energy and charge transport is needed. This is likewise true for molecules and materials important for many endeavors within the DOE energy mission, including transport interfaces within batteries and advanced energy storage capacitors. Photoactive materials for solar energy utilization generally contain distinct domains so that interpretation of time-resolved experimental data acquired using ensemble measurements is complicated by simultaneous excitation of multiple chemically and structurally distinct species. Thus a capability with both spatial and temporal resolution is essential for the characterization of these materials and has motivated our ongoing development of a femtosecond transient absorption imaging technique. As a starting point, we have focused to-date on understanding electronic excited-state dynamics of ensemble photovoltaic materials including copper-phthalocyanine single-crystal nanowires, water-soluble thermoresponsive poly(3-oligo(ethylene oxide)) thiophene derivatives, side- and main-chain deuterium-substituted poly (3-hexylthiophene) (P3HT) polymers as well as their blends with [6,6]-phenyl-C61 butyric acid methyl ester (PCBM). Time-resolved fluorescence measurements on three water-soluble thermoresponsive poly(3-oligo(ethylene oxide)) thiophenes with different side-chain lengths and distinct lower critical solution temperatures (LCSTs) show that their excited-state relaxation dynamics in aqueous solution depend strongly on the side-chain length and temperature. As the side-chain length increases, the fluorescence signals exhibit not only remarkably slower decays but also an increasingly complex decay behavior. Significant acceleration of the fluorescence decay was further observed for the two polymers with x = 3 and 4 (see Figure 3) when the aqueous solutions were heated to their LCSTs (51 °C and 60 °C, respectively) and above. For the polymer with the shortest side-chain (x = 2), the decay is too fast to be resolved. We further found a remarkable linear correlation between the natural logarithms of the mean fluorescence decay rates determined for the two polymers with x = 3 (open circles) and 4 (open squares) at different solution temperatures and the corresponding peak energies (Δ*E*) of their linear absorption spectra. While the observed side-chain length effect can be attributed to the conformational relaxation of the polymer backbones, the temperature effect can arise from intra- or inter-chain excitation energy transfer, conformational relaxation, or both. The linear correlation shown in Figure 3 enables us to unambiguously identify the conformational relaxation as the mechanism underlying the observed temperature effect. Side- and main-chain deuterium-substituted P3HT polymers and their blends with PCBM exhibit clearly faster fluorescence decay than that measured for a pristine P3HT film or its PCBM blend. This observation indicates that the deuterium-substituted P3HT either adopts different conformations or produces more defects when forming thin films and blends than those prepared with pristine P3HT polymer; either of these effects can efficiently quench electronic excitations.

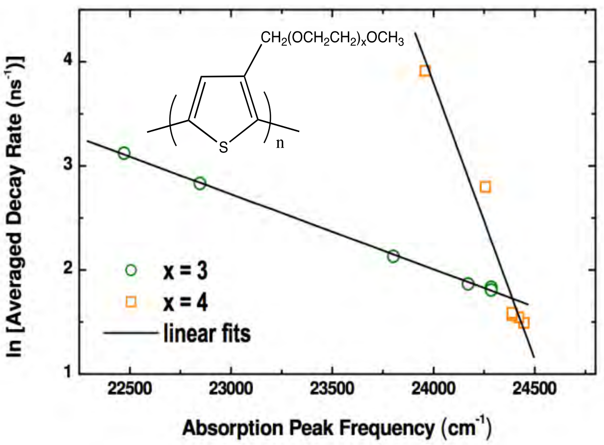

Figure 3. Plot of the natural logarithm of the mean decay rates as a function of the corresponding peak energies (*E*) of linear absorption spectra. The solid lines show the corresponding linear fits.

Science objectives for 2014-2016:

- To improve atmospheric pressure thermal AFM/MS imaging by understanding the means to improve transport and ionization efficiencies of the material sampled by thermal processes from a surface and to understand how to improve the range of compound types amenable to intact molecular MS analysis by this approach.
- To enable liquid exaction-based sampling on an atomic force microscope achieving sub-micrometer sampling resolution, sensitive ionization and detection, and multimodal imaging capability by understanding fully the flow dynamics of possible liquid extraction probe configurations to determine their respective limits for sampling spatial resolution.
- To develop and apply plasmon mediated laser desorption to provide submicron scale chemical profiling with mass spectrometry detection.
- To develop chemical imaging tools and utilize them to characterize molecular and functional domains to understand surface chemistry at space and time scales shorter than those currently accessible using diffraction limited techniques.

- To identify and understand the spatial distribution of electronic excitations and charge carriers in functional assemblies and mesoscale (10-100 nm) domain materials, such as organic photovoltaics and noble metal and oxide nanomaterials, using femtosecond transient absorption (TA) imaging microscopy; and
- To determine the best achievable spatial resolution for ultrafast optical imaging and the techniques to realize it.

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The Nanoporous Materials Genome

Laura Gagliardi
Department of Chemistry, Supercomputing Institute, and Chemical Theory Center, University of Minnesota, Minneapolis, Minnesota, 55455, USA
Email: gagliard@umn.edu; Web: http://www.chem.umn.edu/nmgc/

Collaborators: Christopher J. Cramer, Ilja Siepmann, Donald G. Truhlar, Michael Tsapatsis, University of Minnesota

Aurora Clark,Washington State University

Michael Deem, Rice University

Martin Head-Gordon, Jeff Long, Berend Smit, Omar Yaghi, University of California, Berkeley

Joseph Hupp, Randall Snurr, Northwestern University

Jeff Neaton, Wendy Queen, Lawrence Berkeley National Laboratory

David Sholl, Georgia Tech

Overall research goals: The Nanoporous Materials Genome Center (NMGC) has the objective to create a repository of experimental structures and associated properties of porous materials and of hypothetical structures with characteristics representative of the real materials. In order to achieve these goals, a team of sixteen investigators is working on the project. Five of them are experimentalists, while eleven are computational/theoretical chemists/chemical engineers. In collaboration with the experimentalists, the computational investigators are developing state-of-the-art computational tools to predict the properties of both the experimental structures and millions of as-yet-unsynthesized materials. Data mining tools are also being developed to screen materials performance for a given application.

Significant achievements in 2012-2014: NMGC was funded in August 2012. Since then several papers have been published or submitted on the various topics related to the thrusts of the Center. The Genome has been recently created and data are being uploaded and accessed.

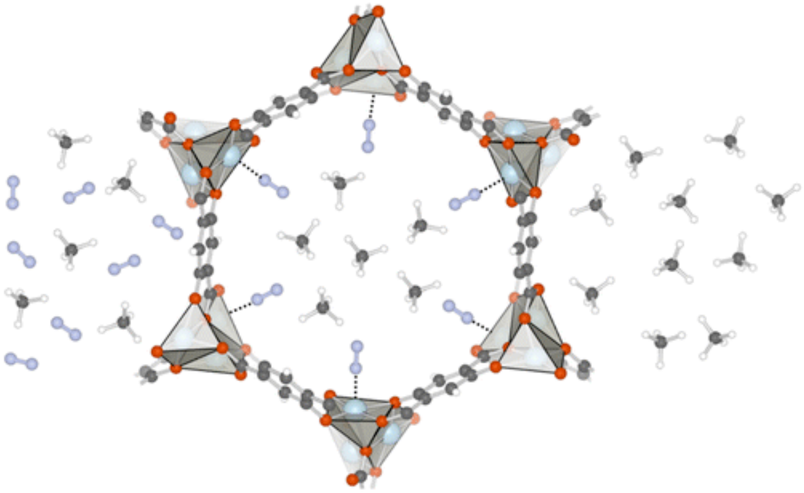

Figure 1. M_2(dobdc) (M= V, Fe and dobdc^{4-} = 2,5-dioxido-1,4-benzenedicarboxylate) for CH_4/N_2 separation.

Science objectives for 2014-2016:

- The collaboration between the theorists and the experimentalists will continue. Novel materials will be predicted and synthesized. Novel adsorption phenomena will be investigated.
- The Genome, for which there is already a working preliminary version, will be expanded and made more accessible to the community.

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Transferable physically-motived force fields for nano-porous materials and beyond

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

Collaborators: Prof. Randy Snurr, Northwestern University, Evanston, IL
Prof. Jeff Long, UC-Berkeley, Berkeley, CA

Overall research goals: The objective of this work is to develop and apply the theoretical framework necessary to generate transferable "physically-motivated" classical force fields for complex systems, with an emphasis on nano-porous materials for gas separation applications. The overarching goal is to develop models which include by construction the right balance of all of the relevant "physics" of inter-molecular interactions, with the physical properties of interest emerging as a natural consequence.

Significant achievements in 2012-2014: We have made significant progress in developing transferable "physically-motivated" classical force field models for a wide variety of metal-organic framework (MOF) materials. Crucially, we recently extended our symmetry-adapted perturbation theory (SAPT) based approach to yield robust and *transferable* force fields, which has allowed us to generate a large "library" of force field parameters that encompasses essentially all of the common MOF linker groups and functionalizations as well as an expanding list of common metal nodes. A key achievement in this regard is our recently-developed methodology for extracting transferable dispersion parameters based upon density functional theory response calculations. This approach yields transferable atomic dispersion parameters that reflect the chemical environment of the atom and allows us to extract a significant amount of information regarding inter-molecular interactions from *monomer* (rather than dimer) calculations on a single member of the interacting pair.

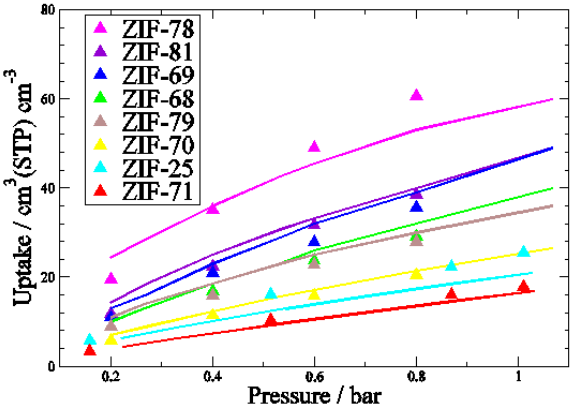

Figure 1. Comparison of calculated (symbols) and experimentally-measured (solid) adsorption isotherms for a diverse set of zeolitic-type MOFs.

Given the accuracy of our models (with no required experimental input!), we are extremely confident in their quantitative *predictiveness.* As such, we are in the initial stages of collaboration with Randy Snurr to integrate our optimized force fields with their ongoing computational screening efforts. Since such screenings incur a non-trivial computational expense (particularly for sophisticated polarizable models), we also recently developed a lattice model-based approach for screening gas adsorption. Briefly, we derive a discrete lattice model from an underlying continuous model (using our physically-motivated force fields for the latter). Using the lattice model instead of conventional molecular simulation techniques yields 2-3 orders of magnitude acceleration in the screening procedure, including the time required to derive the lattice.

In an exciting application of the above work, we showed that we could understand the adsorption behavior of so-called "multivariate" (MTV) MOFs, which contain *mixtures* of multiple organic linking groups. Yaghi and coworkers found that such MTV MOFs sometimes exhibited "synergistic" enhancement of gas uptake as compared to their corresponding pure parent compounds. We used the above methodologies to examine the generality of this synergistic enhancement as well as its molecular origins. We find that the origins lie in the simultaneous interaction of a single adsorbate with multiple linker groups and the associated non-linearity of the Boltzmann factor that governs adsorption. We thus predict that the extent of this synergistic enhancement should depend on both pore and adsorbate size and shape, and might be maximized for "ordered" arrangements of the heterogeneous linkers. The latter prospect is particularly intriguing since recent solid state NMR data suggests some amount of linker orderings, thus potentially opening the door to a new, orthogonal, design axis for MOFs.

The "physically-motivated" approach to force field development described above is entirely general. We recently showed that one can use the same approach to accurately describe the properties of a number of bulk organic liquids (ethane, acetone, methanol…) using only first-principles information. Interestingly, we find that three-body exchange/dispersion contributions are important in achieving quantitative accuracy. This is particularly interesting in that these terms are essentially universally neglected in existing force fields. The resulting error cancellation is likely a significant cause of the lack of transferability between phases in common classical models. Recently, in an emerging direction, we found that we can also extend this approach to ionic liquids. We believe our ionic liquid model to be the most accurate ever developed, with absolutely no empirical parameterization. This is particularly exciting due to the significant interest in ionic liquids in separations and purifications – applications which we are beginning to explore.

Science objectives for 2014-2016:

- Continue *method development* for our physically-motivated force field approach, specifically including strongly interacting systems (e.g. strong chemisorption), high-spin systems (e.g. MOFs with open metal centers) and additional relevant "physics" (e.g. ligand field, spin splitting).
- Expand *applications* of our existing transferable force field parameters, including: to targeted systems of interest (e.g. multivariate MOFs); interaction of flue gas contaminants with MOFs (with Jeff Long); and efforts involving high-throughput computational screenings of MOFs for diverse separation applications (with Randy Snurr).
- Continued development of our highly accurate ionic liquid models and application of these models to separations and purification.

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Theoretical Studies of Spin-Crossover Metal-Organic Frameworks

Francesco Paesani, Principal Investigator

Department of Chemistry and Biochemistry, University of California, San Diego, CA, 92093
Email: fpaesani@ucsd.edu; Web: paesanigroup.ucsd.edu

Overall research goals: The objective of our project is the development and application of an integrated theoretical/computational approach for the characterization of spin-crossover metal-organic frameworks (MOFs) at the molecular level. The ultimate goal is to use *in silico* modeling for the rational design of multifunctional MOFs with magnetic properties for applications in gas storage, separation, and sensing.

Significant achievements since September 2013: In the last years it has been shown that the incorporation of open-shell transition-metal centers into the frameworks provides a promising approach for the development of multifunctional MOF materials in which the intrinsic high porosity and large surface area can be exploited in combination with electronic and magnetic properties. In most spin-crossover MOFs, Fe(II) atoms, which have d^6 electron configurations, are used as metal centers. In the octahedral ligand field generated by the organic linkers, the d-based orbitals split into the well-known t_{2g} and e_g configuration. This provides the possibility for the metal centers to exist in either low-spin or high-spin configurations depending on the temperature and surrounding chemical environment. In particular, it has been shown that the spin-crossover temperature of MOFs is extremely sensitive to the presence of guest molecules inside the pores, thus representing a molecular-level property that can be used for analysis and separation of complex gas mixtures.

In the past six months, we have focused our efforts on the improvement of our molecular dynamics (MD) approach, which includes an accurate description of framework flexibility and electronic polarization, through the inclusion of a new potential-energy term that explicitly describes the ligand field stabilization energy (LFSE). The LFSE term effectively takes into account the change in the energy splitting of the metal d-based orbitals due to the overlap with the ligand orbitals. The LFSE term is parameterized from "first principles" using *ab initio* data for isolated complexes, which we have shown are accurately described at the DFT level using the TPSSh functional.

The first application of our new MD approach focuses on a MOF with molecular formula $[Fe(pz)_2Pt(CN)_4]$ (pz = pyrazine), which undergoes the spin transition between 280 K and 300 K. Importantly, it was shown that this MOF material only exists in the high-spin configuration upon adsorption of benzene, while the spin-crossover temperature increases to ~340 K upon adsorption of CS_2. In our contribution, we will show that our MD approach correctly reproduces the spin-crossover transition for both the isolated complex and the bulk material, thus effectively enabling molecular-level studies of spin crossover in MOFs.

Science objectives for 2014-2016:

- Development of polarizable force fields for guest molecules of relevance for the spin-crossover behavior of MOFs (e.g., benzene, methanol, ethanol, and CS_2).
- Molecular-level studies of the effects of guest molecules on the spin-crossover behavior of MOFs for analysis and separation of complex gas mixtures.
- *In silico* design of new MOF structures with spin-crossover behavior.

References to work supported by this project since September 2013

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High-Throughput Computational Design of Azo-Functional Porous Coordinated Polymers (PCPs)

James P. Lewis, Principal Investigator
P.O. Box 6315, 135 Willey St., Department of Physics and Astronomy, West Virginia University, Morgantown, WV 26506-6315
Email: james.lewis@mail.wvu.edu; Web: http://fireball.phys.wvu.edu

Collaborators: Dr. Oleg V. Prezhdo, University of Rochester, Rochester, NY
Dr. Hongcai Zhou, Texas A&M University, College Station, TX

Overall research goals: Azobenzene functional groups undergo photo-isomerization upon light irradiation or application of heat. Zhou *et al.* (*J. Am. Chem. Soc.* 134:99-102, 2012) showed that porous coordinated polymers (PCPs) that utilize stimuli response, such as light absorption, are potentially highly efficient, and reversible, sorbents, particularly for carbon dioxide uptake. Azo-functional sorbents return to their original state while at ambient conditions for a prolonged period of time or with gentle heating (solar activation). The photo switchable molecules also have potential applications ranging from optical storage devices, photo-orientation of liquid crystals, and control of peptide conformations. Determining optimal functional groups on the photo-responsive organic linkers is a major synthesis and characterization challenge. Our research will provide a unique computational approach to aid in the search for optimal linkers via high-throughput materials-by-design scenarios.

Significant achievements in 2012-2014: Our previous award provided support to initiate research into the properties of photoactive porous coordinated polymers. To that end, our primary proposal objective during that award period was to develop and implement a non-adiabatic molecular-dynamics (NAMD) formalism within our local-orbital density functional theory code, named FIREBALL. We have successfully demonstrated the effectiveness of our approach by examining several excitation processes (*e.g.* the formaldimine molecule, CH_3N) as well as the photo-isomerization of stilbene and azobenzene. There are two key elements regarding our approach. *Firstly*, we explicitly calculate the non-adiabatic coupling vectors (NACVs). The NACVs play a fundamental role in extending first principles molecular dynamic simulations beyond the adiabatic approximation - they provide the link between classical atomic motion and changes in quantum electronic states. In most methodologies, the NACVs are not calculated explicitly. However, it is useful to explicitly calculate the NACVs, for instance, in order to search for conical intersections or avoid crossing regions. Our *exact* expression for the NACVs efficiently extends to NAMD methods so that we can efficiently investigate photo-isomerization processes in large systems (including hundreds or potentially thousands of atoms). *Secondly,* the efficiency of our NAMD approach means that we can also explore very large statistical ensembles of excitation processes. In each of our photo-isomerization investigations, we explore between 500-1,000 trajectories; thereby, we obtain ensembles that are statistically sound. We then explore the properties of the entire ensemble rather than individual trajectories (*photo-isomerization is a probability event*).

More recently, we have been investigating the photo-isomerization processes in azo-functional organic linkers through non-adiabatic molecular dynamics. We are exploring the impact of R-groups on the optical properties, isomerization reaction time, and quantum yield and we find that these properties are strongly dependent on the functional groups attached to the azobenzene derivative. We will report on non-adiabatic molecular dynamics simulation results for a few model azobenzene derivative systems and we will discuss our theoretical understanding of the *trans-* to *cis-* transformation mechanisms, and timescale variations, resulting from different functional groups. Our long term goal is to use high-throughput calculations to rationally design highly efficient photo-isomerization response in porous coordinated polymers for gas separation.

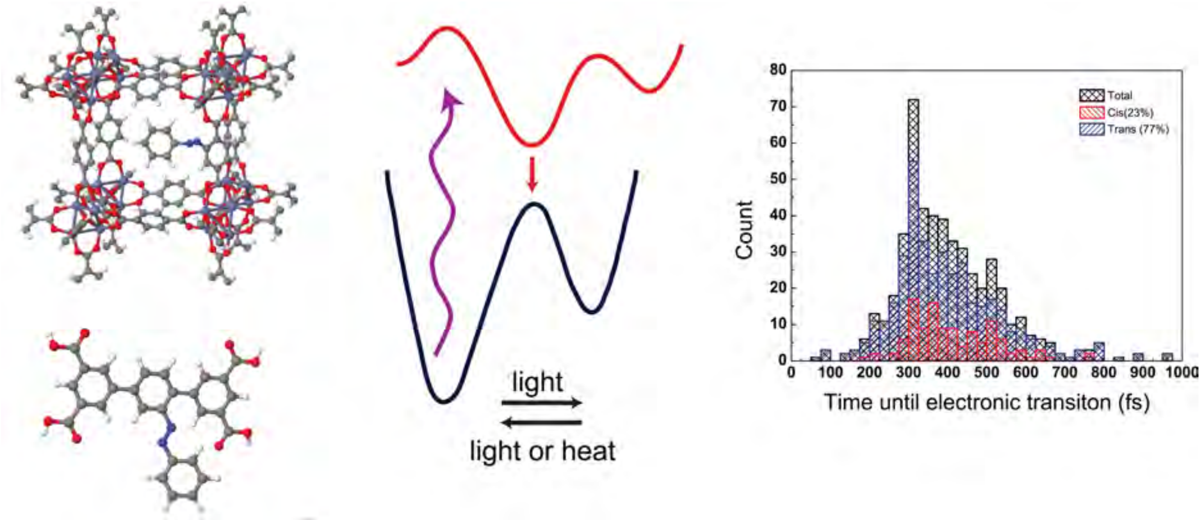

Figure 1. The photo-isomerization process in azo-functional organic molecules (linkers) utilized in metal organic framework nanoporous sorbents (left panel). Azo-functional molecules exist in two stable conformations: *trans* and *cis*, and each configuration is converted to the other through optical excitations (middle panel). In our photo-isomerization simulations, we perform ensembles of trajectories (500 trajectories in this example) to describe the isomerization mechanism, time, and quantum yield (shown in right panel for trajectories starting in the *trans* configuration).

Science objectives for 2014-2016:

- Perfect scripts for organizing ensemble calculations and obtain results for a few model azo-functional linker systems; both isolated linkers and in the porous coordinate polymer structure.

- Develop a fitness function for *scoring* test linkers utilizing tree-searching algorithms. Our goal in searching for optimal linkers is two-fold: 1) We are computationally designing linkers that demonstrate light absorption in the *visible* as well in the ultraviolet. We are searching for photo-functional PCPs that broadly absorb across the UV-*vis* spectrum; 2) We are computationally designing azo-functional linkers that can enhance CO_2 (reversibly) adsorption. The key is to find how photo-functionalizing the azobenzene ring will change CO_2 loading; adding R-groups may improve photo-activity, which is the goal of 1), but these additional functional groups may also decrease CO_2 loading. Our objective is to find how to optimize both 1) and 2).

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Chemical Microscopy of Conjugated Nanomaterials

Michael D. Barnes, Principal Investigator
Paul M. Lahti, Co-Principal Investigator
Adam Wise, Postdoctoral Research Associate
710 N. Pleasant St, University of Massachusetts-Amherst, Amherst, MA 01003
Email: mdbarnes@chem.umass.edu; Web: http://barnes.chem.umass.edu

Overall research goals: This research effort is focused on development of new material platforms and analytical spectroscopy methodologies for probing inter- and intra-molecular electronic processes in conjugated nanomaterials. A detailed understanding of the connection between molecular architecture, supramolecular/polymer assembly, and optoelectronic function is critical to the improvement in polymer-based optoelectronics, yet many questions remain outstanding as to how to 'program' specific inter-molecular couplings via molecular structure in order to achieve desired device performance (photostability, charge-separation and charge-transport efficiency). We combine single-molecule spectroscopy tools and new synthetic methodologies to probe intra- and inter-molecular coupling in small-molecule, oligomeric complex structures and crystalline nanoscale supramolecular assemblies in order to understand in detail, the structure-excitonic property relations and elucidate molecular design rules (distances, angles, etc) for improved performance in organic optoelectronics.

Significant achievements in 2012-2014:

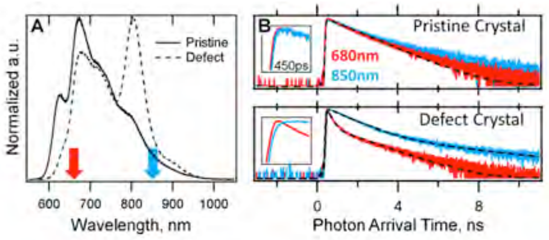

Figure 1. (A) Photoluminescence spectra of two TAT single-crystals – one grown slowly over slow controlled CV conditions, the other (dashed) grown quickly in a hot oven showing deep red (800 nm) defect emission. (B) Time traces of PL emission from pristine and defect crystals showing that the defect emission is fed by direct exciton production.

Single-nanocrystal spectroscopy of a novel small molecule semiconductor. Recent synthetic work has realized a novel (n-type) small-molecule acceptor, 7,8,15,16-Tetra-aza-terrylene (TAT), single-crystals of which can be grown oriented along the c-axis crystallographic direction, and over-coated with pentacene to form a highly ordered donor/acceptor interface for use in organic photovoltaic devices. However, characterization of single TAT crystals reveals highly variable emission spectra and excited state dynamics – properties which strongly influence photovoltaic performance. Through the use of single-crystal widefield imaging, photoluminescence spectroscopy, time correlated single photon counting, and resonant Raman studies, we conclude that this variability is a result of long-lived low-energy trap-emission from packing defects. Interestingly, we also discovered that TAT crystals whose width exceeds ~200 nm begin acting as waveguides and optical microcavity resonators for their own photoluminescence. A manuscript describing this work has recently been accepted for publication in *PhysChemChemPhys*.

Tuning exciton coupling in polymeric semiconductor nanowires. In collaboration with colleages in the Polymer Science and Engineering department at UMass Amherst, we have investigated the photophysics of crystalline nanowires of a polythiophene block-copolymer before and after chemical cross-linking- a process which forms physically and chemically robust nanostructures. Depending on the specific cross-linking strategy (i.e., choice of reactive terminals on the block copolymer and small-molecule cross-linker), we have shown by a variety of photophysical measurements, that exciton coupling can be tuned over a broad range (M. Baghgar, et al. *ACS Nano*, **7**, 8917-8923, 2013). Perhaps most interesting is the observation of a variety of structural morphologies (small and extremely thin (≈ 2 nm) nanowires, nanoribbons, branched sructures, and extended two-dimensional sheets) depending on the chemical specifics of the cross-linking reaction. In addition, combined Kelvin Probe Force Microscopy (KPFM) and polarized photoluminescence imaging on cross-linked poly-3-hexylthiophene (P3HT) nanostructures has revealed a striking dependence of surface potential contrast (SPC) with nanostructure morphology.

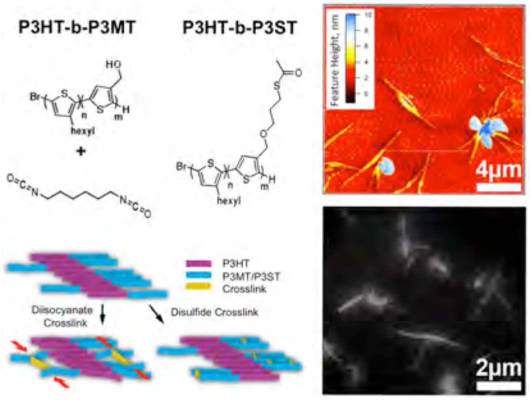

Figure 2. (upper left) Schematic of the P3HT-P3MT/P3ST diblock copolymers, and nanofiber structure (lower left) Purple bars indicate lamellar assembly of the P3HT blocks, while the blue P3MT (P3ST) blocks participate in the cross-linking (yellow). (upper right) AFM surface height image of P3MT-crosslinked nanofibers showing different morphologies (wires, ribbons, and nanosheet "clover-leaf" structures).

<u>Science objectives for 2014-2016:</u>

- Single-molecule probes of inter-chromophore interactions in small-molecule model systems.
- Integrated absorption and photoluminescence probes of isolated polymer and inorganic hybrid nanostructures.
- Synthesis and spectroscopic characterization of foldamer-mimics of H/J aggregate systems Synthesis of slip-stacked oligo-thiophene complexes: A test of the H-J aggregate model

<u>References to work supported by this project 2012-2014:</u>

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Imaging of Conformational Changes

Josef Michl

Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, 80309
michl@eefus.colorado.edu
Collaborators: Thomas F. Magnera, Deborah L. Casher, Alexandre Olive, Cecile Givelet, Jaroslav Vacek, Amanda Z. Lee

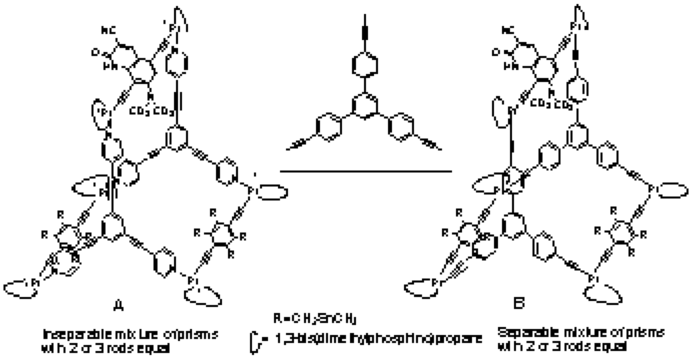
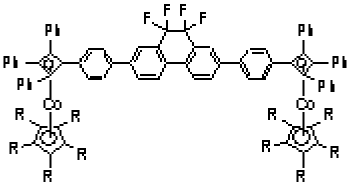
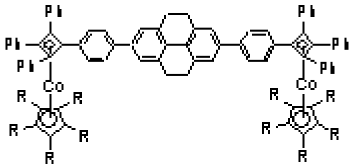


Figure 1. Molecular rotor before (A) and after (B) covalent stabilization.

Overall research goals: This project is directed toward the real-time detection and STM imaging of the conformational rotational change within a single molecule anchored to an atomically flat metal surface by simultaneous tip-enhanced Raman spectroscopy (TERS) and differential barrier height imaging (DBHI). One of our target structures, **B** (Fig. 1), is a two-paddle molecular rotor based on a trigonal prism with differentiated edges: two edges are functionalized for attachment to a Au(111) surface (R = isothiocyanate) and the third acts as an axle for the substituted carbostyril rotor chosen to be in resonance with the TERS excitation beam. Resonance Raman active substituent groups on the chromophore are designed to give signal intensities that will be strongest when the group is closest to the tip plasmon field aligned by the interaction of the chromophore dipole and the electric field created by the STM tip bias voltage. They will be weakest when the group is closest to the surface. This intensity variation is expected to allow the determination of the rotor orientation as the tip bias is changed.

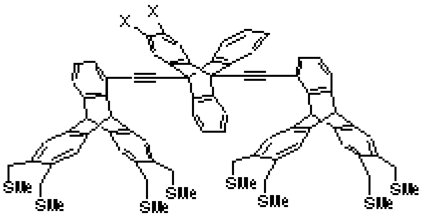


1 R = $HgS(CH_2)_2SCH_3$
2 R = HgO_2CCF_3



3 R = $HgS(CH_2)_2SCH_3$

Significant Achievements in 2012 - 2014: (1) Our approach to the synthesis of the complicated target rotor compounds is to use a self-assembly technique developed by us that relies on simple self-assembly (A) to a weakly bound structure followed by covalent stabilization to yield a sturdy one. The general importance of this approach to the synthesis of complex molecular structures is that it demonstrates a broadly applicable path for reducing a complicated multi-step covalent synthesis to a more manageable two-step one-pot process. A problem discovered is that a very facile spontaneous *cis-trans* isomerization in favor of the all-*trans* isomer occurs at the outset of the



4 X = F
5 X = H

original self-assembly, before the covalent stabilization reaction is even initiated leading to oligomers rather than simple polyhedra. We have developed a remedy to this problem by using a bridging diphosphine, $Ph_2PCH_2CH_2CH_2PPh_2$, (shown in Fig. 1) instead of the originally selected PMe_3 pair. This prevents the rearrangement to a *trans* configuration. (2) The detection of orientational reversal of rotators in altitudinal molecular rotors mounted on Au(111) surfaces by DBHI appears to work as hoped for. Three types of surface-mounted rotor behavior have been observed in DBHI scans Fig 3: (i) Rotors **3** and **5**, whose rotators have no transverse dipole, were invisible, as were the dipolar rotors **4**, attached by eight $-CH_2SCH_3$ residues. (ii) About two-thirds of the dipolar rotors **1**, attached by ten $-HgSCH_2CH_2SCH_3$ substituents, responded to a change in tip polarity and some changed their response with time. (iii) About nine-tenths of the dipolar rotors **2**, attached by ten $-Hg^+$ residues, also responded to a change in the tip polarity, with little if any difference over time. The lack of response of the nonpolar rotors **3** and **5** was expected. The differences in behavior between the rotors **1**, **2**, and **4** are interpreted to reflect the different magnitude of barriers to rotation. TERS was used to spectroscopically verify the features observed under the STM tip. (3) The upgrade of our TERS system to work in the near UV has been successfully completed. The Raman spectrum of DiA (4-(4(dihexadecylamino)styryl)-N-methylpyridinium iodide) (Fig. 4) was obtained by excitation of a Co STM tip with 363.8 nm light from an Ar-ion laser. To our knowledge this is the first time UV-TERS has been demonstrated with a cobalt surface plasmon.

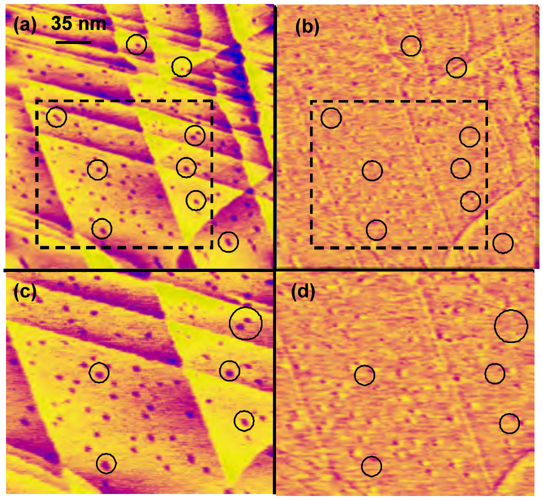


Figure 3. (a, c) Constant-current mode STM image (175 pA, 900 mV) of an Au(111) surface sparsely covered with rotor **2**. (b, d) DBHI scan of the same area. Lower frames are enlargements delineated by the boxes. Circles indicate rotors that are hindered.

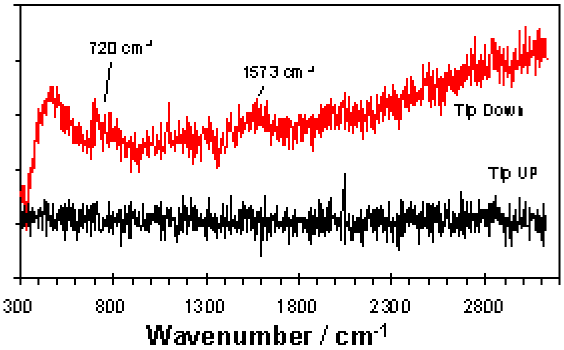


Figure 4. UV-TERS of a LB film of DiA on gold.: 363.8 nm excitation, Co tip, 75 s collection time.

Science Objectives for 2014-2016: Completion of the synthesis of a surface-mounted rotor **B** that will permit the detection of conformational rotation by DBHI/TERS.

Publications (2012-2014) citing this DOE grant:

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Chemistry and Microphysics of Small Particles

Alla Zelenyuk, Principal Investigator
Jacqueline Wilson, Post-Doctoral Associate
Pacific Northwest National Laboratory, Richland, WA 99354
Email: alla.zelenyuk@pnnl.gov; Web: http://www.pnl.gov/science/staff/staff_info.asp?staff_num=5531

Collaborators: Prof. Klaus Mueller (SUNY Stony Brook), Prof. Barbara Finlayson-Pitts (UCI)

Overall research goals: The overall goal is to achieve a fundamental understanding of physical and chemical phenomena underlying analysis and separation of small particles in complex, heterogeneous environments. Our research focuses on developing and applying unique mass-spectrometric tools and single particle *multidimensional* characterization methods for comprehensive quantitative analysis of individual size-selected particles, with particular focus on complex organic-containing particles and particles with multifaceted shapes and morphologies.

Significant achievements in 2012-2014: This project proceeded along four parallel pathways. (1) the chemistry and microphysics of complex organic-containing particles; (2) fundamental physicochemical particle properties and their relation to analysis; (3) particle shape and its effect on particle dynamics and physicochemical properties; and (4) development and application of novel approaches for multidimensional data visualization and analysis.

Our recent studies of the chemistry and microphysics of size-selected complex organic particles enable, for the first time, characterization of their size, composition, morphology, density, shape, viscosity, chemical diffusivity, and evaporation kinetics, providing unique insight into the processes that drive particle formation and transformations. In the absence of experimental data, these particles were assumed for the past 20 years to consist of low-viscosity solutions that maintain equilibrium with the gas phase by fast in-particle mixing and rapid condensation and evaporation. We developed a novel approach to characterize the morphology of these particles, conducted the first measurements of chemical diffusivity in these particles, and quantified their evaporation kinetics, demonstrating that they are semi-solids with viscosities characteristic of tars, have complex multi-layered morphologies, trap volatile organic molecules during formation and growth that follows non-equilibrium pathways, and evaporate orders of magnitude slower than assumed. These findings challenge the most fundamental assumptions, calling for a major change in the way these complex organic particles are treated by models.

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.

Recently we applied our multidimensional characterization approach to study the properties and transformation of fractal particles. We demonstrated the capability to measure mass, mobility diameter, aerodynamic diameter, composition, and morphology of fractal particles and used these measurements to calculate the average primary spherule diameter, number of spherules, their fractal dimension, and void fraction as a function of agglomerate size. Applying this approach to combustion particles revealed the occurrence of two concomitant combustion regimes that produce particles with drastically different properties.

We continued to develop novel approaches for multidimensional data visualization and analysis. We developed a novel structure-based distance metric for high-dimensional space exploration with multidimensional scaling, a novel approach to GPU-accelerated clustering of large datasets with visual feedback, and implemented the parallel coordinates interface.

Science objectives for 2014-2016:

- Advance single particle mass-spectrometric analysis by adding simultaneous detection of negative ions, improving mass-spectral resolution, and developing soft ion generation approach.
- Study phenomena pertinent to non-equilibrium formation, properties, and transformations of complex organic-containing particles, with particular focus on particle phase, morphology, evaporation kinetics, and rates of heterogeneous chemistry.
- Extend our new approaches to image particles with complex shapes and morphologies to fundamental studies of the relationship between shape of nanoparticles and their aggregates and their physicochemical properties, dynamics, and mesoscale phenomena.
- Develop novel approaches for analysis and visualization of complex multidimensional data, including real-time data classification and implementation of the parallel coordinates interface to quantify the relationships between the particle properties and other observables.

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Material Informatics Tools for Discovery of Nanoporous Materials for Energy Applications

Maciej Haranczyk, Principal Investigator
Richard L. Martin, Postdoc

One Cyclotron Rd 50F-1650, Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA 94720
Email: MHaranczyk@lbl.gov ; Web: http://www.maciejharanczyk.info/

Collaborators: BES Nanoporous Materials Genome Center (B. Smit, R. Snurr, D. Sholl, M.Deem)
ASCR Center for Applied Mathematics for Energy Research Applications (CAMERA)

Overall research goals: Our main goal is to develop new computational and material informatics approaches to facilitate efficient discovery of porous materials for energy applications such as separations and gas storage. Our tools, implemented in Zeo++ suite, will enable enumeration, optimization and characterization of increasingly complex advanced porous materials such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs) and porous polymer networks (PPNs). Our second goal is to collaborate with the Nanoporous Materials Genome Center to apply our developments to screen databases of zeolites and MOFs to discover promising materials for CO_2 capture, other separations (e.g. hexane isomers) and storage applications involving weakly interacting guest molecules.

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 enumerate, characterize, 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, which enable building discovery approaches.

In the last period, we have worked on Zeo++ to enable precise control over accuracy of the performed Voronoi decomposition. The 'standard' Voronoi decomposition underlying Zeo++ is only appropriate when atoms all have equal radii, and the natural generalization to structures with unequal radii leads to cells with curved boundaries, which are computationally expensive to compute (Fig. 1). We introduced "sphere-approximation" procedure that replaces all atoms except ones with the smallest radii, with clusters of spheres of radii equal to the smallest atoms. By going so, we can then use the standard Voronoi decomposition, which can be solved accurately. In practice, we used clusters of 50-100 spheres, which allow reducing errors on the calculated pore diameters below 0.02 Å.

In another effort related with further development of Zeo++ code, we introduced fast algorithms for the calculation of two types of pore landscape descriptors: pore size distributions and stochastic rays. These descriptors provide histogram representations that encode the geometrical properties of pore landscapes. Pore size distribution (PSD) histograms indicate the fraction of the void space volume that corresponds to certain pore sizes while the stochastic ray tracing algorithm uses lengths of randomly sampled rays to represent the void space (Fig. 2).

Moreover, we developed a database of MOF-5 analogues, and screened them for the best methane-absorbing materials. Our MOF-5 analogues were constructed from commercially available organic molecules using Zeo++, which was extended to enable generation of these MOF structures. 116 MOF-5 analogues were designed, and characterized in terms of geometric properties and simulated methane uptake at conditions relevant to vehicular storage applications. A strength of the approach is that all of the hypothesized MOFs are designed to be synthesizable utilizing ligands purchasable online.

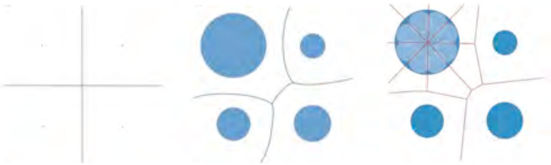

Figure 1. Schematic depiction of Voronoi tessellation around four particles: (left) "standard" Voronoi around point particle, (center) tessellation with curved boundries around atoms of unequal radii, (right) tessellation after replacing the largest atoms with a cluster of smaller atoms.

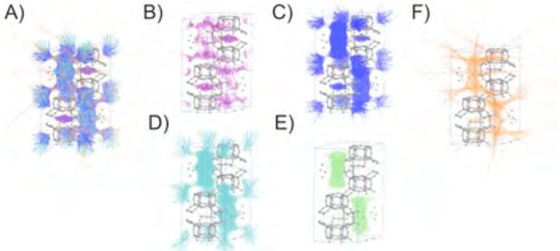

Figure 2. Ray trace method for AFT zeolite. Lines of length (a) 0–100 Å, (b) 0–3 Å, (c) 3–6 Å, (d) 6–9 Å, (e) 9–12 Å, and (f) larger than 12 Å.

Science objectives for 2014-2016:

- 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.
- New databases of advanced porous materials will be developed. This effort will include both enumerations of structures (COFs, ZIFs) as well as curation of experimentally known materials (the latter in collaboration with the Sholl and Snurr groups).
- Demonstrate similarity-based screening of APM for hexane separation. This will involve using query materials with very good performance (such as ones from the Long group, Science 2013) and identification of other materials alike within the databases of experimental and predicted porous materials using similarity measures based on property-governing structure features.
- Demonstrate of a prototype of genetic-algorithm-powered structure optimization w.r.t. properties as a material design tools (in collaboration with the Deem group).
- To enable high-throughput screening of materials for storage or capture of weakly interacting guest molecules such as methane or Nobel gases.

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Surface Chemistry Aspects of Bastnaesite ($Ce,LaFCO_3$) Flotation with Octyl Hydroxamate

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

Collaborators: Dr. Hao Du, National Engineering Laboratory, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China
Dr. Liem Dang and Dr. Hongfei Wang, Chemical Material Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352

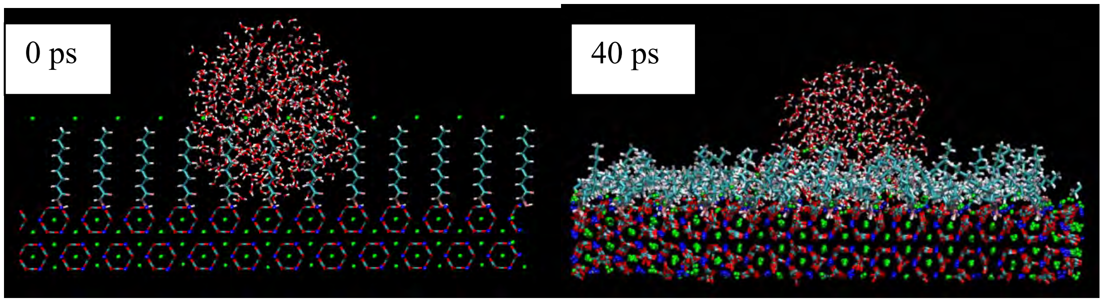
Overall research goals: The primary goal of this research program is to provide a basis for improved flotation separation efficiency in nonsulfide mineral systems by establishing the fundamental features of collector (surfactant) adsorption reactions associated with the hydrophobic surface state and developing appropriate surface chemistry control strategies. Advanced experimental techniques together with more traditional experimental methods are being used to provide crucial information concerning the interfacial surface state and collector adsorption phenomena in various nonsulfide mineral systems. Current research includes the surface chemistry of layered silicate minerals and the rare earth mineral bastnaesite. Spectroscopy of film rupture/bubble attachment is in progress.

Significant achievements in 2011-2014: Before discussion of bastnaesite flotation chemistry for RE recovery, a significant achievement in the surface chemistry of layered silicates should be mentioned. Namely, the experimental procedure for the isolation and preparation of the edge surfaces of 300 nm anisotropic kaolinite particles has been accomplished and the results published in the *Journal of Colloid and Interface Science*, 420, pp. 35-40 (2014).

With regard to bastnaesite flotation chemistry for the domestic recovery of RE values, there is currently a lack of RE production infrastructure and processing knowledge. Thus, extensive research is being conducted in order to make improvements and contributions to domestic RE production. Bastnaesite, a RE fluorocarbonate ($Ce,LaFCO_3$), is an important RE mineral and consists mainly of the cerium subgroup or the lighter REs. Concentration of bastnaesite is mainly achieved through flotation, which involves the surface chemistry aspects of the mineral interface. Consequently, surface chemistry aspects of bastnaesite flotation with octyl hydroxamate collector are being studied including the adsorption features and the corresponding hydrophobic surface state at low levels of hydroxamate adsorption. The chelating octyl hydroxamate collector is a possible collector for bastnaesite flotation because stability constants for the complexes formed between hydroxamic acids and RE metal cations are much larger when compared to other cations. Advanced experimental techniques include adsorption, sum frequency vibrational spectroscopy (SFVS) and molecular dynamic simulations (MDS). Both experimental contact angle measurements and MD simulations have demonstrated that bastnaesite is naturally hydrophilic. The adsorption features as well as the corresponding hydrophobic surface state at low levels of hydroxamate adsorption had not been described. Thus, octyl hydroxamate adsorption from aqueous solution at low concentrations is being studied utilizing the solution depletion method. The stability diagram of bastnaesite was obtained using Stabcal software (W32-STABCAL) for different pH values and the results show that bastnaesite transforms to cerium fluoride at low pH values. The adsorption isotherm at low concentrations indicates an increase in adsorption density when the hydroxamate concentration increases. For both the contact angle and adsorption density results, it appears that full monolayer coverage has been achieved (contact angle = 70-80^o, apparent adsorption density for monolayer coverage = 8.1 $\mu mol/m^2$). Above this point multilayer adsorption begins.

Sum frequency vibrational spectroscopy (SFVS) was used to identify conditions for what appears to be the formation of a well-ordered adsorbed state. Only two peaks appear in the spectra located at 2885-2890 cm^{-1} and 2945-2950 cm^{-1}, which are assigned to the symmetric stretching vibration (r^+) and the symmetric stretching Fermi resonance (r^+_{FR}) with a bending overtone of the CH_3 group, respectively. The absence of CH_2 vibrational modes in the spectra is an indication that the hydroxamate molecules are in an all-trans conformation.

The effects of different levels of hydroxamate coverage (8.3%, 25%, 50%) at the bastnaesite surface were studied using MD simulations. Results show that, when hydroxamate coverage increases, the contact angle from MD simulations also increases indicating an increase in the hydrophobicity. These results are consistent with observations from traditional experimental contact angle measurements.



MDS snapshot of the initial configuration and the configuration after 40 ps for a water droplet at a Ce-bastnaesite surface with 50% hydroxamate coverage.

Science Objectives for 2014-2016: Research objectives include continued surface chemistry study of the phyllosilicate minerals, chemistry of water films associated with air bubble attachment, and the flotation chemistry of bastnaesite. With respect to the flotation chemistry of bastnaesite, research will include adsorption experiments, SFVS, MDS, and contact angle measurements with the following objectives.

- To establish interfacial water structure for different levels of hydroxamate adsorption;
- To study bastnaesite at pH levels below about pH 6 and also with fluoride activation where CeF_3 is expected to be stabilized at the surface;
- To prepare other collectors and compare their adsorption to hydroxamate adsorption;
- To study MDS contact angles with different levels of collector coverage and compare to experimental results.

References to work supported by this project (2011-2014): Selected publications include,

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In addition to 17 journal/proceedings publications, 28 presentations were made between 2011 and 2014.

Fundamental Structure/Property Studies of Gas Separation Membrane Polymers

Benny D. Freeman, Principal Investigator
Kristofer Gleason, Postdoctoral Research Associate
Zachary Smith, Qiang Liu and Kevin Stevens, Graduate Research Assistants
Department of Chemical Engineering, University of Texas at Austin, Austin, TX 78758
Email: freeman@che.utexas.edu; Web: www.membrane.ces.utexas.edu

Overall research goals: Refinery, petrochemical, and natural gas industries, in particular, offer large opportunities for membranes, but they could benefit from more robust, higher performance membrane materials. The overarching goal of this fundamental, experimental research program is to systematically synthesize, characterize, and, ultimately, rationally tailor a novel class of polymeric membrane materials with the chemical and thermal stability as well as separation properties required for gas separation applications. This program will exploit and further develop our discovery that polymers prepared by thermal rearrangement of soluble aromatic polyimides containing *ortho*-positioned functional groups, such as OH, exhibit unusually high gas permeability and selectivity values. Furthermore, early studies of this class of materials suggest that they are very robust chemically (i.e., insoluble in all known solvents) and resistant to plasticization..

Significant achievements in 2012-2014:

Effect of gas mixtures and trace impurities on permeability and selectivity in TR polymers

Often, polymeric membranes have different transport properties for gas mixtures than would be predicted from studying permeation of pure gases. In order to study these differences, a system for studying gas mixtures was constructed, and this system was used to characterize the mixed-gas permeability of CO_2 and CH_4 in TR polymers derived from HAB-6FDA polyimides. The study was conducted as a function of temperature from -15 to 70 °C, and as a function of the degree of TR conversion. For many polymers, CO_2 acts as a plasticizer. As a result, permeation experiments involving mixtures of CO_2 often exhibit lower selectivity. Our mixed-gas studies revealed that these materials are resistant to CO_2 induced plasticization. Competitive sorption affects the transport properties to a much greater degree and acts to increase the overall CO_2/CH_4 selectivity for mixtures. Figure 1A presents CO_2/CH_4 selectivity results at 35°C for an HAB-6FDA TR polymer thermally treated at 450°C for 30 min. At the lowest pressures considered, selectivity for gas mixtures is approximately 20% higher than that predicted by pure gas experiments.

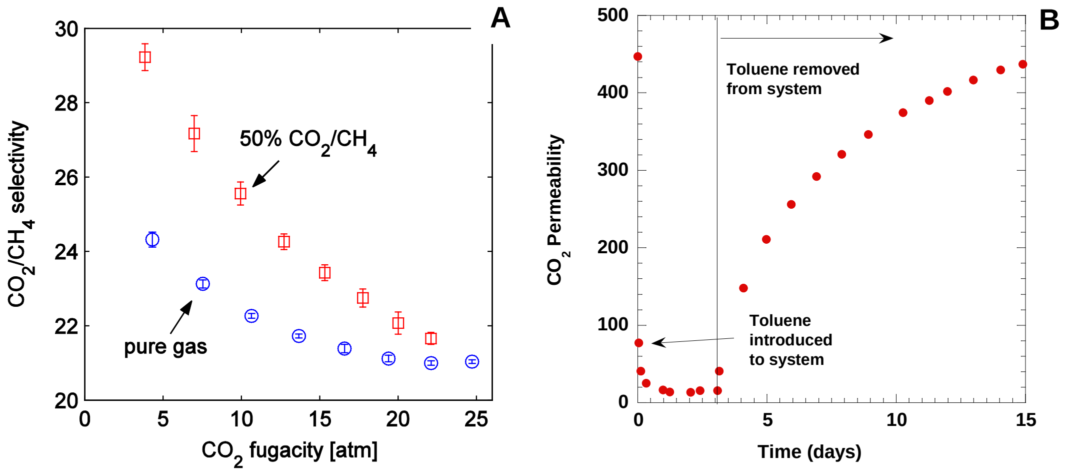

Figure 1: Transport results for an HAB-6FDA TR polymer at 35°C. (A) CO_2/CH_4 selectivity for pure gas and mixed gas experiments, and (B) CO_2 pure-gas permeability at 10 atm before and after film exposure to toluene.

Enhanced CO_2/CH_4 selectivity due to competitive sorption indicates additional implications for transport in TR polymers. Therefore, to investigate this phenomena more thoroughly, we extended our work to study CO_2 and CH_4 permeability before, during, and after exposure to toluene vapor; the results for CO_2 and toluene for the same TR polymer considered in Figure 1A are presented in Figure 1B. Toluene vapor (at 75% saturation) was introduced to a pure gas feed at approximately 10 atm and 35°C using a syringe pump constructed to accurately control the toluene flowrate. Following injection, CO_2 and CH_4 permeabilities decreased by more than 95 percent and CO_2/CH_4 selectivity increased from 19 to 31. Upon removing toluene, CO_2 permeability returned to 60% of the pure-gas value after 3 days and to nearly 100% of the pure-gas value after 15 days. These results indicate strong competitive sorption effects, but also show that CO_2 permeability can be almost completely recovered.

Science objectives for 2014-2016:

- Work will continue with studying the HAB-6FDA polyimide and TR polymer for additional gases and gas mixtures. In particular, we will investigate the effect of water vapor on permeability. These tests are designed to better understand the potential utility of TR polymers in aggressive feed conditions such as those experienced in flue gas streams for carbon capture applications.
- We are furthering our basic structure/property studies by testing a series of polyimides and TR polymers with chemical structures different to that of HAB-6FDA. These tests are focusing on several gases, including H_2, N_2, O_2, CH_4, CO_2, C_2H_4, C_2H_6, C_3H_6, and C_3H_8.
- We are continuing our characterization work on TR polymers to better understand their chemical structure and morphology. For these experiments, we have designed two nearly-identical TR polymer structures, one that is soluble in NMR solvents and one that is insoluble. We are analyzing 1-D and 2-D solution and solid-state NMR experiments to confirm the chemical structure of these polymers, and we are comparing these characterization results with transport properties.

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

Randall Q. Snurr
Joseph T. Hupp, SonBinh T. Nguyen, Omar K. Farha, Co-Principal Investigators
2145 Sheridan Road, Northwestern University, Evanston, IL 60208
Email: snurr@northwestern.edu; Web: zeolites.cqe.northwestern.edu

Collaborators: Prof. Paul Forster, University of Nevada, Las Vegas
Prof. Alexandra Navrotsky, University of California, Davis
Dr. Craig Brown, National Institute of Standards and Technology

Overall research goals: The research objectives are to understand, design, 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).

Significant achievements in 2012-2014: A key development in our recent work on the modeling side of this project has been the development of high-throughput computational screening methods for discovering new MOFs, or identifying existing MOFs, that have superior chemical separation capabilities [1-6]. Subsequent experimental syntheses have confirmed the effectiveness of the approach [1]. The computational approach provides a means for evaluating many more candidate materials than could ever be examined experimentally. In addition to suggesting candidate materials, high-throughput computational screening can also provide new insights and structure/property relationships from the enormous amount of data generated. As one example, we have studied over 137,000 hypothetical MOFs to find structure/property relationships for CO_2 separation and capture applications [3]. The resulting data exhibit sharply defined structure/property relationships that were not apparent when smaller collections of MOFs were considered. We showed clear correlations between purely structural characteristics (e.g. pore size, surface area, and pore volume), as well as chemical characteristics (i.e. functional groups), with five adsorbent evaluation criteria taken from the engineering literature. These relationships can serve as a guide for experimental synthesis going forward. In the past year, we have probed the limits of the methods [4] and applied the methodology to new problems [5].

For particular systems, we have also made detailed comparisons of predictions from molecular simulation with experiments from collaborators [1, 7] and from our own lab [8]. For example, we had previously suggested that MOF-505 should be a good candidate for Xe/Kr separations based on grand canonical Monte Carlo (GCMC) simulations [9]. Our collaborators, Hupp and Farha, synthesized MOF-505 and HKUST-1, and we analyzed the Xe/Kr separation behavior of these materials in a column breakthrough experiment, demonstrating the high selectivity predicted by simulation (selectivity ~ 9-10) [8]. For HKUST-1, we found very good agreement between simulation and experiment for the heats of adsorption of Ne, Ar, Kr, and Xe measured by Forster and Navrotsky [7] as shown in Figure 1, as well as siting locations determined from diffraction measurements by Brown [7]. Other work (e.g. method development [10-13] and propane/propylene separation [14-16]) is also underway.

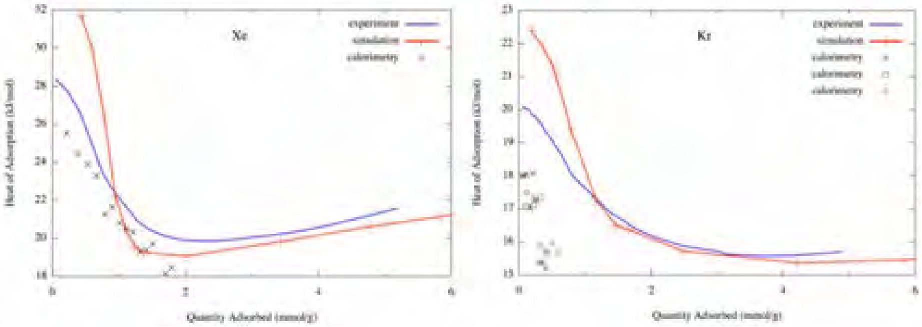

Figure 1. Comparison of heats of adsorption in HKUST-1 determined by GCMC simulation, calorimetry, and variable-temperature isotherms [7].

Science objectives for 2014-2016:

- Expand high-throughput computational screening to a much wider array of MOF topologies and exploit this capability to identify MOFs for desired chemical separations.
- Develop modeling strategies for MOFs with accessible metal sites being developed in the experimental portion of this project.
- Test new MOFs featuring accessible metal sites featuring unusually low coordination numbers for chemical separations in breakthrough measurements.

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Energetics of Nanomaterials

Brian F. Woodfield,[1] Principal Investigator
Alexandra Navrotsky[2] and Nancy Ross,[3] Co-Principal Investigators
[1]Department of Chemistry, Brigham Young University, Provo, UT 84602
[2]Peter A. Rock Thermochemistry Laboratory and NEAT ORU, UC Davis, Davis, CA 95616
[3]Department of Geosciences, Virginia Tech, Blacksburg, VA 24061
Email: brian_woodfield@byu.edu, anavrotsky@ucdavis.edu, nross@vt.edu

Overall research goals: The overarching objective of this project is to develop understanding and predictive systematics for the thermodynamic properties of nanomaterials, their anhydrous and hydrated surfaces, the confinement of molecules in 2D and 3D environments, and to apply such knowledge to systems of importance to DOE fundamental science grand challenges and energy technology.

Significant achievements in 2012-2014:

- 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 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.
- Enthalpies of formation of $Co_x Zn_{1-x}O$ solid solutions (both bulk and nanophase materials) at 298 K have been determined at 973 K. Both the rocksalt and wurtzite phases show an approximately linear dependence of enthalpy of solution on composition, implying a zero heat of mixing in each phase, consistent with negligible lattice parameter changes on substitution of Co^{2+} for Zn^{2+}.

Science objectives for 2014-2016:

- What chemical forces, interactions, and mechanisms drive confinement and reactivity in porous systems?
- What roles do structure, guest-host bonding, and thermodynamics play in confinement of ions, molecules, and water as a function of adsorption, pore size, and local geometry?
- What is the ***emergent behavior*** resulting from host - guest interactions in systems with complex chemistry and complicated multiscale pore systems?

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Plus 14 additional papers

Computer Simulation of Proton Transport in Fuel Cell Membranes

Gregory A. Voth

Department of Chemistry and The James Franck Institute, The University of Chicago, 5735 South Ellis Avenue, Chicago IL 60637

Email: gavoth@uchicago.edu

Web: http://vothgroup.uchicago.edu

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 2012-2014: Continuing our investigations of proton transport in the hydrophilic pores of perfluorsulfonic acid (PFSA) membranes using reactive molecular dynamics simulations, we examined the effect of PFSA side-chain length and polymer morphology. We undertook two separate studies, one comparing Nafion with the medium sized side-chain membrane manufactured by 3M, the other comparing the short side-chain membrane Hyflon with 3M. While we obtained the correct trends in diffusion constant when comparing between these membranes, we do not see the expected magnitude of difference one would expect from the conductivities of these membranes. This suggests the morphology and/or crystallinity differences between these membranes contribute at least as much as the local proton diffusion differences.

In the study comparing Hyflon and 3M, we reparameterized the interaction between the sulfonate group and the hydronium to closer match *ab initio* data. Given the lower attraction of the hydronium to the sulfonate, one would expect faster diffusion, however we did not observe this behavior. On investigating this surprising result, we discovered the proton always resides within two solvation shells of the sulfonate group and so proton passing between sulfonate groups is more important than the protons having to leave the potential well of a sulfonate group altogether (cf. Fig. 1).

Building on observations of sub-diffusive proton transport in amphiphiles like urea, we examined the long-time dynamic behavior of water and excess protons in PFSA membranes. We found that, similar to amphiphilic systems, water and protons show sub-diffusive behavior at timescales up to nanoseconds. The extent of sub-diffusive behavior is strongly dependent on water concentration and so is quite evident in the low water concentration environment of PFSA systems. This highlights the need for longer simulation times as provided by our methodology to fully investigate the long-time dynamics of these systems.

Based on the methodology developed previously in our group using smoothed particle hydrodynamics (SPH), we have extended our study of proton transport in PEM at mesoscale to different morphologies. We have calculated the conductivities for lamellar, cylinder, cluster and random morphologies at different hydration levels (cf. Fig. 1), and our results show that the conductivities of lamellar and cylinder are greater than that of cluster and random morphologies, which arises from the higher porosity and tortuosity of cluster and random morphologies.

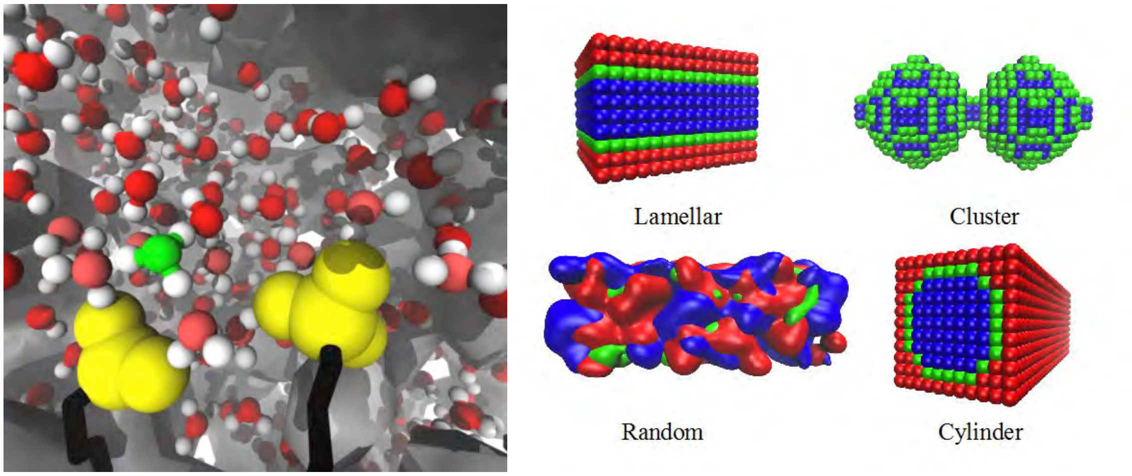

Figure 1 (Left) Detailed information from reactive MD simulations is being used to parameterize large-scale coarse-grained simulations in order to bridge simulation and experiment. (Right) Mesoscopic models for PEMs with different morphologies in SPH calculations.

Science objectives for 2012-2014:

- The coarse-grained SPH methodology is still under further development to obtain better bridging with MD simulation data. We are extracting position-dependent diffusion constants from existing reactive MD simulations and will use these as inputs for our SPH calculations. We plan to take advantage of the parallelizability of the SPH method to simulate extremely large systems beyond the reach of atomistic simulations.
- Using advanced parallelization algorithms for our reactive simulations, we now have the capability to run longer trajectories to investigate the long-time proton and water dynamics in PFSA systems. This will allow us to examine proton transport well past the sub-diffusive regime. We will also be able to study this process under a constant applied potential due to our new advances modeling such systems.
- In order to further investigate the importance of morphology on proton transport, we will examine three morphological models; Schmidt-Rohr's cylinder model, Rubatat's rod model, and Kreuer's lamellar-like model. These simulations will be designed to match experimental dimensions, and will be larger than our previous work in order to examine interactions between pores as well as transport within pores.

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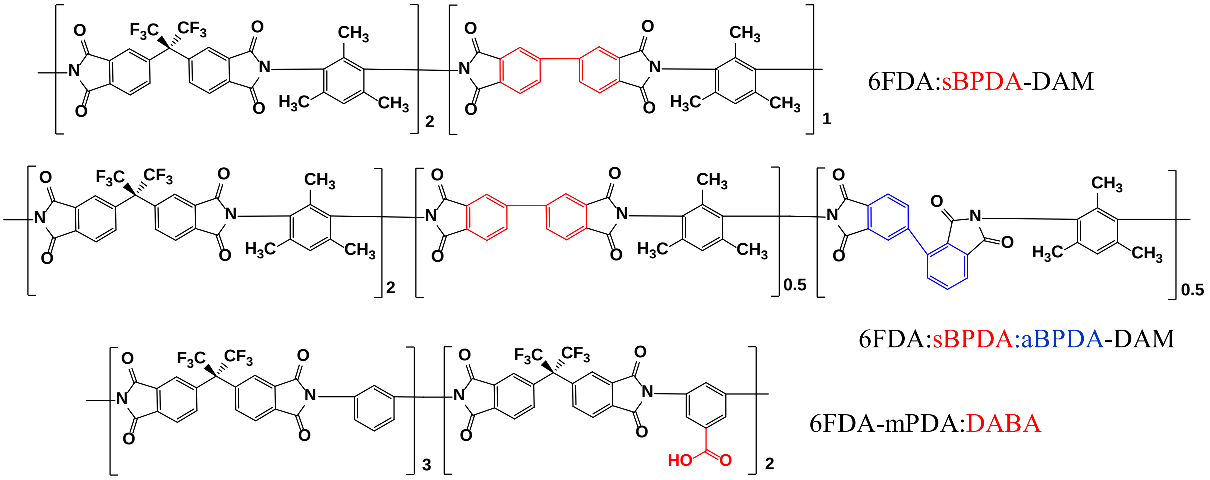
Precisely Tunable High Performance Carbon Molecular Sieve Membranes for Energy Intensive Separations

W. J. Koros, Principal Investigator
Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100
Email: wjk@che.gatech.edu

Overall research goals: The research objective is to develop an improved fundamental framework to guide the systematic understanding and formation of carbon molecular sieve (CMS) membrane materials appropriate for important energy intensive separations. The final gas separation performance of CMS membranes achieved by systematic variations in precursor polyimide structures and pyrolysis protocols is being investigated in the work.

Significant achievements in 2012-2014: More than 10 kinds of precursor polyimides have been designed and synthesized successfully. These polymer sets have systematic and comparable chemical structures, such as polyimides containing *symmetric or asymmetric backbone structure*, polyimides containing block or random backbone structure, polyimides with –CF_3 group was replaced by -CH_3 group, and polyimides containing crosslinkable sites. Typical examples of the precursor polymers are shown in Scheme 1.


6FDA:sBPDA-DAM

6FDA:sBPDA:aBPDA-DAM

6FDA-mPDA:DABA

Scheme 1. Polyimides containing symmetric and asymmetric backbone, and crosslinkable site.

The thermal degradation temperatures, which were used to evaluate the pyrolysis conditions, of the polymers were measured by using TGA. CMS membranes were made from some of the polyimides synthesized, under different pyrolysis temperatures of 500, 550, 675, and 800 °C. These CMS membranes were characterized with FTIR, Raman, WAXD, and XPS.

All polyimide membranes showed typical characteristic imide absorbance peaks at about 1780, 1720, 720, and 1357 cm^{-1}, while the resulting CMS membranes showed quite different FTIR spectra from their precursor polymer membranes after pyrolysis. The intensities of characteristic bands in precursor polymer sample decreased significantly and even disappeared under higher pyrolysis temperature, as can be seen in Figure 1a. WAXD results showed that all these polyimides membranes and CMS membranes are amorphous, and the average interchain distance (*d*-spacing) of all CMS membranes decrease with the increasing of pyrolysis temperature. The amorphous pore structure of CMS membranes was also indicated by Raman spectra, as shown in Figure 1b. The pores in CMS materials are believed to be formed by packing imperfections of small graphene-like sheets, while on the long range CMS materials are amorphous. The crystalline graphite is marked by the G peak at about 1580 cm^{-1}; The peak at about 1350 cm^{-1} is known as D peak (D for defect or disorder). The intensity of the D band and the ratio between the intensities of the disorder-induced D band and the graphite G band provides a parameter that can be used to quantify disorder of the carbon materials. XPS spectra of CMS membranes showed that there are C, O, and N elements in the materials. The C elements were found exist as graphene-like sp^2 C (C-C), N-sp^2 C or C-O, and C=O type bond C; The O elements as C=O, C-OH, O-C-O, COOR types; And the N elements as pyridinic N, pyrrollic N or pyridinium-like N, and graphitic N.

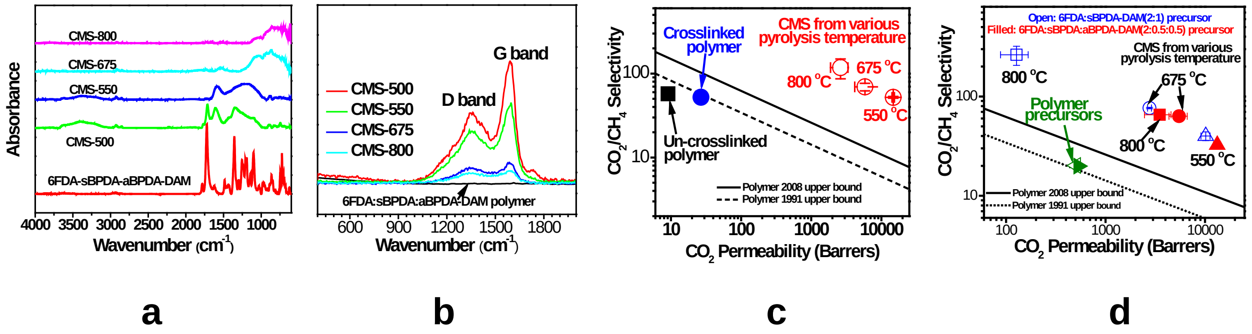


Figure 1. FTIR (a), Raman (b), and separation properties (c) and (d) of typical CMS membranes.

The separation performance of CMS membranes was significantly higher than those of precursor polymer membranes, and exceeded the so-called polymer upper bond. An increase in pyrolysis temperature leads to higher CO_2/CH_4 selectivity, but lower CO_2 permeability. The CMS membranes from crosslinkable 6FDA-mPDA:DABA(3:2) polymer (Figure 1c) showed higher permeabilities than most CMSs from other polymers reported. CMS membranes derived from asymmetric polyimides showed higher gas permeabilities than those from symmetric polyimides, especially made at higher pyrolysis temperature, as can be seen in Figure 1d.

Science objectives for 2014-2016:

- Gas permeation will continue to be performed on the CMS membranes, and sorption will be performed also on specific polymers as well as resulting CMS membranes.
- CMS membrane from other synthesized polyimides will be made, characterized, tested their gas separation performance, and will be connected with structures.
- Fundamental structures and properties of CMS membranes will be studied by using IR, NMR, Raman, XPS, and XRD techniques.

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Understanding the Structure-derived Function of Porous Adsorbents Relevant to Energetically Favorable Industrial Gas Separations

Wendy L. Queen, Principal Investigator
1 Cyclotron Road, The Molecular Foundry, Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA 94720
Email: wlqueen@lbl.gov; Web: http://foundry.lbl.gov/people/wendy_queen.html

Collaborators: Dr. Jeff Long, Department of Chemistry, University of California, Berkeley
Dr. Craig Brown, NIST Center for Neutron Research
Dr. Jeff Neaton, The Molecular Foundry, Lawrence Berkeley National Laboratory
Dr. Berend Smit, Department of Chemical and Biomolecular Engineering, Univeristy of California, Berkeley
Dr. Laura Gagliardi, Department of Chemistry, University of Minnesota

Overall research goals: The research objectives are to understand how varying the structural features of metal-organic frameworks (MOFs) alters gas adsorption/separation properties; elucidate small molecule interactions on framework surfaces; understand effects of various stimuli on frameworks; gain the insight necessary to tune known materials or design new materials for targeted applications.

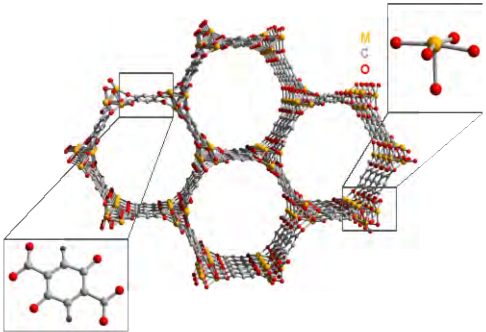

Figure 1. M-MOF-74 framework (M=Mg, Mn, Fe, Co, Ni, Cu, or Zn) showing the open metal-coordination site (top right) and the 2,5- dioxido-1,4-benzenedicarboxylate ligand (bottom left).

Significant achievements in 2012-2014: M-MOF-74 is a family of isostructural MOFs that exhibit a hexagonal array of nanosized channels. This framework is a rarity in MOF chemistry as it can undergo chemical substitution with a wide variety of metals affording us a rare opportunity to probe structure-property relations while changing only one variable. From a fundamental perspective, understanding the structural features that give rise to enhanced or diminished adsorption properties are important for the design of new materials for targeted applications such as carbon dioxide capture. However, synthesizing and screening the nearly infinite number of possible frameworks is inefficient; therefore, the development of accurate computational tools aimed at structure and property prediction is needed. Experimental validation of developing theoretical tools is currently underway.

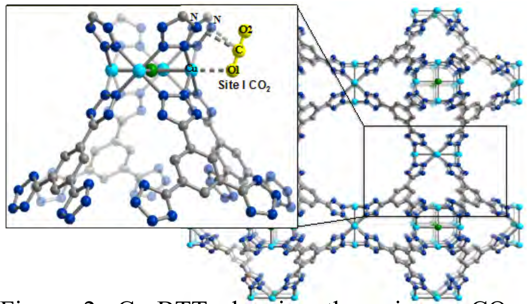

Figure 2. Cu-BTT showing the primary CO_2 adsorption site I at the open Cu^{2+} (cyan) coordination site. Other atoms including N, C, and Cl are drawn as dark blue, grey, and green spheres, respectively.

We have developed *in-situ* methodologies for both powder X-ray and neutron diffraction measurements and utilized these tools in tandem with gas adsorption measurements to unveil molecular level detail of the adsorption of CO_2 and C2 and C3 hydrocarbons within the extensive MOF-74 framework family. Most recently we were able to provide experimental validation to DFT modeling applied to CO_2 adsorption in a family of frameworks known as M-BTT (Figure 1). Our experiment verified that simulations were able to accurately predict binding site locations and binding energies of adsorbed CO_2 molecules within this extensive compound family. We have further begun looking at the adsorption of other small energy-related molecules such as water, and using an ad-hoc dosing apparatus we were able to utilize neutron diffraction to unveil a hydrogen-bonding network within a Zr-containing metal-organic framework.

From the position averaged powder diffraction studies, it is often difficult to discern slight differences in distances between the framework and surface bound guest species and to extract very fine structural detail associated with slight changes in bond distances and angles of surface bound guest species. As such, we have designed an *in-situ* cell for single crystal X-ray diffraction as a means to obtain high-resolution single crystal structures of CO_2 adsorption in MOF-74 and other framework families.

Science objectives for 2014-2016:

- Use the developed *in-situ* techniques to continue to understand the adsorption behavior of small, energy-related molecules such as N_2, O_2, CO_2, H_2O, H_2, H_2S and CH_4 within several new framework families, such as zeolitic imidazolate frameworks, to further understand how to tune these materials for targeted function.
- Utilize these studies as a means to validate on-going computational work meant to predict the structure and properties of porous adsorbents.
- Continue development of *in-situ* cells for single crystal X-ray diffraction, tools that will be incorporated into the general user base of the Advanced Light Source.
- Begin the development of other *in-situ* cells that can be used for spectroscopic characterization as a means to probe, for example, vibrational modes of surface bound guest species.

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Molecular-Level Investigation of Diffusion Behaviors within Cylindrical Nanoscale Pores

Takashi Ito, Principal Investigator
Daniel A. Higgins, Co-Principal Investigator
Rajib Pramanik, Postdoctoral Research Associate; Khanh-Hoa Tran-Ba, Seok Chan Park, Hao Xu, Ruwandi Kumarasinghe, Dol Sapkota, Graduate Students
Department of Chemistry, Kansas State University, Manhattan, KS 66506-0401
Email: ito@ksu.edu; Web: http://www.ksu.edu/chem/people/faculty/ito.html

Collaborator: Dr. Naohiro Kameta, AIST, Japan

Overall research goals: The overall goal of this project is to develop a quantitative molecular-level understanding of mass transport phenomena within solution-filled nanoporous media. Cylindrical nanopores with well-defined sizes and surface properties are employed as model systems to understand key molecular-level mechanisms governing the rate and selectivity of ensemble molecular behavior within nanoporous media. Single-molecule and ensemble mass transport behavior is measured within identical cylindrical nanopores having well-defined diameters and surface properties. New experimental approaches are developed as means to overcome limitations of existing ensemble and single-molecule methods. The knowledge gained will aid in the engineering of nanoporous materials optimized for specific applications relevant to energy science, including membrane separators for fuel cells and batteries and nanoporous supports for catalysis.

Significant achievements in 2012-2014:

1. Quantitative measurements of the restricted orientational motion (wobbling) of single molecules confined within nanopores. We have established simultaneous single-molecule tracking (SMT) and single-molecule emission polarization measurements to assess the translational and orientational motions of single molecules diffusing within cylindrical nanopores (Figure 1). Data obtained for rod-shaped molecules within surfactant-filled silica nanopores indicate that the molecules are, on average, oriented with their long axes parallel to the long axis of the nanopores. Interestingly, the fluorescence emission polarization (FP), calculated from the single molecule emission data, is smaller than expected for perfect parallel orientation. The smaller FP results from orientational motions of the molecules within the nanopore and permits the wobbling angle to be calculated. The wobbling angles are larger for shorter molecules, as expected. The results yield an effective cavity diameter for molecular diffusion (*ca.* 1 nm), which is much smaller than the expected silica pore diameter (*ca.* 4 nm). This difference is attributed to confinement of the dye within the hydrophobic cores of the surfactant micelles incorporated within the silica framework. Measurements of single molecule wobbling will help clarify the molecular-level origins of selectivity in nanoporous materials and will aid in the design of better materials for separations and catalysis.

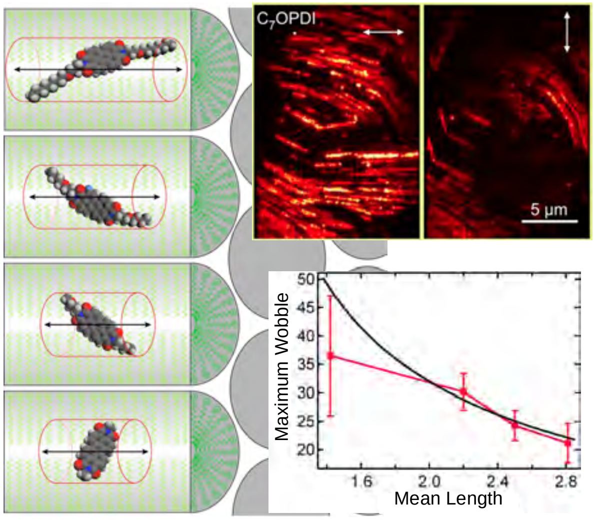

Figure 1. Left: Perylene diimide dyes having different lengths wobble within surfactant-filled cylindrical silica mesopores. Right: (Top) Polarized fluorescence images depicting 1D single-molecule motions in surfactant-templated mesoporous silica. Double-ended arrows depict the detected polarization. (Bottom) Wobbling angle versus molecular length.

2. Quantitative assessment of ensemble and single-molecule diffusion in identical sample regions. We have established a means to assess the ensemble and single-molecule diffusion behavior in the same sample region by combining two fluorescence-based methods: fluorescence recovery after photobleaching (FRAP) and SMT. Thin films of a block copolymer (BCP) with cylindrical domains aligned via solvent vapor penetration are used for this demonstration. Here, FRAP is first employed to measure the ensemble diffusion coefficient. The majority of fluorescent probes are subsequently photobleached. SMT data are then recorded to measure diffusion coefficients for the single molecules. Both methods yield similar diffusion coefficients, though SMT data offer detailed information on the distribution of diffusion behaviors at different depths. These methods can also be used to independently assess domain alignment from the recovery profile in FRAP and the diffusion direction of individual molecules in SMT. Importantly, FRAP data affords a measure of the effective long-distance connectivity of the cylindrical domains. The accuracy of these results is improved by utilizing SMT data on the fractions of fixed and mobile molecules in the analysis.

3. Pursuit of other methods to prepare well-aligned cylindrical nanopores. We have also pursued the following approaches to prepare thin films comprising well-aligned cylindrical nanopores: (i) Flow-induced alignment of mesoporous silica nanopores and BCP domains; (ii) Plasma treatment to remove template surfactants from mesoporous silica films; (iii) Preparation of nanoporous anodic oxides from metallic gallium; and (iv) Aligned immobilization of organic nanotubes.

Science objectives for 2014-2016:

- Systematically investigate single-molecule diffusion and wobbling within the nanopores to understand the influence of electrostatic and chemical interactions on these phenomena.
- Systematically investigate single-molecule and ensemble diffusion behavior in cylindrical nanopores with different dimensions and chemical properties using the FRAP-SMT method.
- Establish simple methods to obtain well-aligned cylindrical nanopores and organic nanotubes.

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Molecular Aspects of Transport in Thin Films of Controlled Architecture

Paul W. Bohn, Principal Investigator
318 Stinson-Remick Hall, University of Notre Dame, Notre Dame, IN 46556
Email: pbohn@nd.edu; Web: http://www.bohnresearchgroup.com

Overall research goals: The research objectives are to develop an understanding of the complex factors that couple reactions to transport under confined/crowded conditions in nanoscale architectures; study reactions in organized geometries that support vectorial transfer of reactants and products in sequential chemical transformations; and determine the role/mechanisms of biofouling in electrokinetically controlled nanoscale architectures.

Significant achievements in 2012-2014: *Tight Coupling of Transport and Reactions*. The coupling of electrochemical potential to electrokinetic flow was observed in nanopore devices containing embedded annular nanoband electrodes (EANEs). The electrochemical signal (current) generated by redox-active molecules passing through EANE-containing pores is enhanced ~40X due to electrokinetically-driven advection in the nanopores, when small voltages are applied between internal EANE electrodes. In addition, we studied the impact of internal and external electric fields on electrochemical measurements performed in both micrometer and nanometer scale channels. When electric fields are induced, the half wave potential ($E_{1/2}$) for the redox process shifts to more negative potentials. Interestingly, the shift in $E_{1/2}$ is linear with the electric field-induced current, rather than the voltage. The use of a secondary electric field allows for increased electrode signal as a function of electrode position and potential, Fig. 1(a).

Nanoconfined Catalysis. Previous BES-supported work from our lab demonstrated that enzyme kinetics are enhanced in nano-confined spaces. These experiments are now being extended by measuring the kinetics of horseradish peroxidise (HRP) immobilized in nanochannels. The activity of HRP is evidenced by the formation of a fluorescent product (resorufin), which is produced during the HRP-catalyzed oxidation of amplex red. A novel experimental structure has been designed and tested which permits kinetics to be studied under multiple reaction conditions simultaneously, by using a gradient mixer, which injects reagents into each of 11 separate nanochannels at different reactant concentrations. Then wide-field fluorescence imaging is used to take a snapshot of the enzymatic kinetics across multiple dimensions of time (position along the axis of any given nanochannel) and concentration (different nanochannels), as shown in Figure 1(b).

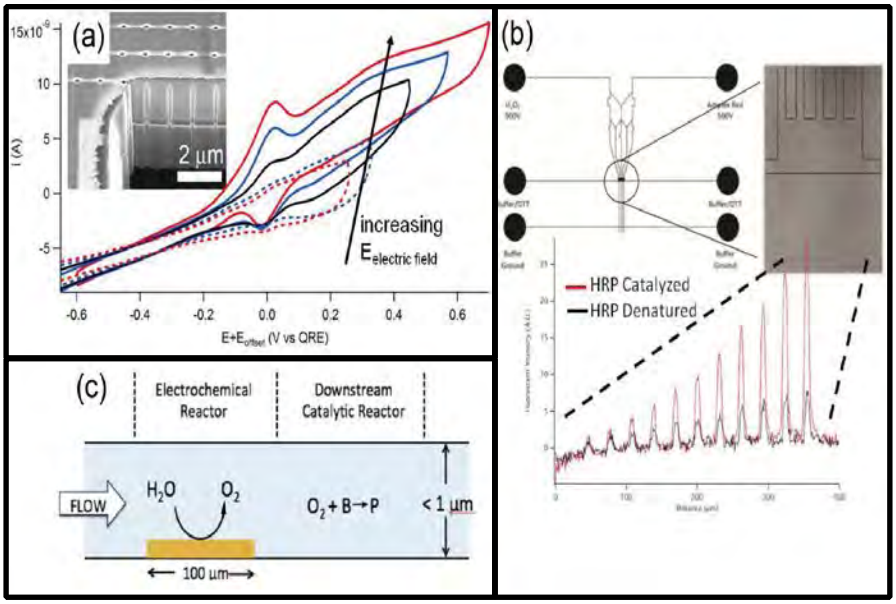

Figure 1. (a) Cyclic voltammetry of 0.1 M $Fe(CN)_6^{3-/4-}$ recorded at EANEs within nanopores (*inset*: cross-sectional SEM image of nanopore-EANE array. (b) Micromixer/ nanochannel used to study biofouling in nanochannels (*insets*: bright field view of nanochannel/micromixer interface and fluorescence intensity in each nanochannel with and without the reaction catalyst, HRP). (c) Diagram depicting sequential processing in a nanoscale system with oxygen generation followed by a downstream catalytic oxidation reaction.

In Situ Reagent Generation. We have also explored the use of water electrolysis in a planar nanoscale device to manipulate the local solution composition with the goal of coupling *in situ* generated species to high efficiency catalytic transformations downstream and using the unique transport characteristics of nanoscale architectures, *e.g.* ultralow Peclet numbers. We have used the fluorescence of a pH-sensitive dye, fluorescein, to monitor the generation of highly concentrated regions of OH^-/H_2 and H^+/O_2 during H_2O reduction and oxidation, respectively, within nanochannels, Fig. 1(c). Finite element simulations were used to model transport and reaction in the nanoscale systems and yielded good agreement with experimental observations. The combined results of experiment and simulation provide insight into the availability of generated reagents (OH^-/H_2 or H^+/O_2) as a function of electrolysis rate and device geometry, guiding ongoing work to incorporate catalytic materials into nanofluidic systems for high efficiency reactions.

Science objectives for 2014-2016:

- Construction and characterization of multiple-EANE structures to combine multiple reaction, detection, and chemical processing steps coupled by vectorial transport within a single nanoscale environment.
- Integration of nanofluidic reagent generation with downstream catalytic oxidation/reduction reactions. Reactor performance will be verified using theoretical calculations and finite element simulations and compared to reactions performed in bulk (unconfined) systems.
- Continuation of studies of enzymatic catalysis in confined geometries under well-defined flow conditions, using fluorescently tagged proteins and/or fluorigenic reactions. We will focus on the coupling between reagent delivery and overall reaction velocity, taking advantage of the low Peclet number flow regimes characteristic of nanofluidics.
- Application of single molecule spectroscopy to study the behavior of nanoconfined oxidoreductase enzymes using both fluorescence correlation spectroscopy and direct emission in nanophotonic structures, *i.e.* zero-mode waveguides.

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Separations and Analysis using Bipolar Electrodes

Richard M. Crooks, Principal Investigator
Stephen E. Fosdick and Kyle N. Knust, Graduate Students
Department of Chemistry, 105 E. 24th St Stop A5300, The University of Texas at Austin, Austin, TX 78712-1224 Email: crooks@cm.utexas.edu Web: http://research.cm.utexas.edu/rcrooks/

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

Overall research goals: The purpose of this research project is to develop the scientific principles underpinning novel electrochemical methods for solving problems related to analysis of materials and continuous-flow, membrane-free separations.

Significant achievements in 2012-2014: **Method development for materials analysis.** During the present contract period, we have developed a simple and effective method for the analysis of electrocatalysts using bipolar electrodes (BPEs). In this analytical method, materials are deposited at the cathodic poles of individual BPEs, the arrays are placed inside a confined fluidic cell containing electrolyte solution, and then a voltage is applied across the array. Figure 1 shows the general scheme of the screening experiment. Initially, the dissolution (oxidation) of Ag microbands was used as a reporter for the oxygen reduction reaction (ORR). The number of microbands removed during the experiment relates to the electrocatalyst activity. The readout is simple: better electrocatalyst materials result in more bands dissolving. We've subsequently developed the technique to test bi- or trimetallic combinatorial electrocatalyst candidates prepared by piezo-dispensing for the ORR and hydrogen evolution reaction (HER). To enhance the reliability and stability of the readout, the anodic reporter was changed from Ag to Cr.

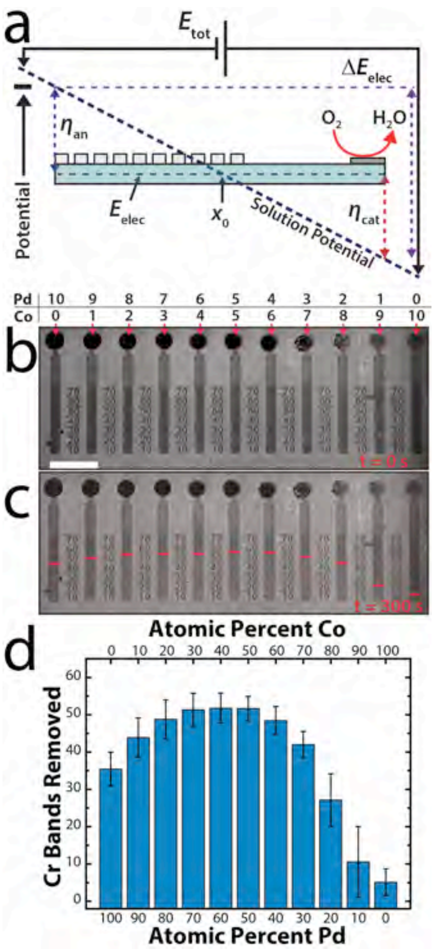

Figure 1. (a) Schematic illustration of the potential differences that drive the BPE. (b, c) Micrographs of BPE arrays before and after screening experiment for the ORR using a Pd-Co bimetallic system. The red bars indicate the last intact Cr microband. (d) Histogram of the performance of the Pd-Co system.

Ion separation from water. The formation of an ion depletion zone and local electric field gradient near a BPE can be used to control the movement of charged species. We're now developing a method to continuously separate ions in solutions containing Cl^-. Importantly, Cl^- oxidation to Cl_2 results in the neutralization of Cl^-, thereby forming an ion depletion zone and local electric field gradient. We demonstrated the bulk separation of ions from water using the device shown in Figure 2a. Our collaborators have performed numerical simulations confirming the local electric field and ion separation is induced by Cl^- oxidation. A pressure driven flow (PDF) results in ionic movement toward the outlets. However, as ions approach the local electric field gradient, they experience an increasing electrophoretic velocity that separates them into the brine stream (Figure 2c). The principle criterion for ion separation is based on differences in electrophoretic mobility, meaning that by tuning the local electric field strength, the varying properties of ions result in different rates of migration, and hence separation. The findings in this part of the project are very important, because they provide a first step toward the development of membrane-free separation methods. The elimination of membranes, if found to be effective, should lead to lower operational costs due, primarily, to energy savings.

Science objectives for 2014-2016:

- Method development of the BPE-based materials analysis tool is now complete and will not be continued under support of this DOE program.
- We plan to continue development of the membrane-free separation method described in the second part of the abstract. This will include further refinements of the theoretical and experimental principles necessary to fully exploit the methodology, including: (1) increased separation efficiency; (2) increased separation selectivity; (3) decreased energy input; (4) simplification of the required apparatus.

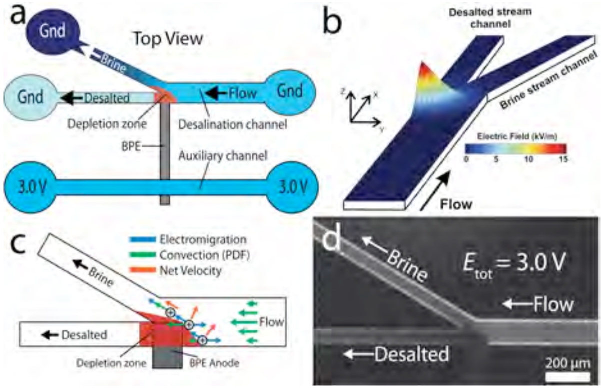

Figure 2. (a) Schematic of the BPE ion separation device. (b) Simulated distribution of the electric field in the central plane (z = 11 μm) of the BPE device for a 0.55 M NaCl solution. (c) Schematic of ion separation near the Y-intersection due to a local depletion zone and electric field strength. (d) Fluorescence micrograph showing the separation of 20.0 μM $[Ru(bpy)_3]^{2+}$ tracer into the brine stream. In all cases, the channel height is 22 μm, with widths of 100 and 50 μm for the inlet and outlets. The total PDF is ~0.08 μL/min.

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Fundamental Studies of Novel Separations

Sheng Dai, Principal Investigator
Co-PIs: De-en Jiang and Shannon Mahurin
Postdoctoral Research Associates: Hongjun Liu, Jinshui Zhang
1 Bethel Valley Road, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831
Email: dais@ornl.gov; Web: http://web.ornl.gov/sci/csd/Research_areas/NC_group.htm

Collaborators: Dr. E. Mamontov and Dr. L. He, SNS, Oak Ridge National Laboratory

Overall research goals: The overarching goal of this program is to investigate fundamental issues of chemical separations by nanostructured architectures and unconventional media that selectively bind and/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 in 2012-2014:

(1) We began measuring the effect of added nitrogen functionality on the gas transport properties through ionic liquids. Varying the functional group enabled us to control the permeability and selectivity thus allowing us to examine how structural properties affected gas transport properties.

(2) We performed detailed and realistic simulations of gas permeation through porous graphene by using classical MD simulations, to obtain permeance and selectivity trend that could be directly compared with experiment. Good agreement was achieved, suggesting that the size is the main factor dictating gas selectivity by porous graphene.

(3) We explored the use of an aromatic trimerization reaction to create polymeric membranes with high microporosity and inherent nitrogen-containing sites.

(4) In effort to develop controlled free volumes in membranes, we have explored a number of synthesis methodologies for making nanoparticle empty spheres.

Science objectives for 2014-2016:

- Examine gas transport properties of porous ionic liquids and polymer membranes by combining carbon nano-shells with a viscous ionic liquid and measuring permeability and selectivity.
- Neutron scattering will be explored as methods to correlate structure and transport properties of CO_2 adsorption and diffusion in ionic liquids and carbon materials.
- Predict gas solubility in ionic liquids by free-energy calculations based on MD simulations; examine the structure and energetics of different N functional groups in carbons; simulate the effect of N-doping on gas adsorption and diffusion.

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Graphene Membranes with Tunable Nanometer-Scale Pores

Rohit N. Karnik
77 Massachusetts Avenue, MIT Room 3-461A, Cambridge MA 02139
Email: karnik@mit.edu; Web: web.mit.edu/karnik/www/home.htm

Collaborators: Dr. Juan-Carlos Idrobo, Oak Ridge National Laboratory, Oak Ridge, TN 37831
Dr. Jing Kong, Massachusetts Institute of Technology, Cambridge, MA 02139
Dr. Tahar Laoui, King Fahd University of Petroleum and Minerals, Saudi Arabia

Overall research goals: The research objectives of this project are to systematically study the effect of ion irradiation, nitrogen doping, and chemical oxidation to create tunable, nanometer-scale pores in graphene membranes, and to elucidate the transport characteristics of the resulting membranes at the single pore and ensemble levels.

Significant achievements in 2012-2014: A central hypothesis of this work is that the transport of different ions and molecules across a layer of graphene can be tuned by creating appropriately sized pores in the graphene. We used graphene composite membranes by transferring graphene grown on copper foil to a polycarbonate track-etched membrane support as a platform for the study of transport through pores in graphene, while transfer to a TEM substrate was used for imaging. We used ion bombardment (8 kV, 52° incidence, at a dose of 10^{13} ions/cm^2) to induce defects in the graphene lattice, and experimented with different oxidizers to identify that a mixture of potassium permanaganate and sulfuric acid (reported by Kosynkin et al to unzip carbon nanotubes) could modulate transport through ion-bombarded graphene (Figure 1). Diffusive transport measurements of KCl and Allura Red (~1 nm sized model organic molecule) illustrated the ability to control selectivity of the membrane based on chemical etch time. Remarkably, we observed cation selectivity at short etch times, which was predicted theoretically for nanoporous graphene but had not been experimentally observed. At longer etch times the graphene layer permitted transport of salt while blocking the larger organic molecule, which could be useful for dialysis and nanofiltration applications. Control experiments attributed this effect to nucleation and growth of pores. Detailed STEM, Raman, and XPS studies revealed sub-nanometer pore size distributions, with pores being stabilized by oxygen-containing groups. This study demonstrated the ability of controlling mass transport across a monolayer of graphene by creation of a high density of tunable sub-nanometer pores. This platform also allows for measurement of the transport properties imparted by different pore creation methods, which is the subject of future study.

In addition to ensemble measurements across macroscopic graphene membranes, we probed isolated pores in graphene to understand the transport mechanisms and heterogeneity between different pores. Towards this goal, we have developed a chemical-resistant flow cell apparatus for measurement of currents through graphene suspended over small (~20-40 nm diameter) pores in silicon nitride membranes designed to isolate pores. These investigations revealed some remarkable ion transport behaviors in intrinsic pore defects in graphene. First, we observed heterogeneous cationic selectivities in sub-nanometer graphene pores (pore size identified based on magnitude of ionic conductance), with all sub-nanometer pores exhibiting extremely high anion rejection. We also observed rejection of a ruthenium salt of 1.2 nm cation size, consistent with steric rejection. Cation selectivity suggests that in-plane ion coordination may play a role in ion transport across graphene, in addition to electrostatic and steric effects. Second, we observed voltage-dependent gating and switching behavior of graphene nanopores. Voltage gating was accompanied by increase in $1/f$ noise and non-linear I-V curves, as is also the case with biological ion channels. In contrast, voltage-independent switching was also observed, which may be due to association/dissociation of charged groups decorating the pore, or transient ion-binding effects. These studies will illustrate parallels and contrasts between the behavior of graphene nanopores and biological ion channels, and will provide insights into the ion transport mechanisms in graphene membranes.

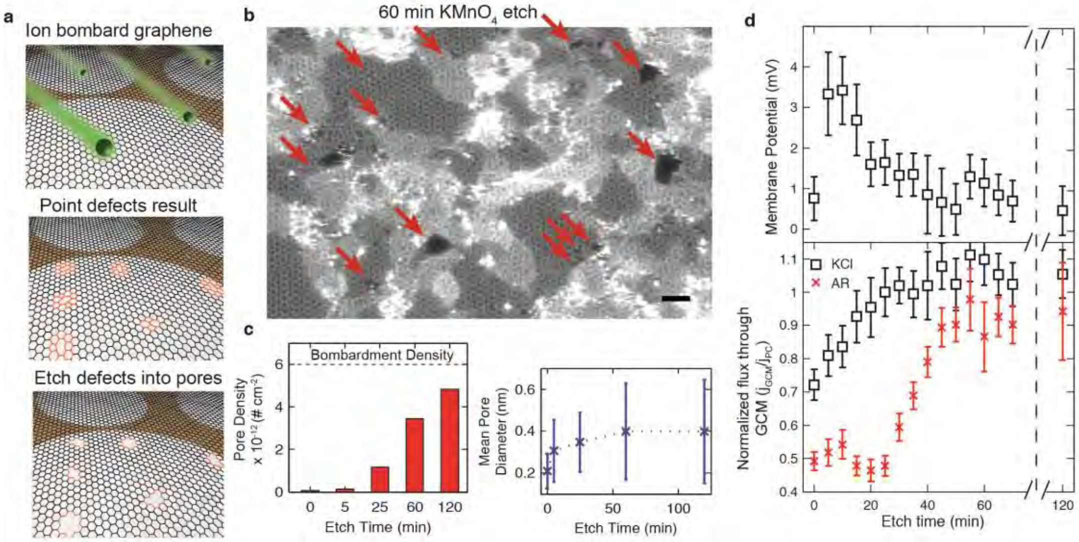

Figure 1. a) Gallium ion bombardment of graphene results in defects that open into permeable pores after potassium permanganate etching. b) STEM image of pores created in graphene. c) Pore density approaches bombardment density at the 120 min time, while the mean pore diameter stabilizes at 0.4 ± 0.24 nm. d) Increase in membrane potential indicates cation selective transport at the 5-10 min etch time, while higher flux of the KCl transport over Allura Red AC (~1 nm model organic molecule) indicates size-selective transport, reaching a maximum selectivity at the 25 min etch time.

Science objectives for 2014-2016:

- Use STEM, Raman spectroscopy, and XPS, to investigate pore structures resulting from nitrogen doping, nitrogen doping and chemical oxidation, and ion irradiation at different angles of incidence and energies that are predicted to correspondingly alter pore size distribution.
- Investigate transport dynamics of isolated pores created in graphene. Behaviors expected to arise from ion coordination effects and association/dissociation dynamics will be studied and compared with those in biological ion channels. Selectivities of these pores for different ions and protons will be examined, which may uncover novel functionalities.
- Characterize ensemble transport properties of macroscopic membranes and relate them to pore fabrication methods and heterogeneity in pore size and behaviors.

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Design, Synthesis and Characterization of Triptycene-Containing Macromolecules with Hierarchically Controlled Architectures as Functional Membrane Materials for Energy Applications

Ruilan Guo, Principal Investigator
Postdoc: Shuangjiang Luo
Graduate students: Jennifer Wiegand, Greg Kline, Joseph Aboki
University of Notre Dame, Department of Chemical and Biomolecular Engineering
182 Fitzpatrick Hall of Engineering, Notre Dame, IN 46556
Email: rguo@nd.edu; Web: http://engineering.nd.edu/profiles/rguo

Collaborator: Prof. Benny Freeman, University of Texas at Austin, Austin, TX

Overall research goals: The ultimate goal of this fundamental, experimental research project is to develop advanced triptycene-containing polymers with hierarchically controlled architecture and morphology over multiple length scales necessary to generate functional membranes for energy and environmental applications. The research will provide fundamental understanding of how the basic yet governing structural parameters, such as factional free volume (FFV) and size distribution, polymer chain packing and self-organization mechanism, determine the membrane properties.

Significant achievements in 2013-2014: The versatile chemistry possibilities, unique spatial configuration and self-assembly characteristics of triptycene-based macromolecules provide great opportunities to produce robust, high performance polymeric membranes for ultra-fast transport and highly selective separation of small molecules and ions. During the first year of this project, we have successfully synthesized a series of triptycene-containing polyimides with systematically varied structures based on a set of newly designed triptycene-1,4-diamine monomers. The obtained robust membranes were shown to be both highly permeable and highly selective. We have established the correlation between the chemical structure, FFV and transport properties for these triptycene-1,4-polyimide membranes, which suggested that a preferred free volume architecture in addition to high fractional free volume were obtained upon the incorporation of triptycene units into polyimide structure. More interestingly, the FFV and free volume architecture were found to be tunable via systematic alteration of the substituent groups neighboring the triptycene moiety along the backbone, which essentially provides a new dimension in finely tuning the membrane transport properties via rational molecular design.

Triptycene diamine monomer synthesis: An efficient synthetic route has been established to synthesize triptycene-1,4-diamine monomers in high yield with high purity, which is critical to produce high molecular weight polyimides in diamine-dianhydride polycondensation reactions. The triptycene skeleton was constructed via Diels-Alder cycloaddition of benzoquinone to anthracene, onto which nitro functionality was introduced at 1,4-position by aromatic nucleophilic substitution (S_NAr) reaction using an appropriately substituted aromatic nitro compound. The final diamine structure was readily obtained by reduction of nitro groups. The synthesized triptycene-1,4-diamine monomers were systematically varied in their structure by introducing various substituents to neighbor the triptycene units, which was found to provide more tunability control of the FFV and free volume architecture as reflected in their membrane transport properties.

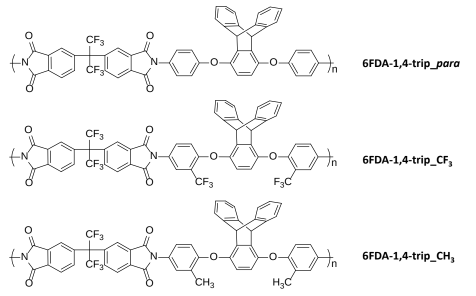

Figure 1. Structures of triptycene-containing polyimides

Polymer synthesis and FFV characterization: A series of newly designed polyimides containing triptycene moiety has been successfully developed based on triptycene-1,4-diamines and 6FDA (Figure 1). The synthesized polyimides exhibited high molecular weight, excellent solvent solubility and excellent thermal stability with very high T_g (up to 300°C) and decomposition temperatures of above 500°C. The polyimides were systematically varied in the substituent groups to test the viability of tunable FFV and free volume architecture in these membranes. Using group contribution method and density measurements, FFV of the membranes was estimated to be 15.1-18.3%, which was shown to be tunable by changing the substituents, i.e., CH_3 and CF_3. An interesting observation was that introduction of $-CH_3$ did not increase FFV as expected, which was attributed to the size difference of the substituent groups. As depicted in Figure 2, the methyl groups are possibly small enough to reside partially in the void space (IFV) already created by the triptycene blades, which reduces the FFV.

Film casting and membrane properties: Tough and ductile thin films were obtained via routine solution casting method. Using a constant-volume, variable-pressure method, the permeabilities to H_2, CO_2, O_2, N_2, and CH_4 were determined. All the membranes exhibited high gas permeabilities due to high FFV generated by triptycene units disrupting efficient chain packing. The permeabilities of the triptycene-polyimides are very sensitive to changes in the substituents in that the permeabilities increased from the $-CH_3$, to the *–para*, to the $-CF_3$ substitution, which nicely agreed with the FFV values for these polymers. High selectivities were also observed, however, were not sensitive to structural change, suggesting formation of favorable free volume (microcavity) size distribution or architecture in all the triptycene-polyimide membranes (Figure 3 and Figure 4). This is very promising as the permeability-selectivity trade-off generally prevents improved properties in both permeability and selectivity for common polymeric membranes.

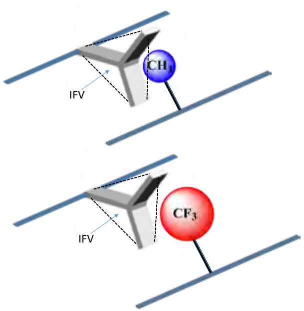

Figure 2. Proposed chain packing mechanism with various substituents

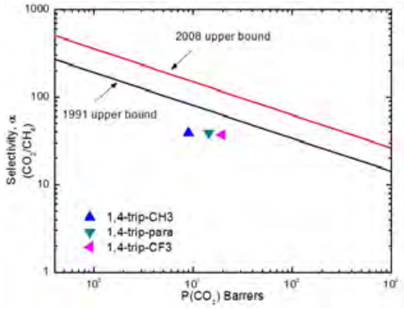

Figure 3. Permeability-selectivity trade-off tuned by chemical structure

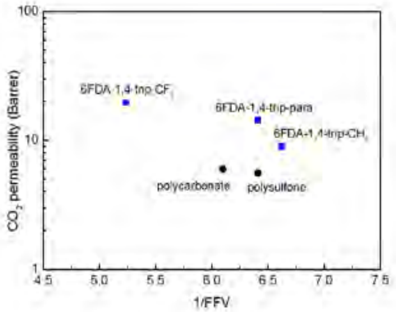

Figure 4. Dependence of CO_2 permeability on FFV

Science objectives for 2014-2016:

- Synthesize triptycene-polyimides with various structural symmetry, i.e., *meta*, *para*, and *ortho* structure to investigate the effects on chain packing, FFV and membrane transport properties.
- Expand the triptycene-polyimides array to other linkage geometry, i.e., 2,6- and 9,10 (bridgehead)-triptycene polyimides, which are expected to have different chain packing efficiency and thus different gas transport properties to meet various separation needs.
- Establish fundamental structure-property relationship in general for triptycene-polyimides and identify the determining structural parameter that can be utilized to construct desired free volume architecture with predictable transport properties.

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Fluoropolymers, Electrolytes, Composites and Electrodes

Stephen Creager, Principal Investigator
Joe Thrasher and Darryl DesMarteau, Co-Principal Investigators
Iqbal Sharif and Jung-Min Oh, Postdoctoral Research Associates
Jamie Shetzline and Hung Pham Doc, Graduate Students
Department of Chemistry, Clemson University, Clemson SC 29634
Email: screage@clemson.edu

Collaborators: Carol Korzeniewski, Texas Tech University; Dennis Smith, University of Texas Dallas; John Goodwin, Coastal Carolina University

Overall research goals: The objectives of this research are to *create and understand new fluoropolymer-based electrolytes and electrodes* suitable for use in electrochemical energy storage and conversion devices such as batteries and fuel cells. The work aims to provide improved understanding of the fundamental relationship between materials properties (e.g. ionic / electronic conductivity, electrocatalytic activity) and materials structure (atomic / molecular / nanoscopic / mesoscopic) with emphasis on properties relating to electrochemical energy conversion and storage.

Significant achievements in 2012-2014: Achievements were realized in all project phases with the most progress in studies on composites of carbon with fluoropolymer ionomer electrolytes. Specific significant achievements are given below.

Carbon nanofoams having zirconia nanoparticles embedded in the carbon skeleton were prepared and characterized. Materials comprised of 10-20 weight percent zirconia with specific surface areas of 700-1000 m^2/g, pore diameters of 10-15 nm, and free volumes of 85% were obtained. Also, fluoropolymer ionomer electrolytes were grafted onto the carbon nanofoam surface (including inside the pores) via covalent binding between phosphonate groups on the fluoropolymer and zirconia particles embedded in the carbon framework. Ion-exchange capacities (IECs) for the carbon / zirconia / ionomer composites in the 0.5-0.6 meq/g range were obtained.

Platinum nanoparticle deposition was realized on the surface of carbon / zirconia / ionomer composites and the resulting materials were characterized as catalysts for the electrochemical oxygen reduction reaction (ORR). Platinum contents of 20 weight percent with platinum particle diameters of 2-3 nm and specific electrochemical surface areas for platinum of 50-60 m^2/g_{Pt} were obtained. ORR activity for thin-film electrodes on glassy carbon supports was studied by rotating disk electrode (RDE) voltammetry. Electrocatalytic ORR activities were between 50 and 80 mA/mg_{Pt} when normalized to platinum mass and between 100 and 150 $\mu A/cm^2{}_{Pt}$ when normalized to platinum surface area, in good agreement with literature reports on benchmark materials (e.g. Pt on Vulcan carbon). Activity was measured at 0.9 V vs. NHE with correction for mass-transfer losses (as recommended by DOE) in aqueous H_2SO_4 (0.1 M) at ambient temperature (20-22 C).

An apparatus was constructed and a method developed to deconvolve ionic and electronic contributions to electrical conductivity in freestanding thin-film samples comprised of carbon and fluoropolymer ionomer electrolytes. The method relies on control of the blocking / non-blocking character towards ions and electrons of interfaces between electrodes and samples. The apparatus operates under variable temperature and relative-humidity conditions. Studies on benchmark materials comprised of carbon black and Nafion^{TM} ionomer in various proportions have been completed and studies on project materials will be undertaken soon.

Collaborative work was pursued with Smith at Texas Dallas, Korzeniewski at Texas Tech, and Goodwin at Coastal Carolina. Smith and co-workers studied wettability of electrospun fluoropolymer fibers with possible applications in fuel-cell electrode water management, Korzeniewski and co-workers are developing infrared (IR) spectroscopic methods for characterizing fluoropolymer ionomers, and Goodwin and co-workers are studying ORR catalysis using cobalt phthalocyanine complexes. For the IR work we provided ionomer materials, and for the ORR work we performed RDE voltammetry studies on catalyst-coated electrodes.

Construction and testing of a barrier facility for the safe handling of tetrafluoroethylene (TFE) and various trifluorovinyl ether (TFVE) co-monomers were completed in summer 2013. The facility is now ready for project use synthesizing a wide range of fluoropolymer electrolytes for integration into carbon electrode supports and also for polyelectrolyte membrane (PEM) formulation.

Science objectives for 2014-2016:

- Carbon / zirconia / platinum / ionomer nanocomposites will be used to fabricate electrodes in PEM fuel cell membrane-electrode assemblies (MEAs) and/or catalyst-coated membranes (CCAs). MEAs / CCAs will be characterized in a fuel-cell test stand in half-cell and full-cell configurations. Studies will focus on the role that covalently grafted polymer electrolytes play in adjusting electrode activity under PEMFC conditions which differ significantly from those in prior studies which utilized aqueous acid electrolytes.
- Synthesis and stability studies on hydroxide-ion-conducting fluoropolymer electrolytes will continue to be pursued with emphasis on guanidinium organocations and NMR stability studies in D_2O/KOD. This project work is behind schedule due to an unexpected medical situation for the graduate student working on the project, which caused him to have to drop out of school and cease working on the project. This work is being transitioned to another team member.
- TFE / TFVE copolymer and terpolymer electrolytes having very high IEC and a small proportion of organophosphonate groups suitable for grafting onto zirconia-containing supports will be prepared and the properties of their composites with carbon / zirconia studied.

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Chemical Analysis of Nanodomains: Diffraction-limited and Subdiffraction Spatial Resolution Imaging

Emily A. Smith, Principal Investigator
Ning Fang, Jacob W. Petrich, Co-Principal Investigator
1605 Gilman Hall, The Ames Laboratory, Ames, IA 50011
Email: esmith1@iastate.edu; Web: www.ameslab.gov/cbs/fwp/nanodomains

Collaborators: Dr. Sumit Chaudhary, Iowa State University, Ames, IA
Dr. Javier Vela, The Ames Laboratory, Ames, IA

Overall research goals: The goal of this research team is to develop the next generation of imaging tools and methodologies for the analysis of phenomena that occur at nanometer length scales and picosecond time scales. This work supports the Grand Challenge mastering energy and information on the nanoscale to create new technologies with capabilities rivaling those of living things. The developed instrumentation and methodology is applied to model systems of interest to the DOE mission, where fundamental insight can be gained with the spatial and temporal resolution afforded by our developed methods. A main focus is thin polymer films used in energy storage and capture devices.

Significant achievements in 2012-2014: The Nanodomains team has investigated properties of bulk-heterojunction organic photovoltaic devices (OPVs) and other polymer films. OPVs based on poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) were measured by scanning angle (SA) Raman spectroscopy and fluorescence spectroscopy. SA Raman spectroscopy simultaneously measures polymer thickness and order. A decrease in polymer order was measured for a P3HT:PCBM mixture on a gold or indium tin oxide substrate compared to pure P3HT. The stability of 3 different OPV films was measured using laser-induced photodegradation (Figure 1). Upon incorporating a ferroelectric polymer as additive in the active-layer, power conversion efficiencies increase by nearly 50%, and internal quantum efficiencies approach 100% – indicating complete exciton dissociation at certain photon energies. Similar enhancements in bilayer-heterojunctions, and direct influence of ferroelectric poling on device behaviour show that improved dissociation is due to ferroelectric dipoles rather than a morphological change. Enhanced singlet-exciton dissociation is also revealed by photoluminescence lifetime measurements, and predicted by simulations using a numerical device model.

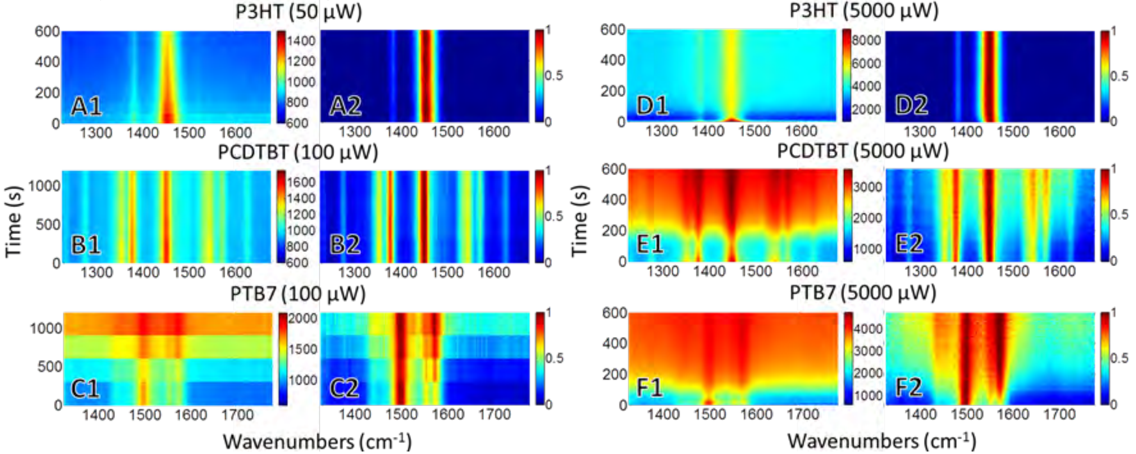

Figure 1. Images of Raman spectra for P3HT:PCBM, poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT):PCBM, or poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]-thieno[3,4-b]thiophenediyl}) (PTB7):PCBM OPVs at different illumination times and powers. A1-F1: raw spectra and A2-F2: normalized background subtracted spectra. Peak broadening is indicative of decreased polymer order and increased background is associated with undesired luminescence.

We have also demonstrated the use of giant CdSe/14CdS nanocrystal quantum dots (g-NQDs) as fluorophores for subdiffraction fluorescence lifetime imaging in a stimulated emission depletion optical format. A spatial resolution of 40 nm was achieved and imaging was performed with negligible photobleaching of the g-NQDs. This is a benefit for STED imaging, where organic fluorophores can exhibit 50% or more photobleaching during image acquisition as a result of high laser fluxes. In order to understand the minimum number of photons required to extract meaningful fluorescence lifetimes, we have analyzed data with 40 ± 30, 70 ± 50, and 100 ± 100 photon counts in the peak channel. In all three cases, similar histograms of 262,144 fluorescence lifetimes were achieved, indicating that as few as 40 ± 30 photons in the peak channel is sufficient to obtain an accurate lifetime. This is important as the number of required photons limits imaging speed and affects photobleaching when using organic fluorophores.

Science objectives for 2014-2016:

- The stability and structure of polymer films suitable for use in organic photovoltaic devices will be investigated with a combination of optical imaging and spectroscopy.
- The mechanism for improved OPV device efficiency will be investigated with time-resolved studies.
- Nanodomain formation in donor acceptor blends and block copolymers will be investigated with subdiffraction optical imaging.

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Strong Field Molecular Photoionization in the mid-IR: Implications for submicron molecule-specific imaging with mass spectrometry

Nicholas Winograd
Andrew Kucher
209 Chemistry Bldg, Penn State University, University Park, PA 16802
Email: nxw@psu.edu; Web: Winograd.psu.edu

Collaborator: Dr. Andreas Wucher, Fachbereich Physik, Universitaet Duisburg-Essen, 47048 Duisburg, Germany

The overall research goal is to utilize laser photoionization techniques to enhance the capabilities of cluster secondary ion mass spectrometry (SIMS) imaging. The program covers a range of studies aimed at acquiring a better fundamental understanding of the cluster/solid interaction, at attaining improved sensitivity for 2 and 3-dimensional molecule-specific imaging and at advancing bioimaging applications.

Significant achievements in 2012-2014: A new fs IR pulsed laser has been acquired that provides a unique opportunity to enhance molecular photoionization. Several systems have been examined, and the results confirm predictions from earlier studies at lower power that more abundant molecular ions can be produced at longer wavelengths with less photofragmentation when compared to UV-Vis wavelengths. After optimization of the photoionization yield, the system has been applied to the imaging of the 3-dimensional distribution of hydrocarbons in *Botryococcus braunii*, a green microalgae which has garnered enormous attention as a potential biofuel candidate for its unique ability to synthesize and accumulate a diversity of long-chain hydrocarbon oils

The commercially available laser system employed in these experiments is based upon chirped pulse amplification (Coherent Legend Elite Duo) and produces pulses of 40 fs duration at 800 nm wavelength, with a repetition rate of 1 kHz and an average power of 10 W. The laser output is used to pump a commercially available optical parametric amplifier (OPA, Light Conversion TOPAS-C-HE), the output wavelength of which is tunable in the 1160 nm - 2580 nm range, with a combined signal and idler conversion efficiency between 30-40% of the pump power. From the power and wavelength dependence of the molecular photoionization yield, we have found that for most biomolecules, ionization with 10^{13}-10^{14} W/cm^2 at 1350 nm provides the most effective analytical signal. With our new laser system, this energy range allows maximization of the spatial overlap between the plume of sputtered molecules and the photon field. A comparison between a SIMS image of the β-estradiol molecular ion compared to the laser-based image is shown in Figure 1.

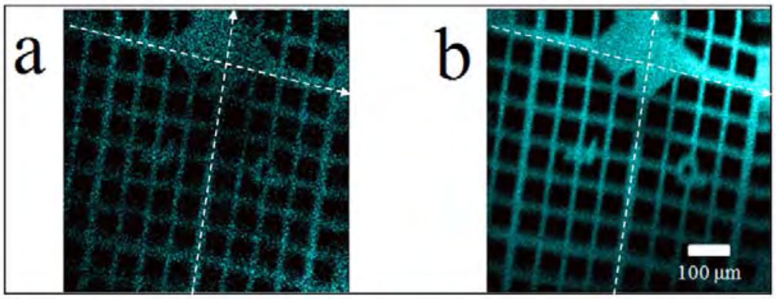

Figure 1. a) SIMS and b) sputtered neutral mass spectrometry (SNMS) images of the molecular ion of β-estradiol, with the sterol vapour deposited onto a 400 mesh Ni London finder grid. Post-ionization was performed at 1350 nm with an intensity of 4 x 10^{13} W/cm^2.

This protocol has been applied to the SNMS imaging of a number of biological samples ranging from rat brain tissue to single algae cells noted above. In all cases, the sensitivity for molecular ions is increased by up to 40-fold over SIMS. A particularly exciting example is shown in Figure 2. The SIMS images are displayed since they require special instrumentation to achieve the 300 nm spatial resolution, not available for our laser-based experiments. The chemical assignments, however, were based upon the high field fs IR spectrum shown in the figure.

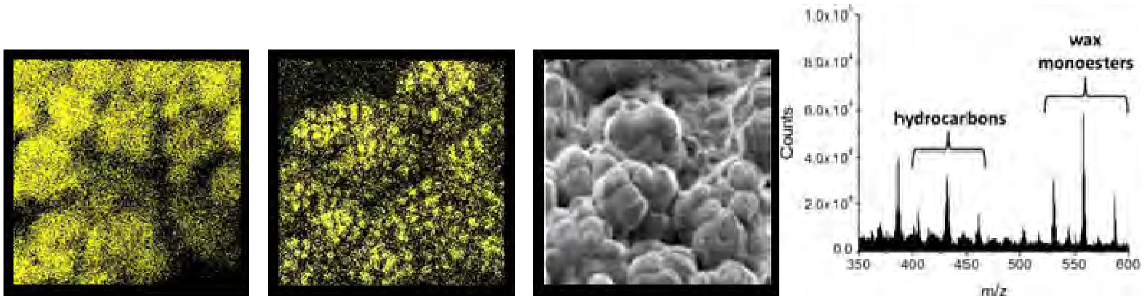

Figure 2. These images show 13 algae cells grown on a Si target, taken in SIMS mode. The first image on the left shows wax monoesters, whose laser photoionization spectrum is shown on the right. After depth profiling with C_{60}^+ bombardment, the wax monoesters are removed, revealing long chain hydrocarbons concentrated into sub-cellular globules shown in the centre image. A total ion image is shown on the right, revealing the overall morphology of the sample.

Science objectives for 2014-2016:

- Investigations into strong field photoionization of long-chain hydrocarbons will continue, with emphasis on determining the relationship between ionization efficiency and chain length
- Preliminary results for B B braunii will be extended to provide a full 3-D representation using both SIMS and SNMS at 250 nm spatial resolution using the C60+ probe.
- Tissue imaging, where matrix effects and charge suppression are problematic with SIMS, will be explored in more detail with SNMS. In general, our emphasis will be on implementing the protocols we have developed over the last several years.

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Fundamental Studies in Plasma Sources for Elemental and Molecular Analysis

Gary M. Hieftje, Principal Investigator
Steven J. Ray, Associate Scientist
Department of Chemistry, Indiana University, 800 East Kirkwood Ave., Bloomington IN 47405
Email: hieftje@indiana.edu; Web: http://www.indiana.edu/~gmhlab

Overall research goals: This program earlier emphasized fundamental studies of the inductively coupled plasma (ICP). However, the scope of studies has broadened considerably in the last two years and now includes other atom, ion, and molecular sources for optical and mass spectrometry. Included is one that requires no gas flow, operates at modest power, but provides the same detection limits as the ICP. A second plasma is employed as a source for ambient mass spectrometry and offers a number of advantages over competitive units. An overview of all three will be provided.

Significant achievements in 2012-2014: Considerable progress has been made in devising strategies for understanding and alleviating matrix interferences in ICP emission spectrometry. Recently, we have begun exploring end-on observation of ICP emission; in this mode, signals are higher and precision is better, but matrix interferences are worse, so recognizing them is even more critical. The method involves measuring either the spatial distribution of analyte emission or the effect of dilution on the magnitude of interference. Because the ICP is spatially heterogeneous, especially in an end-on observation mode, the magnitude of an interference changes from one plasma location to another. The interference-recognition method is then straightforward: a calibration curve is created at several spatial locations in the ICP. The emission signal from an unknown sample is then obtained at each location and its apparent concentration determined from the corresponding calibration curve. If the sample behaves in the same way as the standards, the determined concentrations will be the same for all spatial locations. If the determined concentrations differ, a matrix interference clearly exists. The dilution-based method is similarly straightforward; because different analyte elements are affected dissimilarly by a matrix interferent, the degree of matrix-induced signal enhancement or suppression changes from one element to another during dilution. Ratioing two analyte signals as dilution proceeds then yields a constant value in the absence of an interferent but a changing value when an interference is present.

The second source undergoing fundamental study is a glow discharge sustained at modest power (~75W) in the open atmosphere. Unlike most glow discharges, here the sample solution itself serves as the discharge cathode. As a result, sample species in the solution are atomized directly into the negative glow, where they are excited and can be detected by atomic emission. Detection limits for some elements are even better than in the ICP, despite the simplicity of the arrangement. Moreover, spectra emitted by the Solution-Cathode Glow Discharge (SCGD) are surprising uncluttered, so even a moderate-resolution spectrometer or interference filter can be used for spectral selection. Because the system has a very low dead volume (no spray chamber is needed) we have coupled the SCGD with a flow-injection system and an ion chromatograph. Recent studies have revealed that sample injection into the plasma is complex, and involves a very high field at the sample-solution surface and the consequent electrospray-like ejection of sample material.

The third source is an atmospheric-pressure helium glow within a closed chamber. The effluent from the chamber is relatively hot (~300C) and is rich in helium excited states, He ions, and He_2^+. All three species are important in carrying energy into the open atmosphere, where they produce H_3O^+, $(H_2O)_nH^+$, N_2^+, O^+, NO^+, and others. Some of these species are excellent proton donors whereas others have strong electron affinities and can form ions from other molecules by proton or charge transfer, both of which cause little fragmentation of the target molecules. Unlike the commercial DART source for ambient ionization, the new source has a different structure and current-voltage characteristics. It also can be tuned in temperature without an external heater, and suffers less from matrix interferences caused by competitive ionization. In recent basic studies, we have used schlieren imaging to characterize how the FAPA desorption plume interacts with a solid-sample surface and have employed emission imaging to characterize the reactions that are responsible for energy transport in the plume and in generating reagent ions for analyte ionization.

Science objectives for 2014-2016:

- Extend dilution-based method for identifying ICP matrix interferences to ICP mass spectrometry.
- Explore use of SCGD emission spectrometry for the determination of isotopes by means of molecular-emission spectral shifts. These shifts are predicted to be much more substantial for molecular bands than for atomic emission lines.
- Apply the FAPA source to the detection of counterfeit electronics. Characterize extraction of volatilized sample constituents into MS interface.

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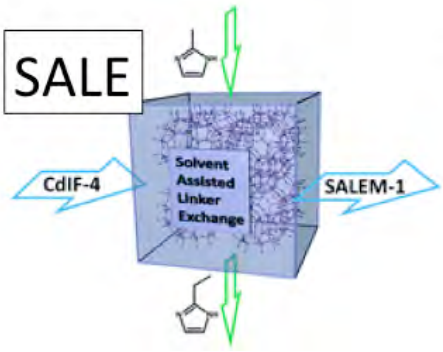
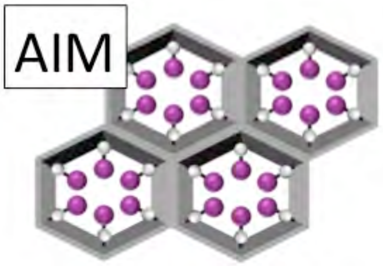
Coordination-Chemistry-Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities: Experimental

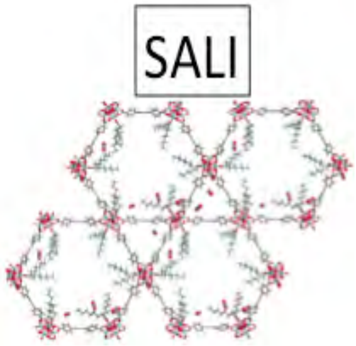
Joseph T. Hupp,
Randall Q. Snurr, SonBinh T. Nguyen, Omar K. Farha, Co-Principal Investigators
2145 Sheridan Road, Northwestern University, Evanston, IL 60208
Email: j-hupp@northwestern.edu; Web: http://chemgroups.northwestern.edu/hupp/index.html

Overall research goals: The research objectives are to understand, design, 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).

Significant achievements in 2012-2014: An enormous number of metal-organic frameworks now exists. Nevertheless, conventional synthesis methods preclude access to many others that clearly would be highly desirable. The issues include chemical incompatibility of functional groups, unwanted recruitment of desired open-metal sites as secondary nodes, linker degradation under solvothermal conditions, undesired framework catenation, and inadequate building-block solubility. We have found that many highly desirable, but otherwise inaccessible, MOFs can be obtained experimentally by using one or more of three powerful new synthesis techniques: SALE (Solvent-Assisted Linker Exchange), SALI (Solvent-Assisted Ligand Incorporation), and AIM (Atomic Layer Deposition In MOFS). In turn, these have opened up new capabilities for gas and vapor separations.







Plans for 2014-2016: With the above synthesis tools in hand, and with computational guidance from the Snurr lab, we are focusing on otherwise challenging or energetically expensive, small-molecule separations including hydrogen/methane, nitrogen/oxygen, and nitrogen/methane.

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Preparation of Chemically Functionalized Surfaces through Ion Soft Landing and Ion/surface Reactions under Vacuum and in the Ambient Environment

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

Overall research goals: The research objectives are to prepare catalytic active surfaces with energy relevance using mass spectrometric methods; to understand the ion chemistry involved in the processes; to characterize the prepared structures of nanoparticles to atomic resolution; to deposition materials on surfaces by ion soft landing; to optimize ion manipulation techniques for controlled surface modification.

Significant achievements in 2012-2014: A new method of nanoparticle synthesis was developed to using electrospray ionization of noble metals to create metal ions and using reductive ion landing to create surface structures (Fig. 1A).[1] The solvated metal ions enter the electrospray plume and form metal nanoparticles upon deposition on a solid or liquid surface in the ambient environment. A variety of nanoparticles has been generated including silver, gold, copper, and palladium and their nano alloy mixtures.[2] This method requires no vacuum and no gas stream, operates at room temperature using in conventional organic solvent. Successful applications has been made in fields including online solution-phase catalysis[1], micro fabrication of nano structured patterns and creation of nano structure modified surfaces for enhancement Raman spectroscopy (SERS).[3] Parallel to reductive landing of the ionized metal, direct ligand binding and collecting for the synthesis of organometallic catalyst has also been demonstrated.[1]

Another achievement is the ambient preparation of atomic metal cluster ions in both positive and negative ion modes. Precursors are metal salts which are electrosonic sprayed and passed through a heated tube. Heating evaporates and oxidizes the counterion to form naked cationic metal clusters (Fig.1B). This ion source has been used to generate $Ag_n^{+/-}$, Pd_n^+, $PdnO_y^+$, $Pd_nO_y^-$, and bimetallic palladium-silver cluster cations ($3<n<20$, $3<y<8$) and to study their high reactivity with various compounds in the gas phase. [4]

Atmospheric pressure ion focusing devices have been developed and characterized.[5, 6] A 3D printing protocol has been implemented to quickly print non-conductive spacer and conductive polymer electrodes. 3D printing allows for rapid turnaround time for manufacture as compared to traditional machining. The printed devices serve are modeled on calculations of ion motion and serve as optimized ion-guide that focuses metal ions and clusters onto surfaces at atmospheric pressure. Surfaces modified by this way show improved homogeneity as compared to previous ion soft landing experiments. A focused ion beam also allows for higher surface coverage in shorter times which is critical in the mass production of active nanostructured surface spots. The guided ion beam also allows for the deposition of different ions from different ion source to the exact same spot, both simultaneously or in one after another. This solves space charging problem for conventional array type ion sources and allows high fluxes of landing ions. All these capabilities open many opportunities for the chemical modification of surfaces.

Science objectives for 2014-2016

- Full characterization of prepared nanostructures and clusters using state of the art instrumentation including transmission electron microscopes and x-ray photoelectron spectroscopy to obtain chemical understanding of nano structures down to atomic resolution.
- Atmospheric pressure focused ion beam lithography using ambient ion focusing and precision moving stage or pre-manufactured masks.

- Atmospheric pressure focused ion beams for advanced chemical synthesis and surface modification.

- Heterogeneous catalytic studies of silver clusters in the epoxidation of propylene; Au, Pd nano particles/alloys in CO oxidation and the water-gas shift reaction. A custom-built mass spectrometer with capabilities of secondary ion mass spectrometry (SIMS), Raman spectroscopy, and temperature programmed desorption (TPD) will be used in the catalysis study.

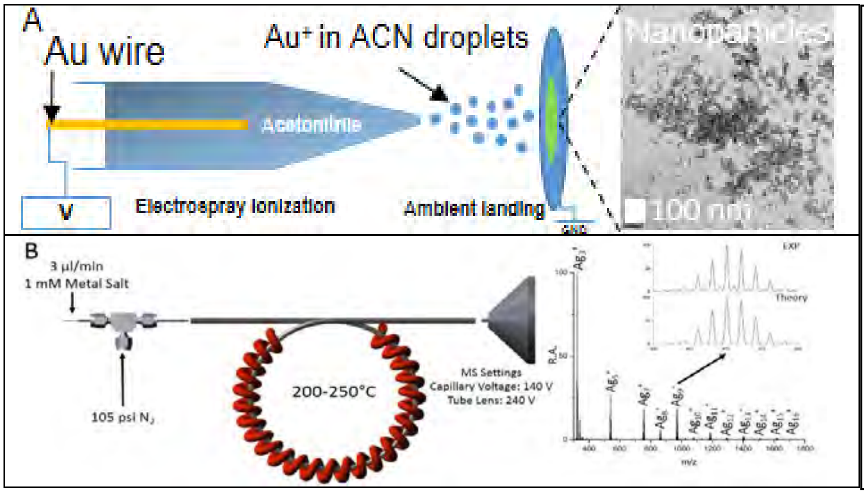

Figure 1. Two new ion sources for materials science applications
A.) Nanoelectrospray ionization source for direct generation of ions from noble metals and subsequent soft landing synthesis of nanoparticles.
B.) Electrospray ionization source with heating transfer loop for generation of small atomic metal clusters.

<u>Patent applications 2014</u>

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Development of Anti-Fouling Membranes via Combinatorial Chemistry and a Novel High Throughput System (DE-FG02-09ER16005)

Georges Belfort, Principal Investigator
Howard P. Isermann Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute (RPI), 110 8th Street, Troy, NY 12180-6590
Email: belfog@rpi.edu; Web: http://www.rpi.edu/dept/chem-eng/WWW/faculty/belfort/index.html

Collaborators: Dr. Yubing Xie, State University of New York at Albany, Albany, NY
Dr. Guohao Dai, Rensselaer Polytechnic Institute, Troy, NY

Overall research goals: This renewal-grant application is an extension of our previous grant in which we continue to expand our approach by focusing on discovery both low fouling (previous grant and this application) and high performing (this renewal proposal) membranes. The goals of the proposed 3-year research program are to expand, refine and optimize the discovery and separation characteristics of new surfaces using the 96-membrane well format with the high throughput-atmospheric pressure plasma (HTP-APP) method and to elucidate the behavior of protein-resistant chemistries. In short, we use combinatorial chemistry to prepare a vastly expanded library of vinyl monomers (AIM 1), graft these newly synthesized monomers, test their efficacy for improving filtration performance, and select winners (AIM 2); fine-tune the grafting and filtration conditions of selected winners (AIM 3), and investigate the underlying mechanistic reasons why the successful monomers are able to perform best (AIM 4).

Significant achievements in 2012-2014: The analysis of our 66 commercially available monomers has been completed. The results from our high throughput screening methods have shown that polyethylene glycol (PEG) monomers (n=4-22 repeats) perform very well when subjected to a static protein fouling test. This is attributed to the hydrophilic nature of PEG, but the exact mechanism is not yet fully understood. We have also synthesized two new sets of monomers. The first set of monomers was used to study the effect of carbon chain length within some of the previous winners. The results correlated extremely well with our predictions based on Hansen Solubility Parameters. These parameters were used based on our hypothesis that water interactions at surfaces play a critical role in filtration processes. We also found that fouling index is exponentially related to the distance between water and monomer solubility parameter points. This shows that monomers that are not similar to water perform exponentially worse as their dispersion, polar, and hydrogen bonding parameters are further away from water (Fig. 1). Selectivity and permeability tests were performed, which correlated with the fouling index and solubility parameters as well.

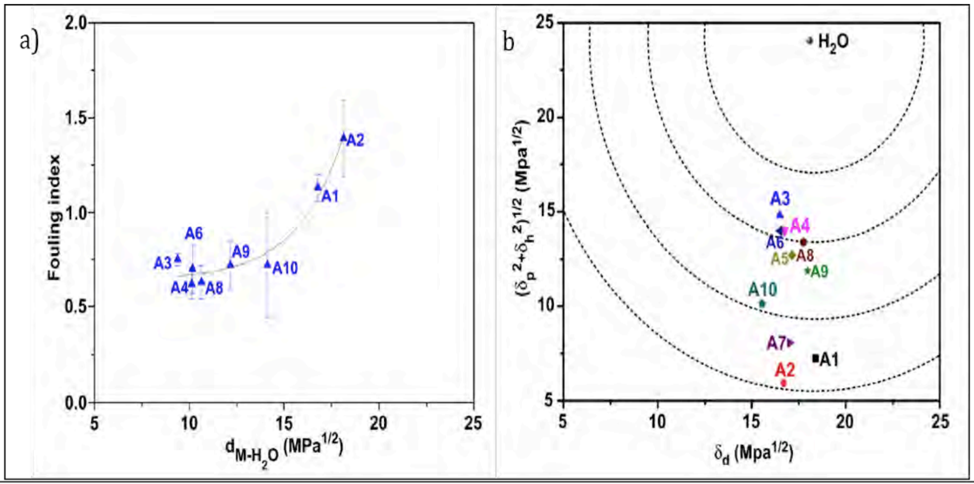
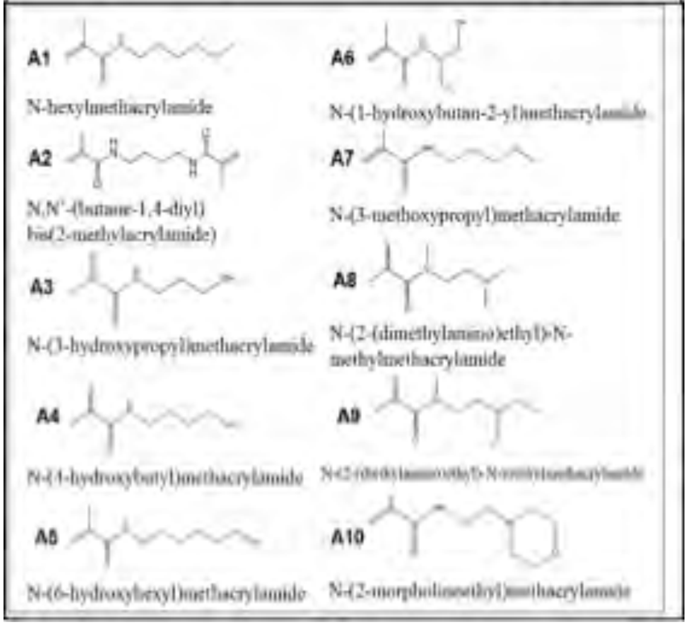


Figure 1. Monomer performance for newly synthesized monomers: (a) Fouling index vs. distance of monomer from water solubility parameter; (b) Plot of polar, hydrogen bonding, and dispersion Hansen Solubility Parameters relative to those of water, dashed circles are radial distances from water to help guide the eye (Gu et al.). Monomers are identified on Table 1.

A list of the monomers used in Fig. 1 can be seen in Table 1.

Table 1. List of monomers described in Fig. 1.



A1 N-hexylmethacrylamide	**A6** N-(1-hydroxybutan-2-yl)methacrylamide
A2 N,N'-(butane-1,4-diyl) bis(2-methylacrylamide)	**A7** N-(3-methoxypropyl)methacrylamide
A3 N-(3-hydroxypropyl)methacrylamide	**A8** N-(2-(dimethylamino)ethyl)-N-methylmethacrylamide
A4 N-(4-hydroxybutyl)methacrylamide	**A9** [illegible]
A5 N-(6-hydroxyhexyl)methacrylamide	**A10** N-(2-morpholinoethyl)methacrylamide

A second set of new monomers was synthesized in order to expand the breadth of our library. Our new combinatorial method utilizes a disulfide starting material, which is then reduced and reacted with a library of maleimides. This allows us to generate a large library starting from one starting material and a library of R groups on the maleimides. We have confirmed synthesis of these new monomers using Thin Layer Chromatography (TLC), High Performance Liquid Chromatography (HPLC), Mass Spectrometry (MS), and Fourier-Transform Infrared Spectroscopy (FTIR). Preliminary experiments indicate that many of these new monomers performed well and exhibited low fouling indices, i.e. repelled proteins. Hansen Solubility Parameters have been calculated as well and we expect the more hydrophilic monomers to perform better based on their solubility parameters being close to that of water.

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

- Synthesize combinatorial library: To use combinatorial chemistry to prepare an expanded library of vinyl monomers for APP-grafting of PES UF membranes.
- Graft, test, and screen: To use our high throughput 96 membrane-well format to graft, test and screen for the best performing graft polymerized membranes from Aim 1 using single protein feed filtration.
- Select, refine, and optimize: To optimize and fine-tune the grafting and filtration conditions of selected winners using our high throughput 96 membrane-well format.
- Mechanism: To investigate the underlying mechanistic reasons why the successful monomers are able to perform best.

<u>References to work supported by this project 2012-2014:</u>

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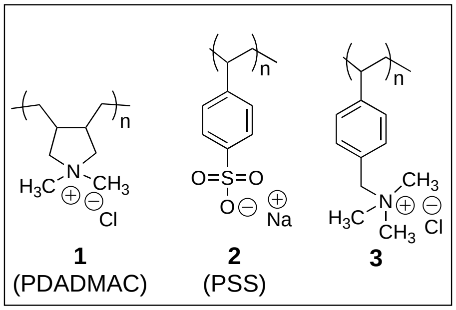
Hyperthin Membranes for Gas Separations

Steven L. Regen, Principal Investigator
Department of Chemistry, Lehigh University, 6 East Packer Avenue, Bethlehem, PA 18015
Email: slr0@lehigh.edu; Web: www.lehigh.edu/~inslr

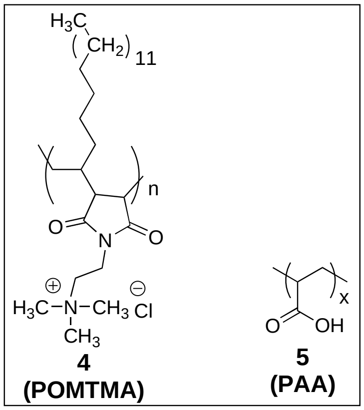
Overall research goals: This research is aimed at understanding those factors that will allow for the rational design and synthesis of hyperthin (<100 nm) organic polymeric membranes having a high flux and a high permeation selectivity towards gaseous permeants. This work is based on the use of Langmuir-Blodgett (LB) and Layer-by-Layer (LbL) methods of film deposition, together with the use of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) as support material.

Significant achievements in 2012-2014:

Unexpected Barrier Properties of Structurally Matched and Unmatched Polyelectrolyte Multilayers. We have discovered that structurally unmatched polyelectrolytes, PDADMAC (**1**) and poly(sodium 4-styrene sulfonate) (PSS) (**2**), afford 14 nm-thick polyelectrolyte multilayers (PEMs) having exceptionally high CO_2/N_2 selectivities (Figure 1). We have also found that structurally matched analogs made from **2** and **3** (having the identical polymer backbone) show similarly high CO_2/N_2 selectivities but permeances that are two to three times greater. Evidence has been obtained, which indicate that this high CO_2/N_2 selectivity is due to the greater diffusivity and higher solubility of the smaller CO_2 molecule. The higher permeances of the structurally-matched analog represents a fundamentally new phenomenon in the PEM area, and its origin is currently under investigation.


1 (PDADMAC) **2** (PSS) **3**

A 7 nm Thick Polymeric Membrane with H_2/CO_2 Selectivity of 200 That Reaches the Upper Bound. A careful study of the effects of pH on the permeability of LB bilayers made from POMTMA (**4**) and poly(acrylic acid) (PAA) (**5**) has led to the fabrication of 7 nm thick membranes having H_2/CO_2 permeation selectivities of ca. 200, which reach the upper bound. Preliminary studies suggest that molecular sieving may be operating. Thus, the permeability of these membranes toward N_2 was found to be only ca. three times lower than CO_2 despite a size difference between CO_2 (0.33 nm) and N_2 (0.36 nm) that is similar to that between CO_2 and H_2 (0.29 nm). We hypothesize that ionic crosslinking between **4** and **5** and hydrogen bonding within **5** lead to a glassy membrane that has gaps, which are large enough for H_2 (but not CO_2 and N_2) to readily cross


4 **(POMTMA)** **5** **(PAA)**

Self-Assembled Versus Langmuir-Blodgett-based Anchors for Polyelectrolyte Multilayers on PTMSP. Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) is unique among all known organic polymers in terms of its exceptionally high gas permeability. Because PTMSP is strongly hydrophobic, we have made extensive use of ionically crosslinked LB monolayers as "anchors" for attaching polyelectrolyte multilayers. We have now found the LbL deposition of PEMs can made, directly, onto PTMSP producing similar thicknesses and similar permeation selectivities. In principle, this advance should greatly simplify the use of PTMSP for fundamental studies as well as practical applications; e.g., the fabrication of PTMSP-coated hollow fibers for the separation of gases.

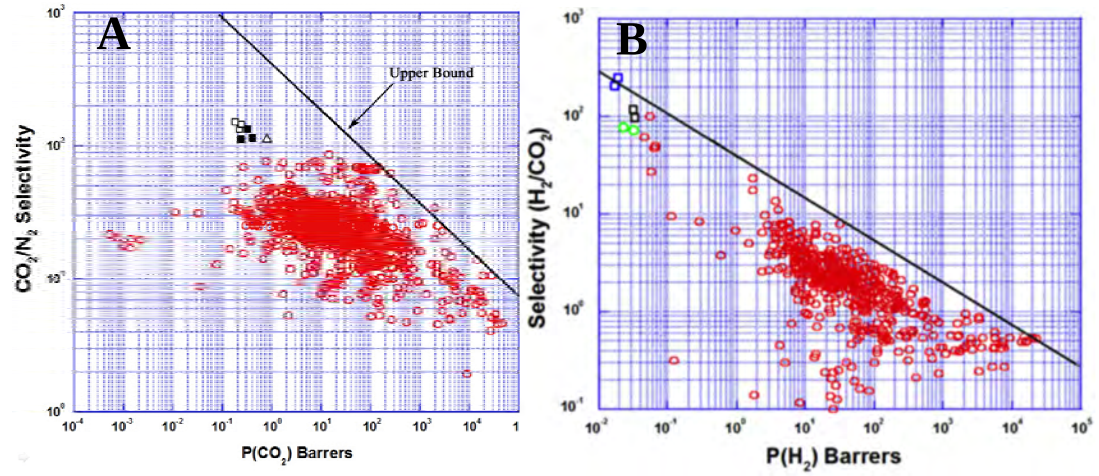


Figure 1. Upper bound plots for CO_2/N_2 and H_2/CO_2. Data for known polymers are shown as red circles. Peformance of (A) 14 nm thick polyelectrolyte multilayers (shown as black open and filled squares and triangles), and (B) 7 nm-single Langmuir-Blodgett bilayers (shown as open green circles and open black squares and blue squares) made from **4** and **5**.

Science objectives for 2014-2016:

- To determine the consequences of hydrogen bonding, positioning of the pendant ions along the polymer backbone, and tacticity on the gas permeation selectivity and permeability of structurally-matched and unmatched polyelectrolyte multilayers.
- To determine the feasibility of introducing uniform micropores into polyelectrolyte multilayers for enhancing permeability and permeation selectivity.
- To determine the consequences of introducing covalent crosslinking on the gas permeation selectivity, permeability and robustness of hyperthin membranes based on polyelectrolyte multilayers and ionically crosslinked ("glued") Langmuir-Blodgett bilayers.

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Electrically Driven Ion Separations in Permeable Membranes

Merlin Bruening, Principal Investigator
Department of Chemistry, 578 S. Shaw Lane, Michigan State University, East Lansing, MI 48824
Email: bruening@chemistry.msu.edu; Web:
http://www2.chemistry.msu.edu/faculty/bruening/index.htm

Collaborators: Dr. Andriy Yaroshchuk, ICREA and Department of Chemical Engineering,
Polytechnic University of Catalonia, Barcelona, Spain

Overall research goals: This research focuses on exploiting electrical potentials to develop membrane-based ion separations with high selectivities. Electrodialysis studies aim to maintain the remarkable diffusion dialysis selectivities of multilayer polyelectrolyte films in high-throughput separations. Other experiments are examining the limits of selectivity in counterflow electrophoresis through microporous membranes. Finally, development of conducting membrane surfaces should afford control of ion partitioning in ultrathin membrane skins to manipulate ion-transport selectivity.

Significant achievements in 2012-2014: Remarkably, polyelectrolyte multilayers on porous membrane supports show K^+/Mg^{2+} selectivities >350 during diffusion dialysis. Transmembrane potential measurements reveal that for $MgCl_2$, the transport number of Mg^{2+} is essentially zero. The low Mg^{2+} transport numbers with both polycation and polyanion-terminated films likely stem from exclusion of Mg^{2+} due to its large size or hydration energy. In nanofiltration, the high asymmetry of membrane permeabilities to Mg^{2+} and Cl^- creates transmembrane diffusion potentials that lead to negative rejections (the ion concentrations in the permeate are larger than in the feed) as low as -200% for trace monovalent cations such as K^+ and Cs^+. Moreover, rejection becomes more negative as the mobility of the trace cation increases. These studies show that a knowledge of single-ion permeabilities is vital for predicting the performance of membranes in the separation and purification of mixed salts.

Unfortunately, the K^+ diffusive flux is relatively low (2.4±0.5 nmol cm^{-2} s^{-1}) in polyelectrolyte multilayers, and nanofiltration, which provides higher throughput than diffusion dialysis, shows selectivities >20-fold lower than diffusion dialysis. Nevertheless, recent result show that electrodialysis can enhance flux and still afford K^+/Mg^{2+} selectivities >100. Similarly, Li^+/Co^{2+} selectivities are >100, which may allow the use of electrodialysis for recycling Li^+ and Co^{2+} from batteries. Current research aims to develop methods for modifying cation-exchange membranes to increase transport numbers (current efficiencies) for the ion of interest. Preliminary studies with films deposited on Nafion membranes show K^+/Mg^{2+} electrodialysis selectivities >50.

Typical multilayer polyelectrolyte membranes exhibit high selectivities between monovalent and divalent ions but not among monovalent or divalent ions. However, recently developed facilitated transport through polyelectrolyte multilayers gives Cu^{2+}/Mg^{2+} selectivities of 50. Formation of these membranes relies on synthesis of polyelectrolytes that contain Cu^{2+}-binding ligands.

Streaming potentials or applied potential gradients across porous membranes should provide selectivity among monovalent ions with different mobilities. The potential creates ion electrophoresis that opposes convective transport. Ions with low mobilities pass through the membrane, but the magnitude of the electrophoretic flux of high-mobility ions approaches that of convective flux to give high rejections. These high rejections should give rise to high selectivities, although thus far selectivities are only around 5. Current research focuses on enhancing discrimination in these challenging separations.

Science objectives for 2014-2016:

- Examine the limits of countercurrent electrophoresis in the separation of monovalent ions with similar mobilities. These studies will include determining the effect of buffer concentration and mobility on these separations.
- Develop permeable membranes with conductive surfaces to control and understand ion partitioning into membrane skins as a function of electrical potential. The applied potential should control ion fluxes in diffusion dialysis and nanofiltration.
- Modify ion-exchange membranes with multilayer polyelectrolyte films to achieve high selectivities between monovalent and divalent ions along with high current efficiencies in electrodialysis separations.

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Ion-Surface Interactions in Mass Spectrometry

Julia Laskin, Principal Investigator
Grant E. Johnson, Co-Principal Investigator
Don Gunaratne and Venkateshkumar Prabhakaran, Postdoctoral Research Associates
Pacific Northwest National Laboratory, P.O. Box 999, K8-88, Richland, WA 99352
Email: Julia.Laskin@pnnl.gov; Web: http://www.pnl.gov/science/staff/staff_info.asp?staff_num=5534

Collaborators: Graham Cooks, Purdue; Sergey Nizkorodov, UC Irvine; Ivan Chu, U Hong Kong, Hong Kong, China; Wen-Ping Peng, National Dong-Hwa University, Taiwan; Alex Laskin, PNNL; Daewon Moon, Daegu Gyeongbuk Institute of Science and Technology; Hao Chen, Ohio University; Murray Johnston, University of Delaware.

Overall research goals: The objective of our research is to achieve a fundamental understanding of physical and chemical phenomena underlying chemical analysis of large molecules in complex heterogeneous environments using mass spectrometry (MS) and to develop preparative MS as a versatile tool for the highly selective synthesis of precisely-defined materials on surfaces. Our research contributes to the BES mission by providing unique tools for fundamental studies in chemical analysis of complex molecules, materials synthesis, catalysis and electrochemical energy storage.

Significant achievements in 2012-2014: Surface-induced dissociation (SID) experiments enabled the first experimental determination of the competition between covalent and non-covalent bond cleavages in non-covalent complexes. Our results emphasize the important role of the activation entropy on dissociation of complex ions. We also used SID to examine the energetics of dissociation of small ammonium bisulfate clusters relevant to new particle formation in the atmosphere. This study identified the presence of a previously unrecognized activation barrier for the incorporation of ammonia and ammonium bisulfate into ammonium bisulfate clusters, which has a significant effect on the rate of the new particle formation process, often described as a barrier-less diffusion-limited process.

Soft-landing of mass-selected ions was used for the first time for preparation of monodisperse layers of ligated metal particles on surfaces. We demonstrated that the charge state and, hence, the reactivity and optical properties of soft-landed ligated metal clusters may be tuned by tailoring the properties of the surface and by varying the surface coverage of ions. Furthermore, our studies showed that soft-landing is uniquely suited for tuning the reactivity of molecules deposited on monolayer surfaces by controlling the acidity of the monolayer. In addition, we developed reactive nanospray desorption electrospray ionization (nano-DESI) for quantitative analysis of selected classes of compounds in complex organic mixtures such as ambient organic particles collected on substrates.

Science objectives for 2014-2016:

- First MS-based studies examining factors affecting nucleation, growth and etching of nanoparticles in scalable solution-phase reduction synthesis.
- Use ion soft-landing for controlled preparation of individual molecules and mesoscale assemblies on surfaces for fundamental studies in thin film electrochemical capacitors.
- Develop methods for quantitative chemical analysis of complex organic mixtures using nano-DESI MS.

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Cryogenic Ion Mobility-Mass Spectrometry (IM-MS): Probing the Structure of Ionic Water Clusters and Hydrated Cluster Ions of Hydrophilic Molecules

David H.Russell
Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, TX 77843
Email: russell@mail.chem.tamu.edu; Web: http://www.chem.tamu.edu/rgroup/russell/

Overall research goals: IM-MS is complementary to X-ray diffraction (XRD), NMR, small-angle X-ray scattering (SAXS), and it provides information that is not readily obtained using techniques that measure sample-averaged signal response. IM-MS can directly measure the molecular heterogeneity, including separation of isomeric species or molecules that differ only in terms of 3-D shapes. Recent developments in cryogenic (80^{o}K) IM show marked improvements in separation efficiency and new approaches for studies of hydrated ionic species.

Significant achievements in 2013-2014: A new cryogenic (80^{o} K) IM-MS was brought on line in early 2013 and this novel instrument has been used to study hydrated hydronium ion clusters, species of the type $H^{+}(H_2O)n$, where n = 1 to > 200. The results reveal new insights on the 3-D shapes of the clusters that are consistent with clathrate cage structures (J. A. Silveira, et al., J. Phys. Chem. A (2013) **117**, 953-961). Studies on polyfunctional molecules, peptides bradykinin and gramicidin S, illustrate new capabilities for studies of solute-solvent interactions. Current studies focus on resolving questions concerning the interactions of water with hydrophilic functional groups, specifically the quanidinium ion (a large, planar ionic species) and substituted ammonium ions (small, high density charged species). **The question:** *are changes in the 3-D shapes of the hydrated ionic clusters an effect of conformational changes of the ionic molecule induced by the solvent or do such interactions alter the local structure of water surrounding the ionic molecule?* Additional studies focus on the fundamentals of ESI, viz. the ability to kinetically trap specific conformers that can be shown to originate from specific hydrated ion conformations.

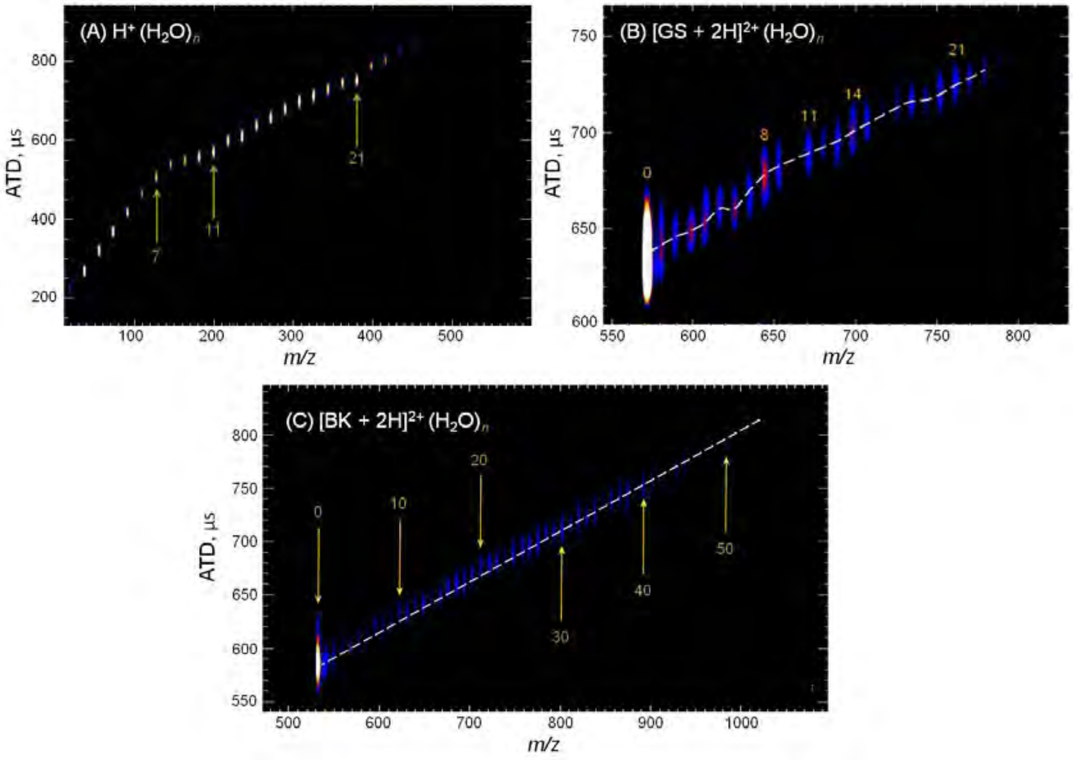

Figure 1. 2-D (mobility vs. m/z) plots of water cluster ions and the hydrated ions of gramicidin S and bradykinin.

Science objectives for 2014-2015:

- Studies of charge state dependence on the extent of hydration are underway and will remain as a major focus area for next six (6) months.
- How does the nature of the solute influence the structure of the solvent; can cryo-IM-MS shed new light on Hofmeister effects? For example, the ammonium ions, which are in the cluster interior, have been reported to promote formation of clathrate structures whereas alkyl ammonium ions are surface-exposed and favor non-clathrate structure...how do such interactions alter ion mobility collision cross sections.
- Metal ions such as La^{3+} have been reported to alter the structure of solvent clusters and these systems are now being explored by using cryo-IM-MS.
- These studies are aimed toward establishing collaborations with groups involved in "cold-ion spectroscopy," i. e., E. Williams (UC-Berkeley) and Tom Rizzo (EPFL).
- Not discussed are projects aimed at broad issues in the development of analytical/separations related to IM-MS.

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The Dynamics and Thermodynamics of Gaseous Macro-ions

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

Collaborators: Dr. Timothy S. Zwier, Purdue University, West Lafayette, IN 47907
Dr. Christopher A. Reed, UC Riverside, Riverside, CA 92521
Dr. Gary L. Glish, University of North Carolina, Chapel Hill, NC 27599

Overall research goals: The overall objectives of this research effort are to expand the range of informative chemistries of gaseous polyatomic ions and their complexes within the context of a mass spectrometry experiment and to provide a deeper understanding of the factors that affect ionic reactions. The specific objectives of the project include study of the selective covalent bond in tandem mass spectrometry via ion/ion chemistry, which promises to greatly enhance the utility of structural characterization by tandem mass spectrometry, the study of ion/ion reactions involving non-covalently bound complex ions with emphasis on hydrated ions, and the spectroscopy of ions derived from energy relevant molecules, such as lignins.

Significant achievements in 2012-2014:
Ion/ion Electron Transfer. In this period, we completed systematic studies on the roles of analyte ion charge state in electron transfer dissociation. This work involved careful measurements of product ion partitioning for a range of charge states of a given ion. We found that the results are consistent with the Landau-Zener based model that we originally developed to examine characteristics of the reagent anions in the competition between electron transfer and proton transfer. We then examined the role of cation recombination energy on product ion partitioning by varying the size of the analyte ion at a constant charge state.

Specific covalent bond formation. We continue to make good progress in our covalent chemistry initiative. We found that we could modify carboxylic acid groups (-COOH) with carbodiimide reagents. We demonstrated this phenomenon with dendrimers and chelating agents, such as EDTA. We also found that quaternary ammonium cations will transfer alkyl cations to carboxylate groups ($-COO^-$) as well as sulphates and phosphates giving rise to a gas-phase esterification.

Dipolar DC in Electrodynamic Ion Traps. We have been exploring the uses of dipolar DC potentials in quadrupolar ion traps in a variety of applications. Considerable emphasis has been placed on this technique for ion heating. This approach turns out to be useful as a broadband means for collisional activation. We are now using it routinely to determine collision induced dissociation kinetics in ion traps. We also explored its use as a means for mass analysis of very high mass-to-charge ions. We found that it a remarkably effect approach for ions with mass-to-charge values in excess of 10^4.

Cold Ion Spectroscopy and Photodissociation. We have made significant progress in our gas-phase ion spectroscopy collaboration with Professor Tim Zwier in our department. We have constructed a triple quadrupole instrument with an ion optical axis that employs a multi-pole cold trap with a recirculating liquid helium refrigeration system. This brings ions down to roughly 10 K so that we can generate high resolution infra-red spectra on conformation selected ions via an action spectroscopy approach. The instrument has been constructed and is generating data. We have collected both IR and UV spectra of well-studied systems, such as protonated tryptophan, and have begun generating data on ions derived from lignins (see Figure 1), which are of interest to the bio-fuels community.

Selective Metal Ion Removal via Ion/Ion Reactions. We began a project this year involving the use of anions of superacids as ion/ion reagents in a collaboration with Prof. Christopher Reed of UC Riverside. These ions have the interesting characteristic of being selective for metal ion removal when there is a mixture of metal ions and protons whereas virtually all other anions that we have used in the past are highly selective for proton removal. This interesting behavior is intimately linked with the low proton affinities of super acid anions.

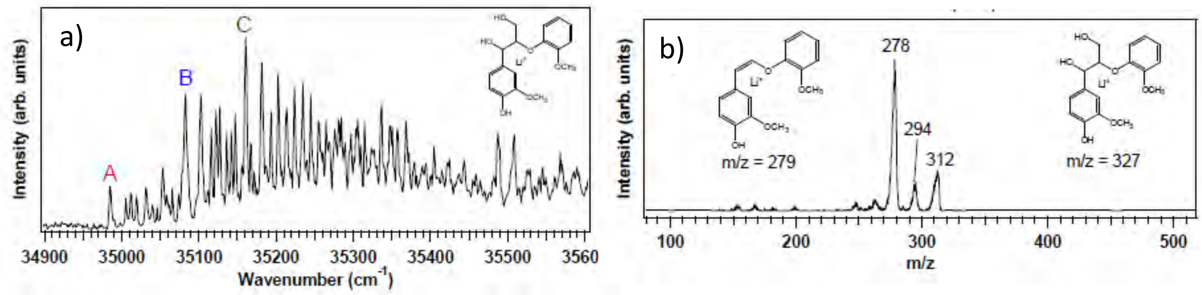

Figure 1 – a) UV photodissociation spectrum of a cold lithiated β-O-4 lignin dimer ((β-O-4+Li$^+$)). b) Photofragmentation spectrum of (β-O-4+Li$^+$) obtained at 35161 cm^{-1} (i.e., conformer C).

Science objectives for 2014-2016:

- Dissociation kinetics studies (using dipolar DC and resonance excitation collisional activation methods) along with DFT calculations will be conducted to investigate the energy surfaces associated with ion/ion reactions that lead to covalent bond formation, as opposed to proton transfer.
- UV and IR photodissociation spectroscopy experiments will be conducted to determine the 3-dimensional structures of cold model ions, such as those derived from lignins, and to explore the complementary structural information that can be obtained from excited state fragmentation .
- The use of superacids as ion/ion reaction reagents will be further explored and developed. Selective metal ion removal from a variety of analyte species that are likely to show a range of interactions with metals will be evaluated.

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Mass Spectrometric Imaging of Plant Metabolites

Basil Nikolau, Principal Investigator
Young-Jin Lee, Co-Principal Investigator
Robert S. Houk, Co-Principal Investigator
3254 Molecular Biology, Ames Laboratory, Ames, IA 50011
Email: dimmas@iastate.edu; Web: http://www.ameslab.gov/cbs/fwp/mass-spectrometric-imaging

Overall research goals: The overarching goal of our research is to understand plant metabolic biology at the level of a single cell, and eventually at the subcellular and possibly the sub-organelle levels using mass spectrometric (MS) imaging techniques. Such information provides unprecedented details about the distribution of metabolites from cell to cell, and enables the visualization of cooperative and antagonistic effects among the metabolites that are programmed by the genetics of the organisms and modified by environmental influences. These details will ultimately lead to a predictive understanding of the mechanisms that multicellular organisms use to regulate metabolic processes.

Significant achievements in 2012-2014: As the technology matures, a critical limitation of MS imaging for practical applications is identifying compounds directly on biological tissues. We have previously developed 'multiplex MS imaging' to acquire both high-resolution MS and MS/MS in a single data acquisition and demonstrated this capability for flavonoids of Arabidopsis flowers. Recently, we have advanced this methodology to include polarity switching, so that we can visualize both positive and negative ions with confident molecular identity (Figure 1).

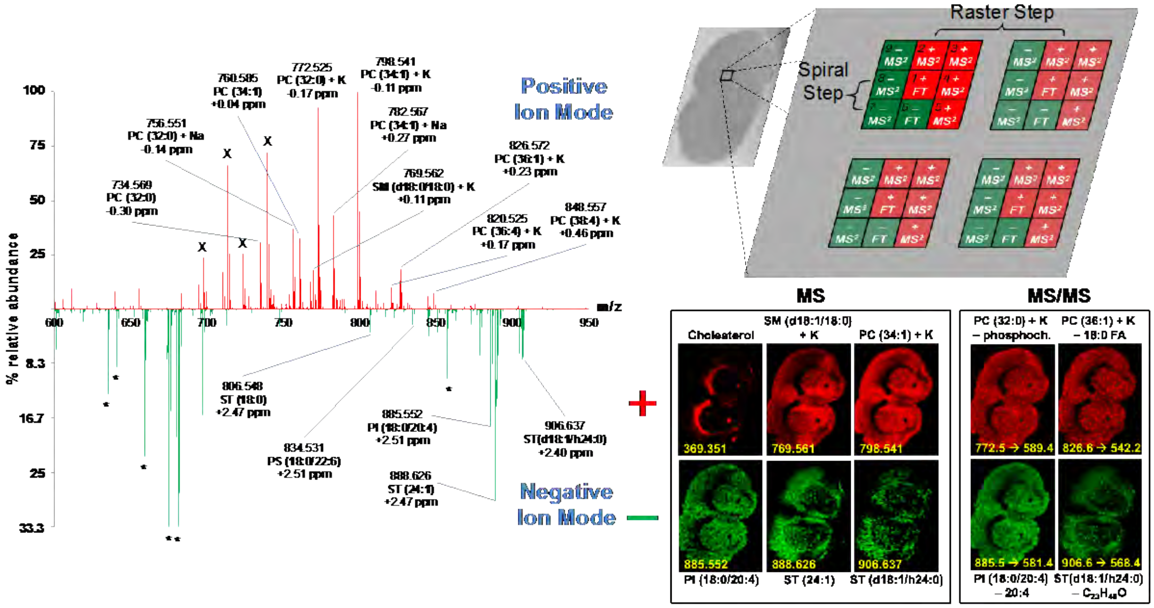

Figure 1. Multiplex MS Imaging with polarity switching. (Left) MALDI-MS spectra in positive and negative ion mode, demonstrating different classes of lipids detected in each polarity. (Top Right) Data acquisition scheme for multiplex MS imaging with polarity switching. Each raster step is split into nine spiral steps: Orbitrap MS (FT; #1, #6) and ion trap MS/MS (#2, 3, 4, 5 or #7, 8, 9) for each polarity. (Bottom Right) Various lipid images obtained from a mouse brain section for both positive and negative ion mode, and in high-resolution MS and MS/MS (ref 2).

Because of wide range of chemical functionalities, ionization of small metabolites has strong matrix dependence and it is challenging to visualize certain metabolites in MALDI MS imaging. To overcome this limitation, we have developed diaminonaphthalene as a new matrix for small molecules in negative ion mode and screened fifteen different nanoparticles for their ability to ionize over thirty different plant metabolites. Previously we had achieved 10 μm spatial resolution in MS imaging, and currently this has been enhanced to a resolution of 5 μm. Such high spatial resolution will enable the investigation of metabolite trafficking at the cellular and subcellular levels. We also have also developed new sample preparation methods, imprinting and fracturing, to visualize internal plant metabolites in lateral resolution and applied these methods to study chemical interfaces in plant-pathogen interactions. Initial results on atmospheric pressure LDI with a new ion mobility TOF-MS will also be presented. This capability is meant to complement the ongoing reduced pressure LDI work by resolving isobaric compounds by ion mobility, and b) allowing experiments in real time on living plants, and c) allowing measurements of volatile metabolites that are lost in reduced pressure experiments.

We have developed unique genetic resources to apply these new MS-imaging technological advancements. These are associated with maize and Arabidopsis genetic isolines that express different metabolic outcomes as a consequence of either loss-of-function alleles or gain-of-function alleles. These mutant lines are affected in processes associated with different aspects of acetyl-CoA metabolism. The ability to visualize these metabolic alterations in acetyl-CoA metabolism is paramount to fully understand and dissect the asymmetric distribution of acetyl-CoA metabolism among different cellular and subcellular compartments. The acetyl-CoA metabolic processes have been selected for these studies because they represent a nexus in capturing solar energy and converting it to valuable, high energy biochemicals that have potential applications in biofuels and industrial chemicals that are currently derived from petroleum, with an associated large, negative environmental footprint.

Science objectives for 2014-2016:

- Study metabolite trafficking in cellular and subcellular level with 5 μm spatial resolution.
- Visualize dynamic metabolic changes occurring in corn seed germination in 2D and 3D chemical images at various germination time points.
- Understand NALDI (nanoparticle-assisted laser desorption ionization) mechanism through comparative study between various nanoparticles.
- Evaluate a 100 fs laser for laser desorption and laser ablation for 3D imaging of plant materials

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New Approaches for Metabolomics by Mass Spectrometry

Akos Vertes, Principal Investigator
Bindesh Shrestha, Postdoctoral Research Associate
Department of Chemistry, George Washington University, Washington, DC 20052
Email: vertes@gwu.edu; Web: vertes.columbian.gwu.edu)

Collaborators: Dr. Éric Maréchal, CEA-CNRS-INRA-Univ. Grenoble Alpes, Grenoble, France
Dr. R. K. Kostiainen, P.O. Box 56, University of Helsinki, Helsinki, Finland

Overall research goals: Our overall aim in this project is to develop new approaches for the direct analysis of small molecules in unprocessed biological samples relevant for energy research. This will enable capturing information on a large variety of metabolites, with the ability to distinguish structural isomers through the combination of new ionization techniques, ion mobility separation (IMS) and mass spectrometry (MS).

Significant achievements in 2012-2014: During the current reporting period we combined laser ablation electrospray ionization (LAESI) with IMS and MS. We utilized this new method for the structural analysis of metabolites, lipids and peptides in small populations of live microalgae that are used as a model system for biofuel research (see Figure 1(a)). LAESI-IMS-MS was extended for molecular imaging of isobaric species in live biological tissues. Other progress included developing an ambient molecular imaging technique (see Figure 1(b)) with enhanced ionization efficiency for nonpolar and neutral compounds, and exploring alternative ion source geometries to achieve smaller ablation spots using focusing optics with higher numerical aperture.

Combining the LAESI ambient ion source with IMS enabled us to separate isobaric ions, including structural isomers, on the fly, and subject the separated ion packets to MS and tandem MS. Direct analysis of a wide variety of biological samples, including aqueous protein solutions, mouse brain sections, *Arabidopsis thaliana* and other plant leaves, megakaryoblast cell lines, and *Chlamydomonas reinhardtii* microalgae, was carried out to test the performance characteristics of this new technique.

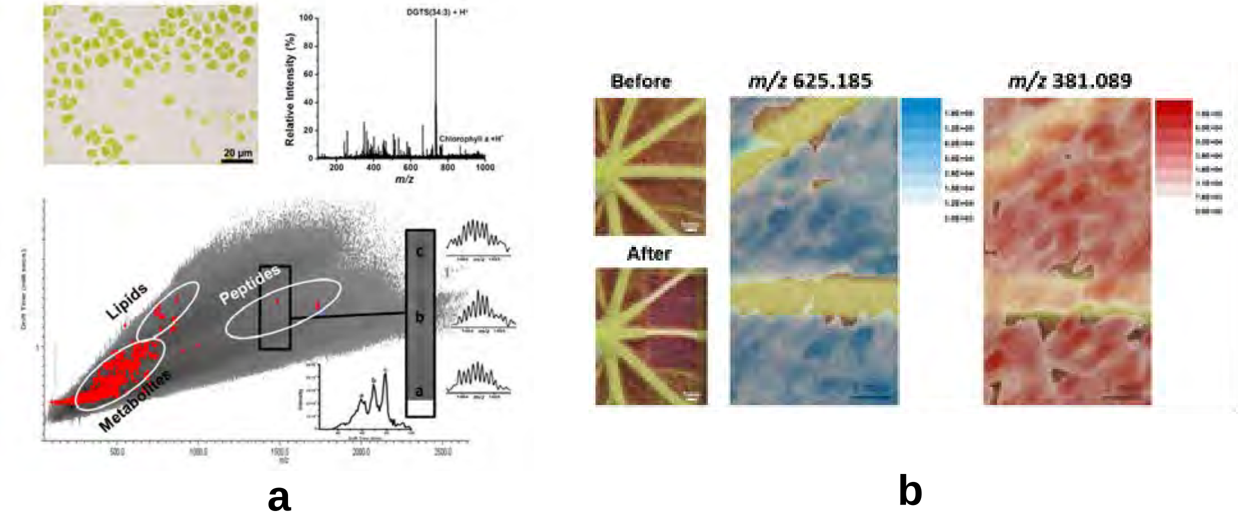

Figure 1. (a) (top) A representative microscope image and a typical LAESI mass spectrum of live *C. reinhardtii* cells and (bottom) corresponding DT vs. *m/z* map with highlighted regions corresponding to metabolites, lipids, and peptides. Inset shows three distinct peaks for a multiply charged ion at *m/z* 1484 at different drift times, suggesting three structural isomers or conformers. (b) Microscope image of ivy geranium leaf abaxial epidermis before and after ablation is shown. Molecular distributions of ions generated by LAESI-IMS-MS from the ivy geranium leaf revealed trihydroxy-methoxyflavone at *m/z* 625 as more prevalent outside of veins, whereas the distribution of the disaccharide ions at *m/z* 381 was more uniform over the tissue.

Science objectives for 2014-2016:

- Exploring the utility of LAESI-IMS-MS to follow the metabolic response to environmental conditions in wild type and genetically modified *Chlamydomonas*. Specifically, we are testing the ability of this technique to discern changes in the type and quantity of lipids, when nutrients or light conditions are altered or certain metabolic pathways are shut down.
- We plan to explore the incorporation of stable isotopes into microalgae by LAESI-IMS-MS using pulse-chase experiments. This will result is a broadly applicable technique to determine the metabolite and lipid turnover rates in plants and microorganisms, and to directly interrogate metabolic networks.
- Transmission geometry laser ablation microsampling will be developed to analyze plant cells using LAESI-IMS-MS.

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Mapping Surface Functionality and Reactivity Using Single Molecule Probes

Daniel K. Schwartz, Principal Investigator
Dept. of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, CO 80309
Email: daniel.schwartz@colorado.edu; Web: www.colorado.edu/chbe/daniel-k-schwartz/

Overall research goals: The goal of this project is to develop and employ real-time imaging methods that use individual reactant/adsorbate molecules as probes of surface chemical functionality (particularly non-covalent interactions) and reactivity. The approach is based on observations of individual molecules using total internal reflection fluorescence microscopy (TIRFM), including high-resolution spectral methods involving resonance energy transfer. These methods are appropriate for the development and characterization – and especially the mechanistic understanding – of heterogeneous materials (including nanomaterials) that are widely employed in separation processes, energy conversion, and catalysis.

Significant achievements in 2012-2014: In previous work, we developed a super-resolution chemical imaging technique, MAPT (Mapping using Accumulated Probe Trajectories), in which a large number of interfacial molecular trajectories are determined using single-molecule TIFRM. By tracking the molecular locations through time, physical properties of probe/surface interactions (adsorption rates, local diffusion, desorption probability and surface coverage) are determined and sorted spatially to prepare surface maps. Recently, we showed that highly-charged probe molecules can be used to map regions associated with surface charge via local electrostatic interactions. We also showed that probe molecules that engage in interactions to specific surface structures (e.g. crystalline vs. amorphous regions) can be used to identify those particular regions while simultaneously determining the characteristic dynamic molecular behavior within those regions.

We have made significant progress understanding the fundamental dynamics of, and interactions between, various classes of molecules at solid-liquid interfaces. For example, we studied the interactions between a hydrophobic adsorbate probe molecule and hydrophobic self-assembled monolayers (SAMs), the effects of specific (Hofmeister) ions on hydrophobic interactions, and the dynamic behavior of biomolecules (proteins, peptides, and nucleic acids) as a function of surface chemical properties. Notably, we discovered a highly-general mechanism of molecular interfacial mobility (see Figure 1) that involves periods of confined 2D diffusion punctuated by occasional long 3-dimensional flights.

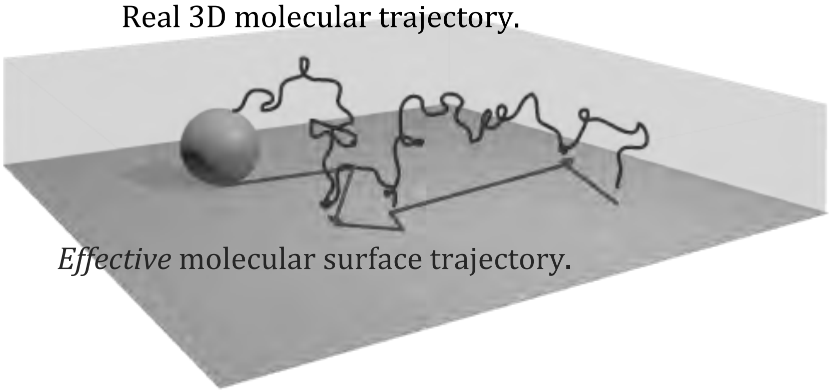

Figure 1. Many molecules (including polymers, proteins, and small aliphatic and aromatic molecules) diffuse at the solid-liquid interface by executing 3-dimensional flights through the liquid phase rather than by executing 2-dimensional random walks at the surface. These trajectories, similar to "forager dynamics" well-known in biology, represent a highly efficient search process and may also enable new approaches to control or direct molecular motion at interfaces.

Science objectives for 2014-2016(style=Stand alone text heading):

- Multi-color surface mapping methods will be developed involving multiple probes as well as individual probes that exhibit spectral shifts associated with specific surface chemistries.
- Experiments will be developed to measure first passage time distributions for interfacial targeting processes. These will be used to directly test the efficiency of intermittent motion.
- Single-molecule tracking methods will be directly to materials and dynamics directly associated with separation processes including reversed phase liquid chromatography.
- Unsupervised machine learning approaches will be developed to mine large datasets of molecular trajectories in unbiased ways.
- Three-dimensional tracking methods will be developed using structured illumination (i.e. double-helix point spread function analysis).

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Analytical Spectroscopy Methods for Liquid/Solid Interfaces

Joel M. Harris, Principal Investigator
Eric Peterson, Postdoctoral Associate; Justin Cooper, Chaoxiong Ma, Jay Kitt, and Jonathan Schaefer, Graduate Students; University of Utah, Department of Chemistry, Salt Lake City, UT 84112-0850
Email: harrisj@chem.utah.edu ; Web: http://www.chem.utah.edu/directory/faculty/harris.html

Collaborators: Dr. Marc Porter, University of Utah

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 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 and the efficiency of chemical separations. 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 Raman and single-molecule fluorescence microscopies capable of *in situ* characterization of sub-monolayer populations.

Significant achievements in 2012-2014: Raman microscopy has been applied to studies of structure and trace-level detection at liquid/solid interfaces. The self-assembly of carboxy-terminated n-alkanethiols onto silver was shown by surface-enhanced Raman scattering (SERS) to be a multistep process, initiated by binding of both carboxylate and thiol groups. In a second step, carboxylate interactions are displaced by thiol-metal bonds, producing an ordered monolayer.[1] Modifying surfaces with functionalized monolayers expands the variety of species that can be SERS detected. Detection of ionic solutes can be enhanced by a charged surfactant adsorbed to an n-alkane-modified SERS surface. The surfactant attracts ionic solutes of opposite charge where they are detected at 2-orders-of-magnitude lower concentrations than in free solution.[2] We used Raman microscopy to detect of polycyclic aromatic hydrocarbons extracted into single C18-silica particles serving as 100-fL collectors.[3] A *48,000-fold concentration gain allowed detection of 10-nM pyrene* from solution, an exceptional result for Raman scattering without surface enhancement. Comparable results were achieved with a new porous particle material made by vinyl polymerization of an acrylate-carboxylate surfactant, which does not require subsequent silane surface modification.[4]

A new research area for the group is imaging single-molecules and their surface dynamics at liquid-solid interfaces using fluorescence microscopy. Our initial goal was to provide quantitative analysis of interfacial molecular populations, used to address the question of how electric fields influence polyelectrolyte populations at an interface. We adapted ITO electrodes to single-molecule imaging of individual polyelectrolyte molecules a potential-controlled surface, which showed counter-ions screen much of the polymer excess charge.[5] We also investigated surface charging of ITO by photo-excitation at energies well below the band gap of the semiconductor using charged fluorescent nanoparticles as interfacial potential probes.[6] Most recently, we employed single-molecule tracking to report the first observations of transport dynamics and retention trajectories of individual molecules within *authentic, commercial reversed-phase chromatographic silica particles*.[7]

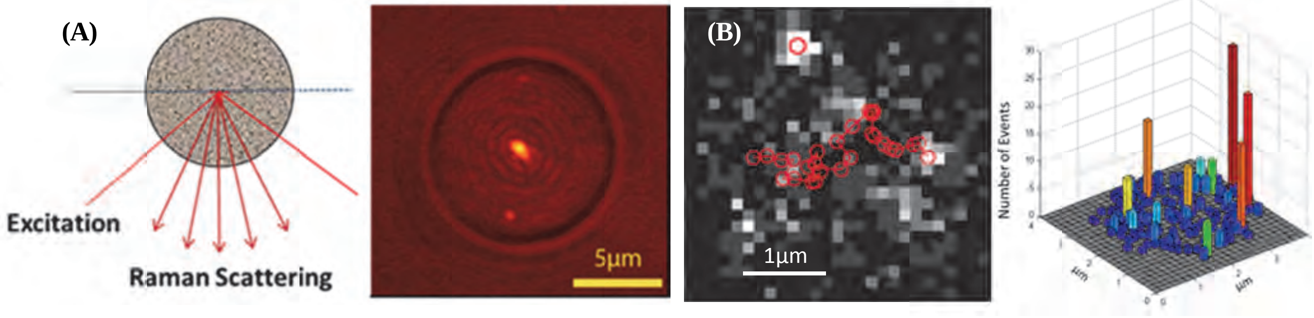

Figure 1 A. Excitation and collection of Raman scattering from within an individual C_{18}-modified silica particle.
B. Imaging single- molecular retention trajectories in a 3-μm C_{18}-silica particle and stuck molecule events (right).

Science objectives for 2014-2016:

- Confocal-Raman microscopy will be applied to studying the interior composition and interface structure of chromatographic silica particles. The time dependence of solute accumulation will provide information about kinetics of transport and partitioning of non-fluorescent molecules within porous particles. The influence of the solute structure on conformations of n-alkyl chains will be investigated to provide molecular-scale understanding of chromatographic retention.

- Confocal-Raman microscopy of the interior composition of porous particles will be applied to measurements of octanol-water partitioning in individual silica particles, whose pores filled with octanol. This is a very sensitive and fast approach to determining the partitioning of aromatic carboxylates, which is critical to their use in enhanced oil recovery, and the partitioning of naphthenic acids, which controls their environmental impact in the extraction of tar sands.

- While octanol-water coefficients is relevant to partitioning between water and continuous organic phases such as petroleum, their use in assessing bioactivity of compounds is not ideal, because they lack the interfacial interactions present in lipid membranes of cells. To address this question, we assemble lipid bilayers on the interior surfaces of porous silica. The structure and phase transitions of these bilayers are comparable to phospholipid vesicle membranes, but they provide 500-times greater surface area. They will be used to study small-molecule interactions with lipid membranes and membrane-bound redox-active proteins relevant to energy research.

- Molecular transport dynamics that impact the efficiency of chromatographic separations and catalysis will be investigated by imaging single-molecule trajectories within individual particles of commercial chromatographic media and catalyst supports. With astigmatic imaging and real-time image analysis, the microscope stage can follow the z-axis motion of molecules, which will allow tracking of molecular trajectories through a particle in all three dimensions.

- Fluorescence imaging correlation spectroscopy can report diffusion at rates that exceed the speed of single-molecule tracking of molecular motions. The method employs a fast-framing CCD camera that can map diffusion on inhomogeneous surfaces, where the size and location of a test area are controlled electronically. We will use this method to measure fast diffusion within porous particles under conditions that better represent chromatographic elution and catalyst applications.

References to work supported by this project 2012-2014:

1. Chaoxiong Ma and Joel M. Harris, "Surface-Enhanced Raman Scattering Study of the Kinetics of Self Assembly of Carboxylate-Terminated n-Alkanethiols on Silver," Langmuir **28**, 2628-2633 (2012).
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Optical Mass Spectrometer and Photoacoustics

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

Overall research goals: Several research objectives have been proposed for this project. Experiments and theory have been initiated to investigate a photoacoustic pyrometer, photoacoustic double resonance, the generation of the photoacoustic effect with an unmodulated laser beam, the properties of the photoacoustic effect in a periodically modulated structure, the production of the ultrasonic vibration potential using a colloidal jet, and investigation of the motion of an optically levitated particle with the goal of determining particle masses.

Significant achievements in 2010-2013: Although it is not commonly known, the photoacoustic effect can be generated by emission of infrared radiation from a photoacoustic cell when a chopping wheel is placed in the path between the cell and a cooled body. The resulting production of sound in the photoacoustic cell is referred to as the "inverse" photoacoustic effect, which has a sensitivity of on the order of 1 part in 10^5 of SF_6 in N_2 when a cell at room temperature views a body at 77 K. We have used this effect as the basis for a photoacoustic pyrometer, which operates by having a photoacoustic cell located between two chopping wheels. One side of the photoacoustic cell views a reference at a known temperature and the other side views the object whose temperature is to be determined. The method produces a null when the object and reference are at the same temperature.

The production of the photoacoustic effect in a phononic structure constructed so that the sound speed varies sinusoidally along the length of the device has been studied. Solutions to any problem involving optical excitation of such a structure can be expressed in terms of either Mathieu functions, or the integer or fractional Mathieu functions. A solution has been found for excitation in a finite region of the structure where the results are expressed in terms of new, traveling wave Mathieu functions. Results of the calculations show a confinement effect of photoacoustic waves in space when the excitation frequency generates waves within band gaps. It is of note that it is possible to excite waves within ban gaps in the case of the photoacoustic effect. The results obtained are found to be applicable to heat diffusion problems. That is, for a structure where thermal properties of a structure vary sinusoidally in space, solutions for the time varying temperature can be found in terms of complex Mathieu functions.

The ultrasonic vibration potential is a voltage that arises when ultrasound propagates through an ionic or colloidal solution. In the case of colloidal particles, charged chemical groups are attached to the particles and a counter charge lies in a spherical distribution around each particle. If the particles and fluid have different densities, the fluid and the particles move differently in response to the oscillatory force of ultrasound, executing motions that are of different amplitude and phase with respect to the ultrasonic wave. Since the charges are chemically affixed to the particles, the differential motion of the fluid and particle results in a distortion of the normally spherical counter charge distribution resulting in the production of a dipole at the site of each particle and a macroscopic voltage in the fluid. Experiments here have shown that the vibration potential can be generated in aqueous colloidal suspensions by rapid deceleration of a stream of suspension striking a fixed electrode. That is, the differential deceleration of the particles in suspension relative to the fluid when a jet of the suspension strikes a flat conductor produces a voltage between the electrode and the metallic tubing used to produce the jet, the voltage being constant unless the jet is interrupted. The features of this method of production of the vibration potential are the simplicity of the experimental apparatus required and the high signal-to-noise ratio in the recorded signals.

Science objectives for 2014:

- Work is continuing on the production of the photoacoustic effect by a continuous laser beam directed into a photoacoustic cell containing an absorbing gas. A theory of this effect has been given by the author that shows that a mode locking effect is produced by a feedback mechanism that involves an increase in absorption and sound production at a pressure antinode in the cell. Further experiments with different temperature references and absorbing gases are in progress in testing the photoacoustic pyrometer. Further experiments with the jets of colloids are in progress to determine if the method is viable as a basis for determining zeta potentials. Experiments with optically levitated particles are in progress. An electrostatic trap has been constructed to operate together with the optical trapping beam to permit trapping of particles at low pressures.

References to work supported by this project 2011-2014:

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2. "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)

3. "Photoacoustic effect in a sinusoidally modulated structure", Binbin Wu and Gerald J. Diebold *Appl. Phys. Lett*. **100**, 164102 (2012)

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Design of Stratified Functional Nanoporous Materials for CO_2 Capture and Conversion

Karl Johnson, Principal Investigator
Jingyun Ye, Postdoctoral Researcher
University of Pittsburgh, 1249 Benedum Hall, Pittsburgh, PA 15261
Email: karlj@pitt.edu; Web: puccini.che.pitt.edu

Collaborators: Dr. Nat Rosi, University of Pittsburgh

Overall research goals: We will use a hierarchy of computational methods to design and screen a large number of functional groups that can be incorporated within metal organic frameworks (MOFs) for their potential to bind and catalytically reduce CO_2 through the addition of hydrogen. We will compute reaction pathways and energy barriers for the most promising candidates identified from screening. We will also estimate diffusivities of reactants and products into and out of the functionalized MOF to screen for transport limitations. The most promising materials will be synthesized and tested experimentally by our collaborator.

Significant achievements in 2012-2014: The work on this project started in February 2014. We therefore only have preliminary results at this time. We have begun by investigating frustrated Lewis pairs (FLPs) as potential functional groups for binding and reducing CO_2. A large number of potential FLPs can be synthesized, providing a significant design space for tuning chemical and steric interactions. Moreover, existing FLPs have been shown to heterolytically cleave H_2 producing hydridic and protic hydrogens bound to the Lewis acid and Lewis base sites, respectively. These hydridic and protic hydrogens are very active for reducing CO_2 at the carbon and oxygen sites, respectively. Frustrated Lewis pairs require significant steric hindrance in solution to prevent formation of the Lewis acid-Lewis base adduct. However, our hypothesis is that FLP moieties bound within MOFs do not need to have their acid and base sites sterically hindered because they are immobilized. An example of a FLP having both Lewis acid and base sites within a single molecule is 1-[bis(pentafluorophenyl)boryl]-3,5-di-*tert*-butyl-1*H*-pyrazole [**1** in Fig. 1(a)]. This FLP is known to heterolytically cleave H_2 and bind CO_2, and therefore is a good candidate for a starting point in designing FLPs functionalized MOFs. We have modified **1** by removing the *tert*-butyl groups and replacing the bulky C_6F_5 moieties with F atoms. This modified molecule, **2** (1-(difluoroboranyl)-4-methyl-1*H*-pyrazole), is shown in Fig. 1(b). We have incorporated **2** inside UiO-66 [shown in Fig. 1(c)], which is a chemically and thermally stable MOF that can be modified post-synthetically. A snapshot of UiO-66 having two functional groups based on **2** is shown in Fig. 1(d).

We have computed binding energies for CO_2 and H_2 bound in UiO-66 having one or two functional groups based on **2**. The fully relaxed geometry of CO_2 bound to 2 inside UiO-66 having one functional group is shown in Fig. 2(a). We see that the C atom in CO_2 binds to the N atom in the β position to the boron group and one O atom binds to the boron atom, analogously to the known binding mode for CO_2 to **1**, as reported in the literature. The binding energy for this complex is -0.93 eV, as computed from DFT with the PBE functional, using the CP2K code. The binding energy for CO_2 in UiO-66 having two functional groups is -0.66 eV [Fig. 2(b)]. This indicates that the binding energy can be tuned to some extent by modifying the pore functionality. The binding energies for dissociated H_2 in these same structures are -0.59 and -0.20 eV, respectively.

Science objectives for 2014-2016:

- Screen multiple functional groups for their potential to bind CO_2 and dissociate H_2 within one or more MOFs.
- Compute reaction pathways for CO_2 reduction for the most promising candidate structures identified through screening.

- Identify underlying physics and chemistry governing the reaction pathways and barriers. Look for connections between electronic properties, charge densities, binding energies, and favorable reaction pathways.
- Compute diffusivities of reactants and products to identify diffusion pathways and mechanisms and how they impact potential transport limitations and the efficiency of CO_2 conversion.

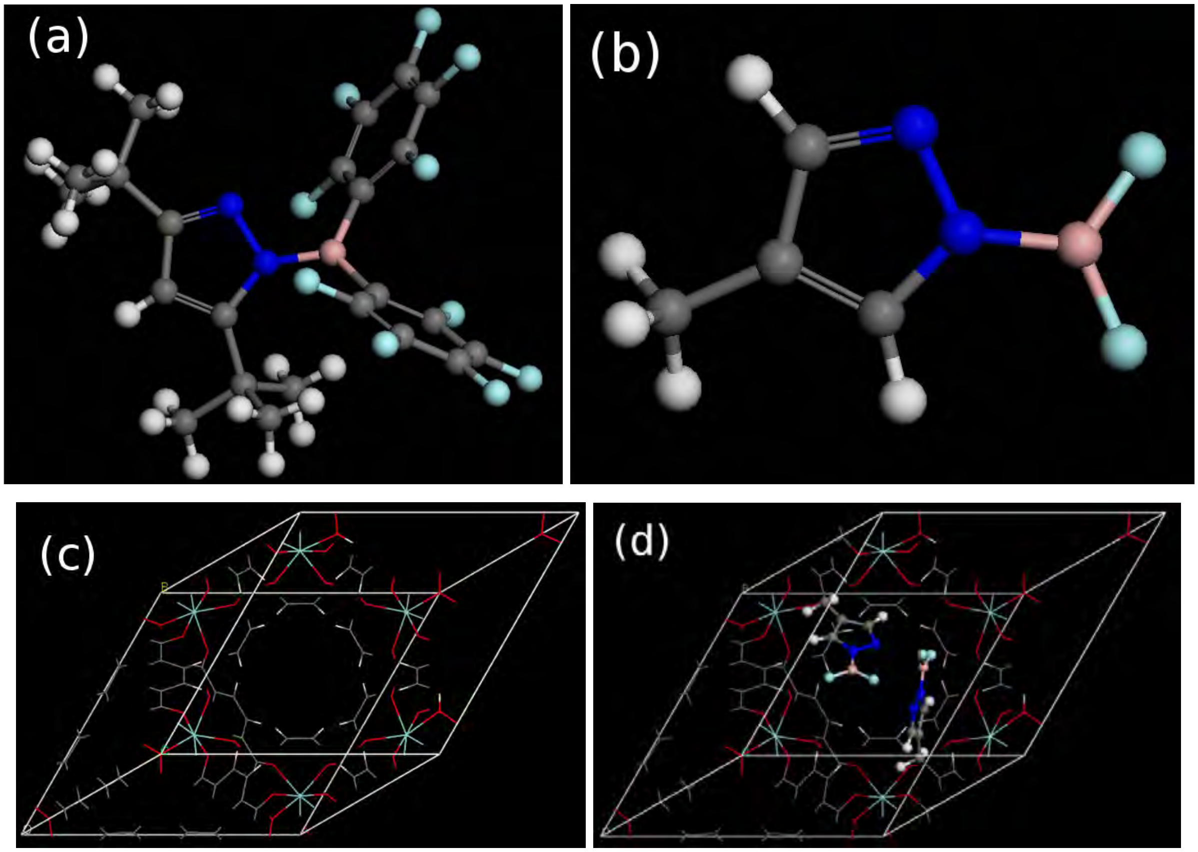

Figure 1. (a) Structure of 1-[bis(pentafluorophenyl)boryl]-3,5-di-*tert*-butyl-1*H*-pyrazole, **1**, a frustrated Lewis pair. (b) Structure of 1-(difluoroboranyl)-4-methyl-1*H*-pyrazole, **2**, a modified version of **1** for inclusion in UiO-66. (c) UiO-66 unit cell. (d) UiO-66 functionalized with two functional groups based on structure **2**.

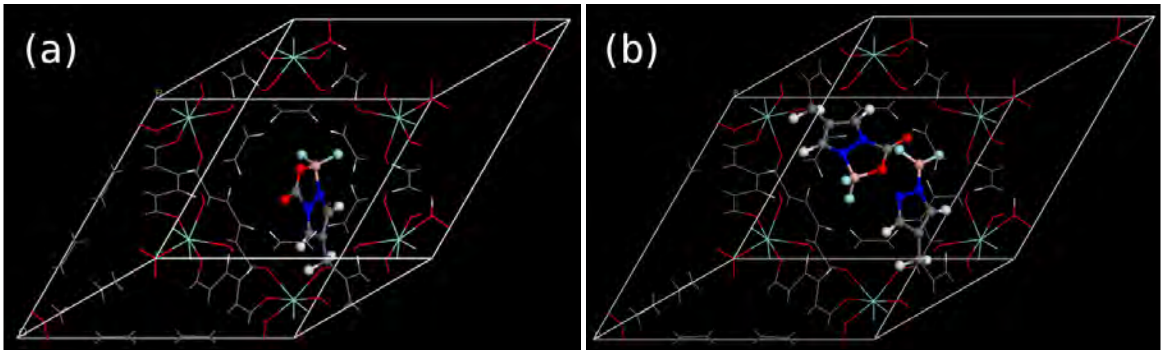

Figure 2. (a) CO_2 bound to UiO-66 functionalized with one functional group based on **2**. The computed binding energy is -0.93 eV. (b) CO_2 bound to UiO-66 functionalized with two functional groups based on **2**. The computed binding energy is -0.66 eV.

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