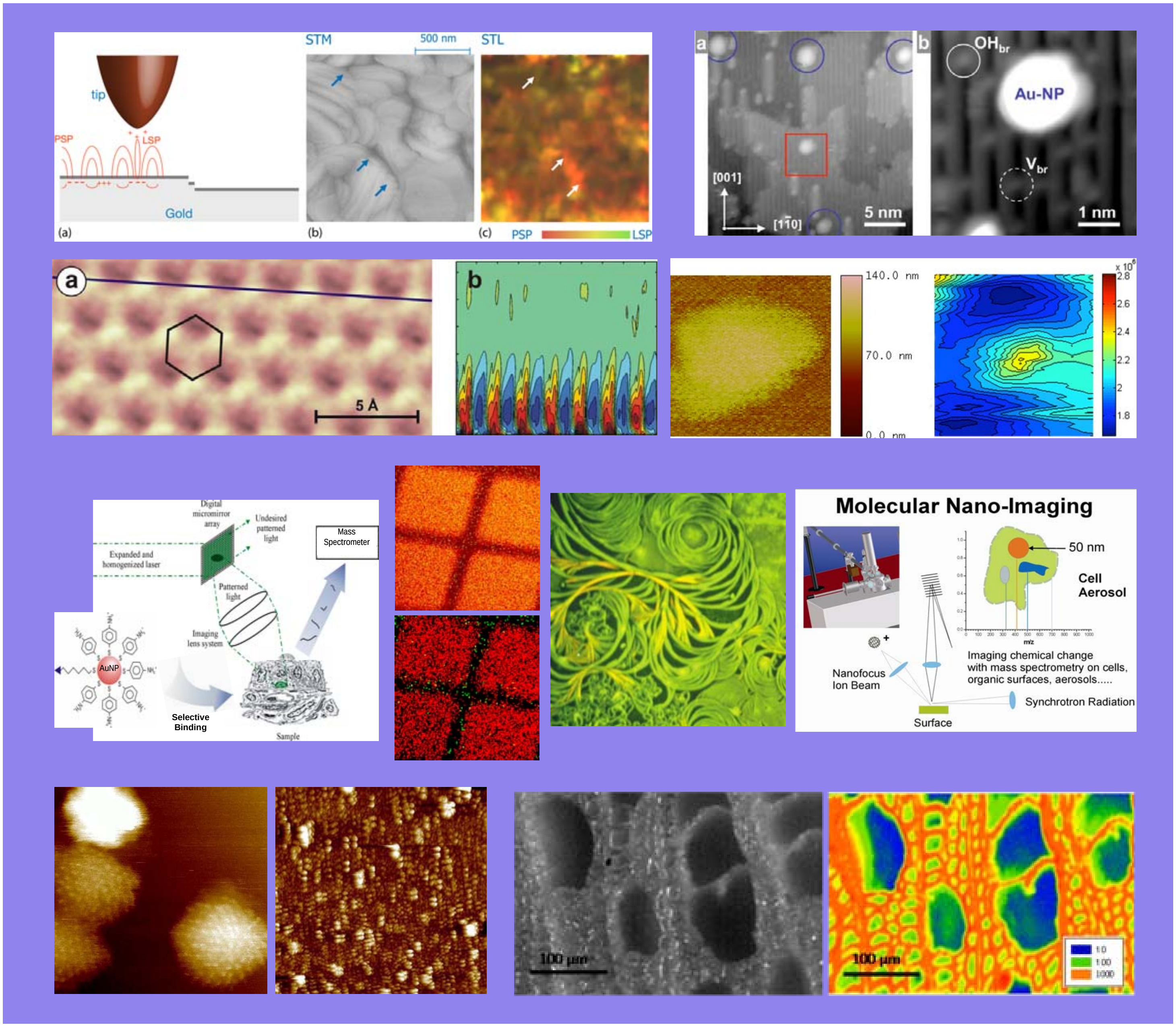
2008 Analysis, Imaging, and Separations Research Meeting

Program and Abstracts

O'Callaghan Annapolis Hotel, Annapolis, MD May 4-7, 2008



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

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DOE Contractors' Meeting
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Cover Graphics:
The cover artwork is a sampling of chemical-imaging and analysis related graphics taken from the following abstracts submitted to this meeting (upper left to lower right);

S3-2, Jao van de Lagemaat – Plasmon Resonance Imaging
S2-1, Peter Sutter – Ultrafast and Chemically Specific Microscopy for Atomic Scale Imaging of Nano-Photocatalysis
S3-3, Udo D. Schwarz – Atomic Resolution Imaging and Quantification of Chemical Functionality of Surfaces
P1-3, Robert W. Shaw – Laser Spectroscopy/Imaging at the Nanoscale
P1-1, Kate Stumpo et al., – Nanoparticles as Selective Matrices for Imaging Mass Spectrometry
S5-3, Nicholas Winograd – Chemical Imaging with Cluster Ion Beams and Lasers
S7-2, Steven K. Buratto – Photophysics of Organic Semiconductors Probed by a Combination of High Resolution Fluorescence Microscopy and Ion Mobility Mass Spectrometry
S1-1, Musahid Ahmed - Investigating atoms to aerosols with vacuum ultraviolet radiation
S5-2, David Tiede – Ultrafast Imaging of Photosynthetic Solar Energy Flow
S5-1, Garth J. Simpson - Molecular Insights from Polarization-Dependent Nonlinear Optical Measurements

The program managers at DOE BES sincerely appreciate the extra effort and accommodation that have made it possible to present projects funded in the Chemical Imaging Initiative across the Chemical Sciences, Geosciences, and Biosciences Division in the context of this Separations and Analysis Program Contractors' Meeting.

This document was produced under contract number DE-AC05-06OR23100 between the U.S. Department of Energy and Oak Ridge Associated Universities.

The research grants and contracts described in this document are supported by the U.S. DOE Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division.

Foreword

This abstract booklet provides a record of the second U.S. Department of Energy contractors' meeting focused on separations and analysis sciences. This year the meeting is co-chaired by Professor Mary Wirth (University of Arizona) and Professor Paul Bohn (University of Notre Dame) and includes reports from projects funded in the recent Chemical Imaging Initiative across the Chemical Sciences, Geosciences, and Biosciences Division. Meeting participants also greatly benefit from interactions with a number of invited presenters selected by the co-chairs.

The objective of this meeting is to provide a fruitful environment in which researchers with common interests will present and exchange information about their activities, will build collaborations among research groups with mutually reinforcing strengths, will identify needs of the research community, and will focus on opportunities for future research directions. The agenda has invited talks, oral presentations, and 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.

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

We thank all of the researchers whose dedication and innovation have advanced DOE BES research and made this meeting possible and productive. We hope that all of you will build on your successes and that we will assemble in a very few years for our next meeting.

We thank Diane Marceau of the Chemical Sciences, Geosciences and Biosciences Division, and Margaret Lyday and Camella Mitchell of the Oak Ridge Institute for Science and Education for their important contributions to the technical and logistical features of this meeting.

William S. Millman
Larry A. Rahn

Greg Fiechtner
Raul Miranda
Mark Spitler
Nicolas Woodward

Agenda

2008 Analysis, Imaging, and Separations Research Meeting
O'Callaghan Annapolis Hotel, Annapolis, MD May 4 - 7, 2008

Sunday, May 4, 2008

5:00 – 6:30 p.m. **Registration**
6:30 – 7:30 **Dinner**

Session 1 – Chemical Imaging I – Mary Wirth, Chair

7:30 – 7:45 p.m. Welcome – Bill Millman, Mary Wirth, Paul Bohn,
7:45 – 8:30 Invited – Dr. Musahid Ahmed - Investigating atoms to aerosols with vacuum ultraviolet radiation

Invited Poster Introductory Presentations:

8:35 – 8:40 Professor Ryan C. Bailey – Real-Time Observation of Interfacial Binding and Reactivity with Optical Ring Resonators
8:40 – 8:45 Professor Amanda Haes – Nanoparticle-Enhanced Capillary Electrophoresis
8:45 – 8:50 Professor Masaru Kuno – Flickering semiconductor nanowires
8:50 – 8:55 Professor Jennifer S. Shumaker-Parry – Plasmonic Structures and Assemblies with Tunable Optical Properties
8:55 – 9:00 Professor Zuzanna S. Siwy – Measuring ion currents carried by ionic liquids in nanopores of well-defined geometry and surface chemistry

Monday, May 5

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

Session 2 – Chemical Imaging II – Alexandra Navrotsky, Chair

8:10 – 8:35 a.m. John Miller – DOE Update
8:35 – 9:00 Peter Sutter – Ultrafast and Chemically Specific Microscopy for Atomic Scale Imaging of Nano-Photocatalysis
9:00 – 9:25 Glen Waychunas – Time-resolved and Ultrafast Imaging of Redox Processes on Mineral Surfaces
9:25 – 9:50 Ning Fang – Single-Molecule Imaging
9:50 – 10:15 Carrick Eggleston – Synthesis and Characterization of Nanocrystalline α-Fe2O3 Films for Waveguide Scanning Photocurrent Microscopy

10:15 – 10:45 **Break**

Session 3 – Chemical Imaging III - Scott A. McLuckey, Chair

10:45 – 11:30 a.m. Invited - Professor Michael D. Barnes – Chemical Microscopy of Novel Nanostructures
11:35 – 12:00 p.m. Jao van de Lagemaat – Plasmon Resonance Imaging
12:00 – 12:25 Udo D. Schwarz – Atomic Resolution Imaging and Quantification of Chemical Functionality of Surfaces

12:25 – 1:20 **Working Lunch**

1:20 – 1:30 Put up posters for Poster Session 1
1:30 – 5:00 **Interaction Time**

Session P1 - Poster Session 1

5:00 – 6:00 p.m.
P1-1 David H. Russell - Nanoparticles as Selective Matrices for Imaging Mass Spectrometry
P1-2 Invited – Jennifer S. Shumaker-Parry - Plasmonic Structures and Assemblies with Tunable Optical Properties
P1-3 Robert W. Shaw - Laser Spectroscopy/Imaging at the Nanoscale

P1-4 Invited – Ryan C. Bailey - Real-Time Observation of Interfacial Binding and Reactivity with Optical Ring Resonators
P1-5 Joel Harris - Analytical Spectroscopy Methods for Studying Liquid/Solid Interfaces
P1-6 Richard E. Russo - Laser-Material Interactions (ablation) for Chemical Analysis
P1-7 Professor J. Thomas Dickinson - Laser-Material Interactions Relevant to Analytic Spectroscopy of Wide Band Gap Materials
P1-8 Julia Laskin - Ion-Surface Interactions in Mass Spectrometry
P1-9 Akos Vertes - Nanostructured substrates and imaging applications of soft laser desorption ionization
P1-10 Invited – Zuzanna S. Siwy - Measuring ion currents carried by ionic liquids in nanopores of well-defined geometry and surface chemistry
P1-11 Paul W. Bohn - Molecular Aspects of Transport in Thin Films of Controlled Architecture
P1-12 Alexandra Navrotsky - Energetics of Nanomaterials

6:00 – 7:00 **Working Dinner**

Session 4 – Membranes and Media I – Dr. William Millman, Chair
7:00 – 7:25 p.m. Georges Belfort – Chemical Interactions Between Protein Molecules and Polymer Materials
7:25 – 7:50 Benny D. Freeman – Nanostructured Hybrid Materials for Advanced Membrane Separations
7:50 – 8:15 Omar M. Yaghi – Zeolitic Imidazolate Frameworks and their Applications to Clean Energy

Poster Session 1 (Cont'd)
8:15 – 10:00 p.m. No Host Bar

Tuesday, May 6
7:30 – 8:10 a.m. **Continental Breakfast**
Session 5 – Chemical Imaging IV - Joel M. Harris, Chair
8:10 – 8:55 a.m. Invited - Professor Garth J. Simpson - Molecular Insights from Polarization-Dependent Nonlinear Optical Measurements
9:00 – 9:25 David Tiede – Ultrafast Imaging of Photosynthetic Solar Energy Flow
9:25 – 9:50 Nicholas Winograd – Chemical Imaging with Cluster Ion Beams and Lasers
9:50 – 10:15 Piotr Piotrowiak – Femtosecond Kerr-Gated Fluorescence Microscopy

10:15 – 10:45 **Break**

Session 6 – Analysis I – R. Graham Cooks, Chair
10:45 – 11:30 a.m. Invited - Dr. Randall Winans – Small-Angle and High-Energy X-ray Scattering Studies in Catalysis and Gas Storage
11:35 – 12:00 p.m. Gary M. Hieftje – Fundamental Studies of the Inductively Coupled Plasma and Glow Discharge as Analytical Sources
12:00 – 12:25 Jeanne Ellen Pemberton – Vibrational Spectroscopy of Chromatographic Interfaces

12:25 – 1:20 **Working Lunch**

1:20 – 1:30 Take down Session 1 posters, Put up Session 2 posters
1:30 – 5:00 **Interaction Time**

Session P2 - Poster Session 2
5:00 – 6:00 p.m.
P2-1 Invited – Masaru Kuno - Flickering semiconductor nanowires
P2-2 Invited – Amanda Haes - Nanoparticle-Enhanced Capillary Electrophoresis

P2-3 Richard M. Crooks - A Fundamental Study of Transient Electrokinetic Effects within a Microfluidic Device incorporating a Nanoporous Membrane
P2-4 Alla Zelenyuk - Chemistry and Microphysics of Small Particles
P2-5 Scott A. McLuckey - Electron Transfer, Proton Transfer, and Metal Ion Transfer in Gas-Phase Ion/Ion Reactions
P2-6 J. Michael Simonson - Self-Assembly of Polyelectrolyte Structures in Solution
P2-7 Mary J. Wirth - Suspended lipid bilayers for membrane protein separations
P2-8 Paul B. Farnsworth - Ion Production and Transport in Atmospheric Pressure Ion Source Mass Spectrometers
P2-9 Douglas Goeringer - Sampling, Ionization, and Energy Transfer Phenomena in Mass Spectrometry
P2-10 Gerald J. Diebold - Shock Waves in Thermal Diffusion
P2-11 R. Graham Cooks - Ion Soft Landing for Catalyst Preparation

6:00 – 7:00 **Working Dinner**

Session 7 – Analysis II - Robert W. Shaw, Chair
7:00 – 7:25 p.m. Jan D. Miller– Adsorption States of Amphipatic Solutes at the Surfaces of Naturally Hydrophobic Minerals
7:25 – 7:50 Steven K. Buratto – Photophysics of Organic Semiconductors Probed by a Combination of High Resolution Fluorescence Microscopy and Ion Mobility Mass Spectrometry
7:50 – 8:15 Frank V. Bright– Studies of Solvation Processes in Supercritical Fluids

Poster Session 2 (Cont'd)
8:15 – 10:0 p.m. No Host Bar

<u>Wednesday, May 7</u>

7:30 – 8:10 a.m. **Continental Breakfast**
Session 8 – Membranes and Media II – Richard M. Crooks, Chair
8:10 – 8:35 a.m. Osman A. Basaran **-** Fundamentals of Electric Field-Enhanced Multiphase Separations and Analysis
8:35 – 9:00 J. Douglas Way – Investigation of Transport Mechanisms in Surface Modified Inorganic Membranes
9:00 – 9:25 Joseph T. Hupp - Coordination-Chemistry-Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities
9:25 – 9:50 William Koros – Synthesis and Analysis of Polymers with High Permeabilities and Perselectivities for Gas Separation Applications
9:50 – 10:15 Merlin Bruening – Exploring New Methods and Materials in the Formation of Selective, High-Flux Membranes for CO2 Removal

10:15 – 10:30 **Break**

Session 9 – Close Out Session – Paul W. Bohn, Chair
10:30 – 12:00 p.m. Presentation of program summaries and discussion
12:00 – 1:00 **Working Lunch** – box lunch for those who have to leave early
1:00 – 3:00 Open Discussion and take down posters

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Session 5 – Chemical Imaging IV

Session 6 – Analysis I

Session P2 – Poster Session 2

Session 7 – Analysis II

Session 8 – Membranes and Media II

Abstracts Not Presented

Investigating atoms to aerosols with vacuum ultraviolet radiation

Musahid Ahmed
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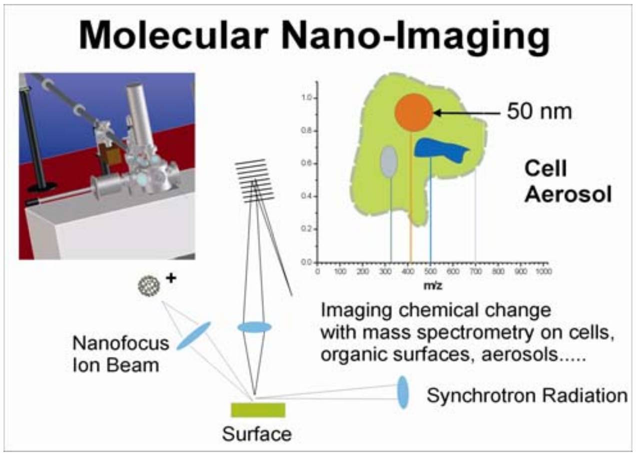
The Chemical Dynamics Beamline at the Advanced Light Source (ALS), is a synchrotron user facility dedicated to state-of-the-art investigations in combustion dynamics, aerosol chemistry, nanoparticle physics, biomolecule energetics, spectroscopy, kinetics, and chemical dynamics processes using tunable vacuum ultraviolet (VUV) light for excitation or detection. A major theme at the beamline is utilizing molecular imaging and aerosol mass spectrometry towards a rigorous understanding of the chemical properties of nanoparticles that are important in energy science and global climate change.

Molecular nano-imaging- A truly integrative tool for visualizing chemical change on surfaces would be to generate chemical specificity at the molecular level coupled with spatial resolution down to the nanoscale. A major effort in this direction is being developed in our group to probe chemical modifications of inter and intra molecular dynamics of various cells and organic aerosols and nanoparticles. The basic principle is to build upon the exciting advances in secondary ion mass spectrometry (SIMS) microscopy by adding enhanced molecular specificity, which is essential to probe more complex aspects of biological systems. As the spatial resolution is increased, the number of detected ions decreases dramatically. Furthermore, ion signals measured by the energetic desorption method fluctuate dramatically due to the competition of different ionization mechanisms, which can be strongly influenced by surface properties and substrate effects. The efficiency of producing molecular ions is also low due to extensive fragmentation. Neutral molecules produced by ion sputtering are typically 3 to 6 orders of magnitude greater than secondary ion yields. Consequently, post-ionization of desorbed neutrals can improve the sensitivity over traditional SIMS. Sub-micron resolution has been achieved with post-ionization; the theoretical lateral limit of static SIMS is about 5-10 nm while depth profiling can be performed at the monolayer level. Single photon ionization (SPI), where absorption to intermediate levels is not required, shows much promise as an efficient method of ionizing fragile molecules. VUV photoionization has been shown to be a selective, yet universal technique in elucidating molecular specific information from gas phase studies of the building blocks of life (DNA bases, amino acids, polypeptides). Imaging by chemical species mass, by detecting the parent ion mass intact, is unique in microscopy in that labeling is not required due to the high molecular specificity of the mass spectrometry method.



Aerosol Chemistry - Ambient aerosols are known to play a significant role in a variety of atmospheric processes such as direct and indirect effects on radiative forcing. Chemical composition can be an important factor in determining the magnitude of these effects (optical density, hygroscopicity, etc.). However, a major fraction (80 – 90%) of organic aerosols cannot be resolved on a molecular level. Recent identification of high mass oligomeric species as a major component in laboratory and ambient organic aerosols has received much attention due to the possibility that these species may account for much of the unknown organic mass in ambient aerosols. Although, a few mechanisms have been proposed, the origin and formation processes of these compounds remain largely unknown. Using VUV photoionization aerosol mass spectrometry we provide strong evidence for a previously unidentified mechanism of rapid molecular growth, via OH radical initiated oxidation of organic aerosols. This process appears capable of converting a sizable fraction of an organic particle to higher masses within only a day of exposure to OH radicals at typical atmospheric concentrations. We propose that such a rapid processing is possible due to a radical chain reaction which quickly propagates throughout the entire particle and is only initiated by the surface OH reaction.

References (2006-2008)

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2. K. R. Wilson, S. Zou, J. Shu, E. Rühl, S. R. Leone, G. C. Schatz and M. Ahmed, "Size-Dependent Angular Distributions of Low Energy Photoelectrons emitted from NaCl Nanoparticles." *Nano Letters* **7**, 2014 (2007)

3. L. Belau, K. R. Wilson, S. R. Leone, and M. Ahmed, "Vacuum-Ultraviolet photoionization studies of the micro-hydration of DNA bases (Guanine, Cytosine, Adenine and Thymine)." *J. Phys. Chem. A.* **111,** 7562 (2007)

4. M. Ahmed, "Photoionization of desorbed neutrals from surfaces." *Encyclopedia of Mass Spectrometry, Vol. 6, Elseiver* (2007).

5. E. Gloaguen, E. R. Mysak, S. R. Leone, M. Ahmed, and K. R. Wilson, "Investigating the chemical composition of mixed organic-inorganic particles by "soft" VUV photoionization: the reaction of ozone with anthracene on sodium chloride particles." *Int. J. Mass Spectrom.* **258**, 74 (2006).

6. J. Shu, K. R. Wilson, M. Ahmed, and S. R. Leone, "Coupling a versatile aerosol apparatus to a synchrotron: vacuum ultraviolet light scattering, photoelectron imaging, and fragment free mass spectrometry." *Rev. Sci. Instrum.* **77,** 043106 (2006)

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10. C. Nicolas, J. Shu, D. S. Peterka, M. Hochlaf, L. Poisson, S. R. Leone, and M. Ahmed, "Vacuum ultraviolet photoionization of C_3." *J. Am. Chem. Soc.* **128**, 220 (2006)

Ultrafast and Chemically Specific Microscopy for Atomic Scale Imaging of Nano-Photocatalysis

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Nicholas Camillone III, Principal Investigator
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Overall research goals: The objective of this interdisciplinary research program is to develop and apply new techniques to study the atomic-scale mechanisms of photocatalytic reactions. Experimental approaches are explored for probing photoinduced nonequilibrium charge populations (‘hot carriers’) and their relaxation to the ground state – key elements of photocatalysis – with combined sub-picosecond temporal and sub-nanometer spatial resolution. To assess the temporal evolution, optical pumping by correlated ultrafast laser pulses is employed. High spatial resolution will be demonstrated by combining detection by scanning tunneling microscopy (STM) with a model system, small metal (Au, Pd) nanoparticles supported by a wide-bandgap oxide (TiO_2), which allows the selective excitation and probing of hot carriers in individual nanoscale structures. If successful, the combination of ultrafast laser excitation and STM will enable studying the effects of atomic-scale inhomogeneities (steps, point defects, impurities, etc.) at photocatalyst surfaces on the lifetimes of excited charge carriers. When complemented by chemically specific microscopy to survey chemical reactions induced by electronic excitations, such a novel tool has the potential to provide unprecedented insight into the mechanisms underlying photocatalytic reactions.

Significant achievements in 2006-2008: The demonstration of ultrafast chemical imaging involves electronic excitation in oxide-supported metal nanoparticles by femtosecond laser pulses, and probing of signatures of this excitation by cryogenic STM in ultrahigh vacuum (UHV). During the initial phase of the project, the two required major instruments, an ultrafast Ti:Sapphire laser-based optical system and a low temperature STM, were installed and commissioned.

A new Ti:Sapphire laser system dedicated to this project was installed and its output characterized. The system provides ~60-fs pulses at 80 MHz repetition rate with an average power of up to 2.7 W (i.e., ~ 34 nJ/pulse). The optics, opto-mechanics, and electronics necessary to provide a stable coupling of the laser beam into the STM, manipulation of the pulses for correlation measurements, and data acquisition have been designed, constructed or purchased. This effort included the construction of a high-precision interferometer complete with modulated delay line, focusing optics to achieve a small (10 μm) laser spot on the sample held in the STM, and a custom optical bench for the STM system. Final work on introducing the laser beam into the STM chamber and on aligning a tightly focused beam with the STM tunneling gap is currently underway.

In parallel with the development of the optical sub-system, we have performed low-temperature STM experiments with two initial objectives: i) development of experimental protocols to achieve small metal nanoparticles supported by rutile $TiO_2(110)$, the model system chosen to demonstrate local detection of laser-induced electronic excitations. And ii) exploration of novel paradigms for characterizing surface defects on $TiO_2(110)$, and for inducing and imaging chemical reactions of small adsorbates at the single molecule level on this surface.

We successfully identified suitable (partially reduced) initial states of the TiO_2 crystal that reproducibly allow the formation of small (1.5 nm to 5 nm diameter) Au nanoparticles by evaporation of Au in UHV (figure 1). Within this size range, a transition from metallic to semiconducting behavior has been observed previously with decreasing particle size. Indeed, we find that scanning tunneling spectroscopy on 2 nm Au particles shows clear signatures of a bandgap

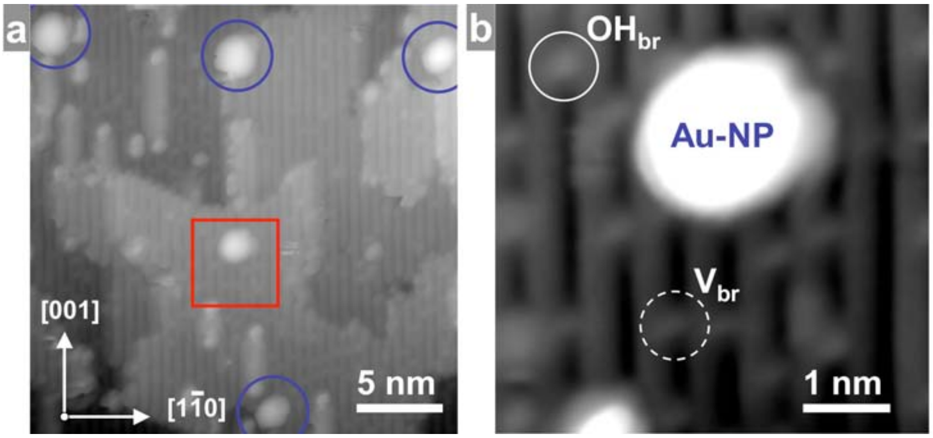

Figure 1. Cryogenic STM on small Au nanoparticles on rutile $TiO_2(110)$. a) Overview scan, showing several Au particles with lateral dimensions of 2 – 3 nm and height of ~ 0.5 nm (blue circles). b) High-magnification view of the area marked red in a). Circles mark $TiO_2(110)$ surface defects, whose nature (OH_{br} – bridging hydroxyl; V_{br} – bridging oxygen vacancy) was directly identified by manipulation techniques.

with negligible density of states. The capability of assembling either metallic or semiconducting nanoparticles is important to the next stage of this project, the demonstration of local probing of excited electronic states, since it will provide a means for tuning hot carrier lifetimes from very short (metal) to much longer values (semiconductor).

Our $TiO_2(110)$ model photocatalyst can exist over a range of stoichiometries, and its surface exhibits a variety of defects that largely determine its reactivity. Cryogenic STM has been used to establish the nature of surface defects, small adsorbates, and their interactions and reactions in unprecedented detail. This work has provided a basis for chemically specific microscopy of hot-carrier driven reactions of small molecules on TiO_2 – a core element of this project – and demonstrated novel general pathways for studying chemical reactions on oxide surfaces.

Science objectives for 2008-2009:

- Ultrafast photoinitiated and electron-mediated diffusion and reactions: combined fs-laser excitation and STM will be used to drive and observe non-thermal diffusion and reactions of adsorbates (H_2O, O_2, OH) and defects (O_{br} vacancies). These experiments – performed with the STM tip retracted or engaged during laser exposure, and with conventional or energy-filtering probes – will pave the way for time-resolved measurements of the carrier dynamics using pulse-correlation techniques and will serve to develop protocols for chemically specific microscopy.
- Non-thermal melting of supported metal nanoparticles: Establishing conditions for STM detection of excited carriers will include the identification of the laser fluence threshold where supported metal particles melt. This threshold likely depends on particle size, and size effects may be particularly interesting near the metal to non-metal transition.
- Hot carrier dynamics in nanoparticles: two-pulse correlation measurements with STM detection will be implemented to probe the dynamics of electronic excitations in individual supported nanoparticles, thus demonstrating simultaneous ultrafast time and nanometer spatial resolution.
- Correlation of hot carrier dynamics with photoinduced surface processes, such as desorption, diffusion, and chemical reactions on metal nanoparticles and on the surrounding TiO_2 surface.

Time-resolved and Ultrafast Imaging of Redox Processes on Mineral Surfaces

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Dr. Peter Eng, Univ. of Chicago, CARS, Argonne, IL
Dr. Robert Schoenlein, LBNL, Materials Science Division

Overall research goals: The overall goal is to measure molecular changes at nanoparticle and crystalline surfaces due to electron/hole transfer. These are fundamental processes in geochemistry, with electron transfer to iron oxide surfaces responsible for reductive dissolution, and hole transfer to pyrite surfaces responsible for the initial step in oxidation and acid mine drainage (AMD) formation. Realization of the goals requires parallel development of experimental techniques and appropriate chemistry to enable reaction measurements on the microsecond to picosecond time scale. Study of reacting crystal surfaces via x-ray scattering provides the most complete description of interfacial reactions through the generation of electron density maps consistent with reaction pathways post electron or hole injection. Such imaging allows comparison with simulations of extremely rapid chemical, structural and thermal phenomena. Nanoscale phases present specific benefits and challenges for time-resolved research on interfacial processes. Although no direct methods exist for nanoparticle surface structure determination, their large surface area may enable valence changes that occur at the surface to be detectable via x-ray spectroscopic methods.

Significant achievements in 2007-2008: The first funding year saw progress on two fronts.

(1) For rapid crystal truncation rod (CTR) surface diffraction we have purchased and implemented the new Pilatus 2D x-ray 100,000 element pixel detector on the 6-circle diffractometer 13ID line at the APS and developed software to control the system in fast timing mode. Static experiments on goethite single crystals were used to optimize detector and software operation. At the time of this writing we are adapting the Pilatus for the time-resolved station on 11ID, and developing a fast motion x-y stage with chemical flush for rapid sample restoration. Initial experiments with the Pilatus showed at least a 50x gain in acquisition time for CTR data, and organic ligands that injected electrons into the hematite R-plane surface were successfully tested.

(2) We have synthesized and characterized two high-surface-area systems possessing a large proportion of chemically active interfacial sites: <3 nm iron oxide nanoparticles coated with photosensitizing molecules and manganese oxide nanosheets intercalated by cationic photoactive dyes. Although both systems demonstrate facile electron injection, in preliminary studies at 11ID the spectral signal associated with changes in iron valence could not be acquired with sufficient statistical weight before sample damage occurred. These data strongly constrain the sample characteristics, such as ligand coverage and laser fluence and repetition rate, that will be required for time-resolved experiments and critically inform the planned work.

Science objectives for 2008:

- We will begin the first pump experiments using C and R-plane hematite single crystals on beamline 11ID. Initial static experiments will examine the effect of the pump femtosecond laser in terms of local heating and possible surface damage. Damage and heat transfer relaxation effects for dry crystals then will be studied in time-resolved mode for varying amounts of laser power and numbers of activation pulses. This will establish a baseline for all future timing experiments.

- Subsequent static and timing experiments will utilize aqueous conditions on the hematite crystal surfaces, then solutions with active ligands, and finally sorbed electron-injection ligands. Here we wish to characterize the effect of pump pulses on aqueous species and solvated organic ligands separately from the complete system with sorbed ligands.

- With completion of our specially designed diffractometer x-y stage we will be able to examine a large number of sites on a crystal surface with varying numbers of pump pulses and time-resolution delays. Experiments will test the ability to refresh an activated surface with new solution and/or sorbed ligand without ceasing data collection, and initial experiments into the nanosecond time-resolution domain will be initiated.

- Katz is presently conducting a systematic study of the sorption density of a suite of photoactive ligands that bind to iron oxide surfaces via a range of chemical linkages. The most favorable ligand will be studied using transient absorption laser spectroscopy in the Falcone/Schoenlein lab to determine the lifetime of ferrous states formed at the surface.

- Gilbert has synthesized aqueous molecular clusters that sorb to mineral surfaces and which undergo nanosecond-scale photochemical transformations to generate reactive species including reduced metal ions and molecular oxygen. We will use static (chemical assays) and time-resolved (laser spectroscopy) studies to test the suitability of these photoactive species for pump-probe x-ray experiments. In particular, we will investigate the oxidation of iron sulfide (mackinawite) nanoparticles using optical and x-ray spectroscopy as a prelude to studies of single crystal pyrite oxidation using CTR diffraction and GIXAS analysis.

References to work supported by this project 2007-2008:

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Single-Molecule Imaging

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Overall research goals: The Ames team focuses on the development of new concepts for chemical analysis and the evaluation of structure-function relationships at nanometer length scales and in microenvironments. The projects of the team range from characterizing dynamics at solid/gas and solid/liquid interfaces to probing details of chemical reactions and of chromatographic processes.

Significant achievements in 2006-2008:

- Three powerful tools – capillary electrophoresis (CE), computer simulation, and single-molecule imaging – were united to study the adsorption properties of model autofluorescent protein R-phycoerythrin (RPE) on the fused-silica surface. Simulated and experimental CE results together provided convincing support for the proposed mobility-based adsorption isotherm. This constitutes the first report of quantitative analysis of the adsorption capacity factor of target molecules on the bare fused-silica or coated capillary wall. In parallel experiments, total internal reflection fluorescent microscopy (TIRFM) revealed the activities of individual molecules within the evanescent field (EF) at the fused-silica prism surface. These microscopic observations were complementary to the ensemble averages obtained from actual and simulated CE experiments. The adsorbed molecules were counted with confidence by extrapolation of the data points constructed from the adsorption times of individual molecules. The CE results and single-molecule detection results demonstrated good agreement. The ability to measure the adsorption strength with CE or with single-molecule detection is an important step forward in understanding the basic separation mechanisms of CE and LC. (Publication 11)
- Single-molecule studies can reveal stochastic behavior that is normally averaged out in bulk experiments. Measurements of the single-molecule activities of lactate dehydrogenase (LDH) and of alkaline phosphatase (ALP) have been reported. Fluorescent products accumulated from individual enzyme molecules were confined in nL to pL volumes in capillaries or in micro-fabricated vials. It was found that individual molecules of the enzymes exhibited activities that varied between 5 to 20 fold. Several different factors may account for the broad and non-Gaussian distribution of activities. First, glycosylation of proteins affects both their flexibility and dynamic stability. Glycosylation and isoforms, however, were not present in the hLDH-H4 samples that were studied. Second, proof of the existence of only one molecule in each reaction zone was based solely on statistical analysis and dilution factors. Third, contributions from wall effects cannot be excluded. Here, we determined single-molecule enzyme activities under conditions that the presence of one and only one enzyme molecule and the absence of wall interactions were both confirmed by direct observation. (Publication 9)
- Recent gene expression studies at the single bacterial cell level have primarily used green fluorescent protein (GFP) as the reporter. However, fluorescence monitoring has intrinsic limita-tions, such as GFP maturation time, high background and photobleaching. To overcome those problems, we introduce the alternative approach of chemiluminescence (CL) detection with fire-fly luciferase as the probe. Firefly luciferase is roughly 100 times more efficient and is faster in generating CL than bacterial luciferase but requires the introduction of luciferin, a species that is not native to bacteria. The difficulty of luciferin diffusion into the cells was solved by making use of cell membrane leakage during bacteria dehydration. In this scheme, the overall sensitivity of the system approaches the single protein molecule level. (Publication 1)

Science objectives for 2008-2009:

- Variable angle evanescent field microscopy (VA-EFM) will be improved upon current designs, and novel image reconstruction algorithms will be developed to record events in a time scale below 1 s and display sectional images that are 1-10 nm thick over a range of several hundred nm.

- Microfluidic devices will be designed and fabricated to combine their unparallel abilities of single-particle and single-cell manipulation with VA-EFM's new ability of producing full 3D images to provide better understanding of the electric double layers under different buffer conditions.
- We plan to explore how surface topology and surface functional groups affect reactions and diffusion. We will take advantage of the unique capability in the group of Dr. Victor Lin, to design surfaces that have well defined nm-scale structures and chemical functionality, as the platform for testing novel single-molecule technologies.
- We plan to quantify the effects of the microenvironment on enzyme activities with respect to electrostatic, hydrophobic, and steric properties of the surface. The location of the enzyme molecules will be monitored by VA-EFM so that one can sort out molecules that are near the surface, at the entrance, and inside the channels. To gain further control of the location of the reactions, we plan to use optical tweezers to direct individual enzyme molecules trapped inside vesicles (e.g. 0.5 μm in diameter) to the desired physical location before electrically disrupting the membrane to release the molecule.

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Synthesis and Characterization of Nanocrystalline α-Fe_2O_3 Films for Wavguide Scanning Photocurrent Microscopy

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Overall research goals: The research objective is to assemble and demonstrate a waveguide scanning photocurrent microscope taking advantage of optical tunneling (evanescent wave) at a waveguide-solution interface at which a photocatalyst-coated tip scatters light out of the evanescent field and serves to detect the outscattered light. A side-effect of the research is to synthesize inexpensive but reasonably efficient and stable photocatalyst coatings that have applications outside the target microscopy.

Significant achievements in 2006-2008: The first and perhaps most important task was the develop the ability to synthesize nanocrystalline photocatalyst films on solid surfaces. We chose to start with hematite (α-Fe_2O_3) doped with Si because it is stable under a wide range of pH conditions and because recent photocatalytic work has shown that this material can be considerably more efficient that previous studies had indicated. We have successfully synthesized Si-doped hematite films by chemical vapor deposition. These films are highly photoactive, achieving photocurrents for water oxidation that are comparable to the best films made by others. An example of a chopped-light photocurrent characterization experiment is given in Figure 1.

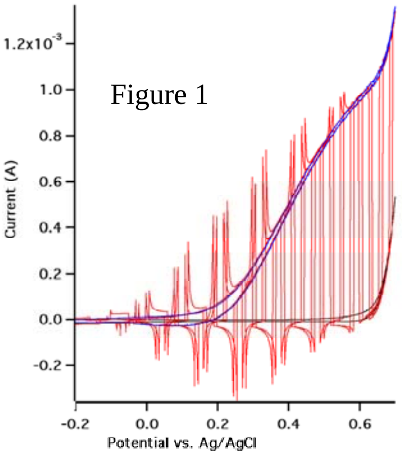

Figure 1 (left): Hematite photocurrent measured in 1M NaOH as a function of potential, in the dark (black lines near 0 current), in AM1.5 light from a Xenon lamp (blue) and in chopped light (red). The photocurrent transients are most likely due to the relatively slow buildup of reactive oxygen species because of water oxidation at the surface, and cathodic electron transfer to these species upon interruption of the light.

A significant issue for the hematite photocatalytic films is their anisotropy with regard to conduction and the deleterious effects of water as an impurity in the synthesized hematite. Below, Figure 2a demonstrates that photocurrent densities are a factor of 5 to 10 greater when illuminating single crystal edges rather than faces, indicating that hematite preferred orientation in synthesized films will be advantageous. Fig. 2b demonstrates that films prepared in water-saturated carrier gas give lower photocurrents than dry CVD preparations.

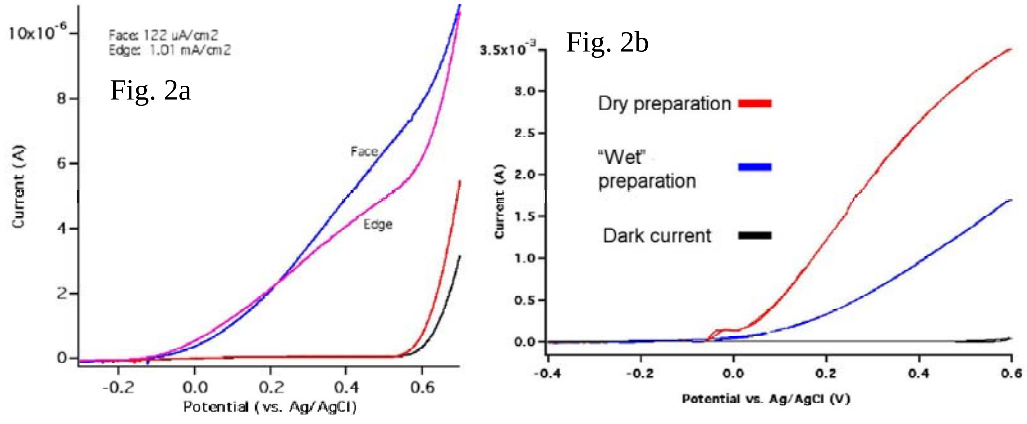

Figure 2: (a) higher photocurrent density on hematite edges than faces; (b) higher photocurrent from dry CVD preparations than from those made using water-saturated air.

The next step in developing the microscope was to synthesize photoactive films on Pt/Ir tips akin to those used in scanning tunnelling microscopy. Figure 3 shows the photocurrent generated by a hematite-coated Pt/Ir tip in blue laser light. We are able to achieve ~5 μA currents in blue laser light.

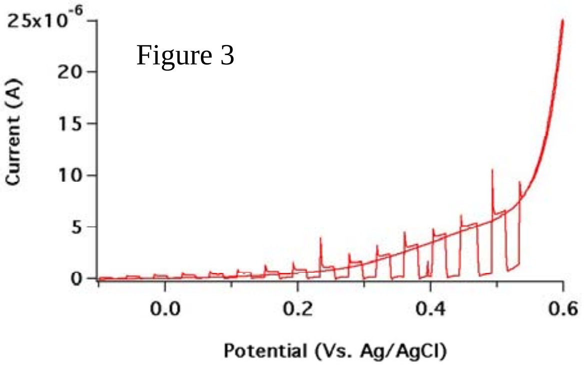

Figure 3 (left): Continuous and chopped-light photocurrent measurement from a hematite-coated Pt/Ir tip manufactured for the microscope using chemical vapor deposition.

We have built an initial microscope frame that incorporates a total internal reflection system for input 432 nm laser light, and an incorporated stand for a Molecular Imaging STM stand that will serve as piezo-positioning device and electrochemical current amplifier in the ~30 pA range. The final step is to assemble the separately-tested components into a working microscope. In addition, we have synthesized $SrTiO_3$ nanoparticles and demonstrated that photocurrent generation by hematite, presumably on the basis of water oxidation, is enhanced in the presence of $SrTiO_3$ nanoparticles dip-coated on the hematite films.

Science objectives for 2008-2009:

- With a pA-sensitive potentiostat we will measure photocurrents from the evanescent wave using our photosensitive tips (demonstrated above).
- We will convert the Molecular Imaging STM head to that we can use the photocurrent as a feedback signal.
- Use hole-scavengers to enhance the photocurrent output of synthetic film tips.
- We will run our initial imaging trials using the photocatalytic photocurrent microscope, concentrating on cytochromes. Our initial interesting in photocurrent microscopy was prompted by our desire to locate individual cytochromes adsorbed on surfaces on the basis of their Soret band optical absorption, which is very close to the peak in photocurrent efficiency (incident photon to current conversion) of hematite, so our initial trials will focus on imaging these large molecules (5 to 10 nanometers).

References to work supported by this project 2006-2008:

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2. The effect of water vapor on chemical vapor deposited iron oxides: Induced phase impurities goethite and maghemite. Langmuir (submitted)
3. Hydrothermal atomic force microscopy of hematite dissolution at pH 1, 125°C: Dehydration defects enhance the dissolution rate of annealed hematites. American Mineralogist (in preparation)

Chemical Microscopy of Novel Nanostructures

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Prof. Todd Emrick, Dept. of Polymer Science and Engineering, UMass-Amherst

Overall research goals: Our research explores the optoelectronic properties of complex nanostructured materials and the relationship with morphology and structure. Our approach employs a suite of ultrasensitive optical and scanning-probe techniques to correlate fluorescence properties with morphology and details of molecular structure in isolated nanostructured systems or single molecules.

Significant achievements in 2006-2008: The chemical systems under investigation in our group have relevance to a wide variety of energy-harvesting and other optoelectronic applications. We have focused on three main areas of research: quantum-dot/organic composite nanostructures, semiconducting polymers, and chiral materials. In collaboration with Todd Emrick (Polymer Science and Engineering Dept., UMass-Amherst) we are investigating the photophysics of individual quantum dot systems whose surfaces have been derivatized with conjugated organic ligands. Our research has revealed some fundamentally new photophysics associated with energy and charge-transfer within individual nanostructures relevant to application of these materials in photovoltaic systems. Recently, we have observed linearly polarized emission from individual CdSe-oligo(phenylene vinylene) nanostructures whose orientation is correlated with the external polarization of the excitation field, suggesting a route to directional control over energy or charge transport in these systems.

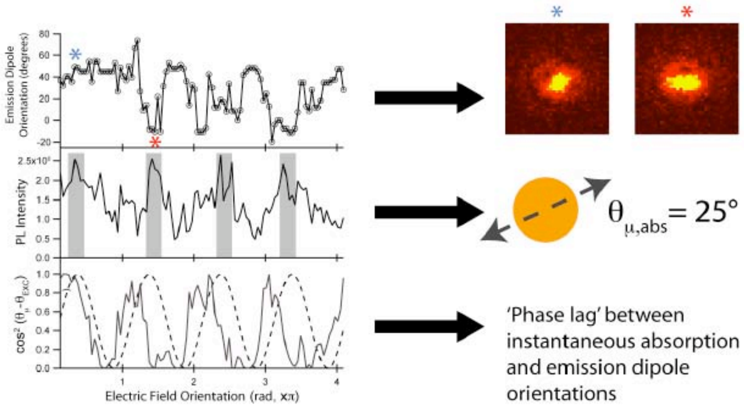

Figure 1. (Left) Comparison of emission moment orientation (top) and polarization anisotropy (middle) from a single 12-nm CdSe-oPV nanostructure. (Right) Defocused fluorescence images (filtered to include only the CdSe emission) show linear polarized emission with dipole orientation correlated with excitation polarization, with a phase-lag of ≈ 25° between the absorption and emission moments.

In the area of single-molecule spectroscopy of semiconducting polymers (specifically polyfluorene species with applications to blue-emitting organic LEDs) our collaborative work with Prof. Paul Lahti (Dept. of Chemistry, UMass-Amherst) has identified the origin of green "trap" impurities as an oxidative defect, thus providing a means of enhancing efficiency of conversion of electrical energy to light emission (at specific wavelengths) in those devices. In the case of chiroptical spectroscopy of individual fluorescent helicene molecules, our experiments probe the "*inhomogeneous broadening*" of the chiroptical response associated with chiral molecular species in polymer-supported films, and provide some fresh insights into the interaction of light with chiral materials. Our preliminary work on this system quantified for the first time the heterogeneity of dissymmetry factors in fluorescence excitation of chiral fluorophores in polymer-supported films.

Science objectives for 2008-2009:

- Photon pair correlation functions in the luminescence of individual CdSe-oPV nanostructures will be measured to determine the bi-(or multi) excitonic character of emission .
- We will develop an apertureless NSOM capabililty by adapting our existing Bioscope AFM hardware to probe composite films of inorganic semiconductors and conjugated polymers.
- We will measure distributions of dissymmetry parameters in luminescence from single chiral chromophores.

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Plasmon Resonance Imaging

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Dr. M. Al-Jassim, NREL

Overall research goals: The objective of this research is to develop and demonstrate new high spatial-resolution time-resolved imaging techniques that enable the study of energy and charge transport in nanoscale systems, to study energetic, surface chemical, and opto-electrical properties of individual quantum systems and superstructures of such, and to study energy and charge transport in relevant nanoscale supramolecular systems and especially the interaction with surface plasmons

Significant achievements in 2006-2008: Two different plasmon modes that are active in the tip-substrate system in our microscope were identified: A localized surface plasmon (LSP) and a propagating surface plasmon(PSP) (see Figure 1). It was shown that the relative intensity of the two modes depends on the excitation energy and on the local morphology of the substrate. This allows for control of the size, symmetry and energy of the nanoscale lightsource generated beneath the tip. The ability to distinguish between the two also allows us to distinguish between localized electronic processes in the tip-substrate cavity and longer-range processes. This result, combined with earlier data obtained preliminary to the current project where the quenching of the LSP modes by single quantum dots was demonstrated (Romero et al. *Nanolett.* **6**, 2833 (2006)), is essential to understanding the interaction between the surface plasmons excited by the tip-to-substrate current and nanoscale species present in the gap.

We demonstrated light emission from surface plasmons on single silver nanoparticles that were vapor deposited on Indium Tin oxide substrates. Similar samples have been demonstrated to work to plasmonically enhance photocurrent when used as substrates in organic solar cells by us in another project (Morfa et al. *Appl. Phys. Lett.* **92**, 013504 (2008)).

Light emission from 100-nm radius nanoholes prepared in silver layers using nanosphere lithography was demonstrated, showing that the holes are plasmonically active. The light originates mostly from the annulus as can be expected from electromagnetic calculations performed by others in the field.

We procured separate institutional equipment funding to build a new “plasmon resonance imaging” microscope. This microscope will be dedicated to the current project and will allow many of the future extensions to the imaging technique.

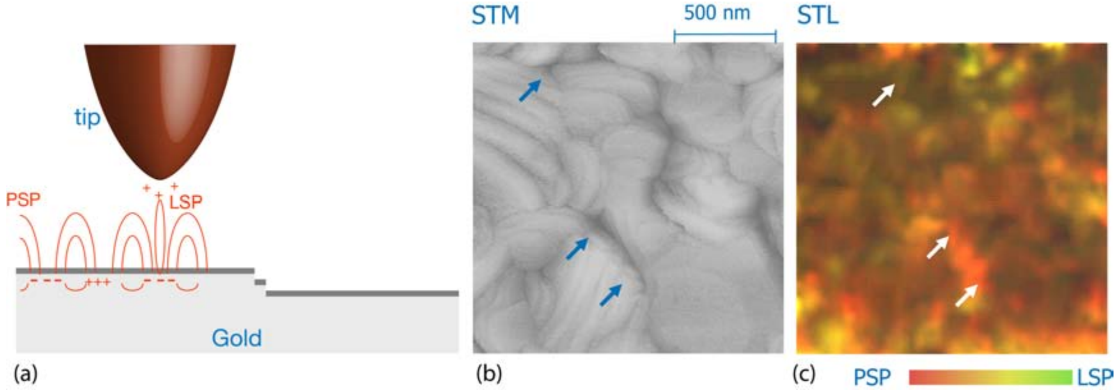

Figure 1. Imaging of plasmon modes on a Gold substrate covered with a 1,6-hexane-dithiol self-assembled monolayer. (a) Illustration of the two possible modes. (b) STM image of the imaged area (c) simultaneously collected tunnelling luminescence image. The color indicates which mode is active where.

<u>Science objectives for 2008-2009:</u>

- The new microscope will be used to measure the absorption spectrum of single quantum dots and other molecular or nanoscale systems. This will be done by using the nanoscale lightsource created by the emission of plasmons created by tunneling in the tip/substrate cavity.
- The tunneling luminescence experiment will be enhanced by employing force feedback using a tuning fork instead of current feedback. This will solve the problem of the luminescence images being convoluted by the height of the tip being varied in response to changes in surface conductivity and is expected to lead to far better detection limits.
- Initial steps will be performed to add time resolution to the plasmon imaging technique. We envision several possible avenues that make possible different time regimes. Firstly, we will use simple current pulses to excite the nanoscale system yielding time resolutions longer than microseconds. Secondly, tapping mode AFM will be employed using a conducting tip that excites the system only during the tap event, yielding resolutions potentially up to nanoseconds. Lastly in the much longer term, femtosecond laser excitation will be used to induce tunneling current leading to luminescence from the sample.

<u>References to work supported by this project 2006-2008:</u>

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Atomic Resolution Imaging and Quantification of Chemical Functionality of Surfaces

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Overall research goals: The goal of this project is to demonstrate new capabilities in atomic-scale *imaging* combined with local interaction strength *quantification.* This will be achieved by atom-specific local spectroscopy (3D force spectroscopy) using a unique low temperature (6 K), ultrahigh vacuum combined non-contact atomic force microscope/scanning tunneling microscope (NC-AFM/STM) in combination with chemically sensitive tips. In particular, we aim at investigating the specifics of the atomic interactions that give rise to chemical sensitivity in NC-AFM as well as the factors that govern stability, resolution, and the ability to quantify the strength of chemical interactions in NC-AFM measurements made with chemically modified tips.

Significant achievements in 2006-2008: After an initial testing and debugging phase, measurements performed with our home-built low temperature, ultrahigh vacuum NC-AFM focused on the establishment of the 3D force spectroscopy capabilities essential for achieving the research goals outlined above. As a test material, we chose highly oriented pyrolytic graphite (HOPG) due to its ease of surface preparation by in-situ cleavage, but also because for this material, the site-dependent interaction mechanism between tip and surface atoms is still highly under debate.

As shown in Fig. 1, we were able to map the complete three-dimensional force field with atomic resolution, which demonstrates the feasibility of our approach. Simultaneously, the tip-sample interaction potential and the energy dissipation of the oscillation process were recorded. From such a data set, representations of cuts in any direction can be produced, which allow deep insight into site-dependent chemical interaction mechanisms. While constant height images show atomic resolution with pN force resolution (Fig. 1a), vertical cuts visualize how the attractive force fields of the atoms extend

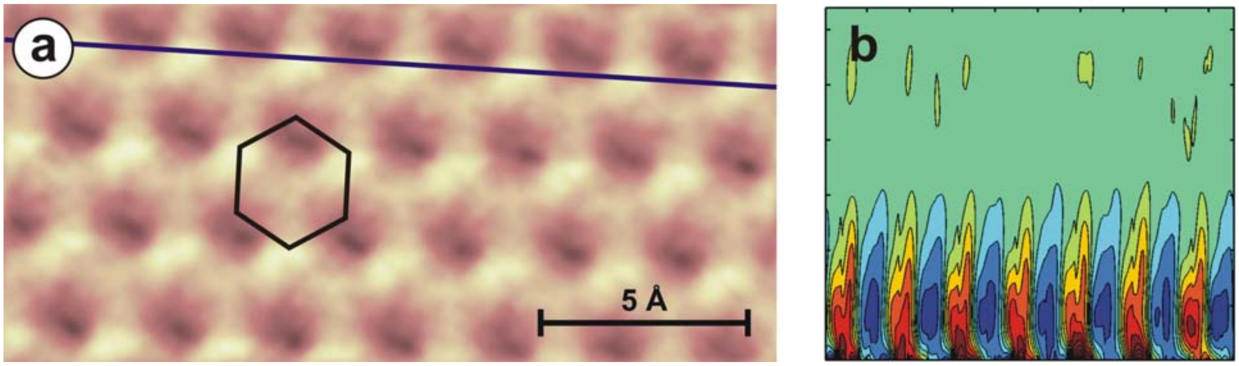

Figure 1. Results obtained with 3D force spectroscopy on HOPG as a test material. (a) Planar cut through the 3D force data at constant *z* height. Please note that in contrast to similar results achieved with NC-AFM in the past, this image reflects the *true tip-sample interaction force*, which *directly quantifies the strength of the chemical interaction between tip and sample*. The average attractive force for this image is –2.306 nN with a total force corrugation of about 50 pN. Even though only three of the six atoms in a hexagon are detected at this height, the exact positions of all atoms have been unambiguously determined using additional information on the energy dissipation at larger tip-sample distances. (b) 2D cross section of the 3D data set along the line indicated in a) showing how the sample's surface force field as probed by the tip extend into vacuum. The average force at each height has been subtracted to enhance contrast. Contour lines mark force differences of 8 pN at every height. Atomic corrugations are visible up to a height of about 150 pm (total height in *z* direction is 300 pm).

into the vacuum space (Fig. 1b). Using information contained in the distance-dependent energy dissipation data, we could clearly pinpoint the exact positions of all atoms in the lattice. This result proves the method's usefulness to gain additional chemical information about the imaged surfaces, allowing the identification of the chemical nature of specific sites.

In a parallel effort, we are working on the preparation and analysis of oxide surfaces ideally suited to further develop the chemical imaging capabilities of the instrument. Among other materials, we started growing (110)-oriented Co_3O_4 thin films, which were characterized in-situ with LEED, RHEED, and XPS. LEED data show a change in the terminating plane with surface treatment, and our NC-AFM images reveal a morphological change in the surface as this occurs. Thus far, atomic resolution imaging has been hampered by deficiencies in surface preparation. Alternative routes pursued include the preparation of $MgAl_2O_4$ and TiO_2 surfaces, which will be used for depositing molecules and for imaging with chemically sensitive tips.

Science objectives for 2008-2009:

- Preparing clean, well-ordered surfaces of (110)-oriented $MgAl_2O_4$, Co_3O_4, or similar spinel-type surfaces featuring broken surface symmetry of anions and cations for chemical imaging.
- Preparing clean, well-ordered (110)-oriented TiO_2 surfaces for chemical imaging of adsorbed molecules or imaging using chemically sensitized tips.
- The next step will then aim at functionalizing tips through molecular assembly in order to probe more complex chemical interactions that require the ability to modify tips using different functional groups. Initially, Au tips are functionalized through thiol self-assembly to create acidic, basic, and neutral tips. These tips will be tested by probing their interactions with individual acidic, basic, and neutral molecules anchored to a TiO_2 surface. By comparing the strengths of the tip–sample interactions measured through force–distance curves with the expected values for these simple interactions, the ability to quantify the strength of individual functional groups on a surface will be determined. To increase the stability of chemically sensitive tips, rutile tips functionalized through carboxylic acid adsorption will be also explored.
- Once robust, controllable chemically sensitive imaging is achieved, the atomic-scale variations in the reactivity of a bare rutile (110) surface will be mapped out as a technologically relevant test case.
- As an ultimate goal, we will try to establish procedures that allow us to pick up different functional molecules with the tip so that the reactivity of the same surface feature to different chemical functionalities can be sequentially probed.

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Nanoparticles as Selective Matrices for Imaging Mass Spectrometry

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Nanomaterials offer chemically unique platforms for many important analytical problems, esp. laser desorption/ionization (LDI) of polar, thermally labile molecules. [McLean, *et al.*, *J. Am. Chem. Soc.* **2005**, 127, 5304] We are designing novel nanomaterials for LDI and developing laser patterning strategies to improve spatial resolution, sensitivity, and sample throughput using imaging mass spectrometry techniques. The nanomaterial research focuses on using tailored metallic nanoparticles to provide both analyte selectivity and enhanced ionization capabilities. The nanoparticles absorbs the ionizing laser irradiation and nanoparticle surface chemistry is tailored to perform a myriad of functions by i) modification of the nanoparticle composition or ii) surface modification of the particles using self assembled monolayers (SAMs). **Figure 1** contains LDI spectra of a mixture composed of ten peptides (***** denotes peptide signals), a lipid and cholesterol, (left panel) organic matrix + $AgNO_3$ and (right panel) from Ag nanoparticles, which cleary illustrate selective ionization of cholesterol by using AgNPs. We have also demonstrated that the capping of gold nanoparticles with compounds such as 4-aminothiophenol (4-ATP) increases ion yield, decreases ion fragmentation, and increases the useful analyte mass range for LDI-MS. [Castellana, *et al.*, *Nano Letters* **2007**, 7, 3023]. The organic (4-ATP) monolayer (i) acts as a source of protons (under acidic conditions) and (ii) decouples the analyte from the nanoparticle surface thereby lowering the energy required for analyte desorption. The end result is a softer desorption/ionization process, which produces lower internal energy ions and less fragmentation of the analyte ions.

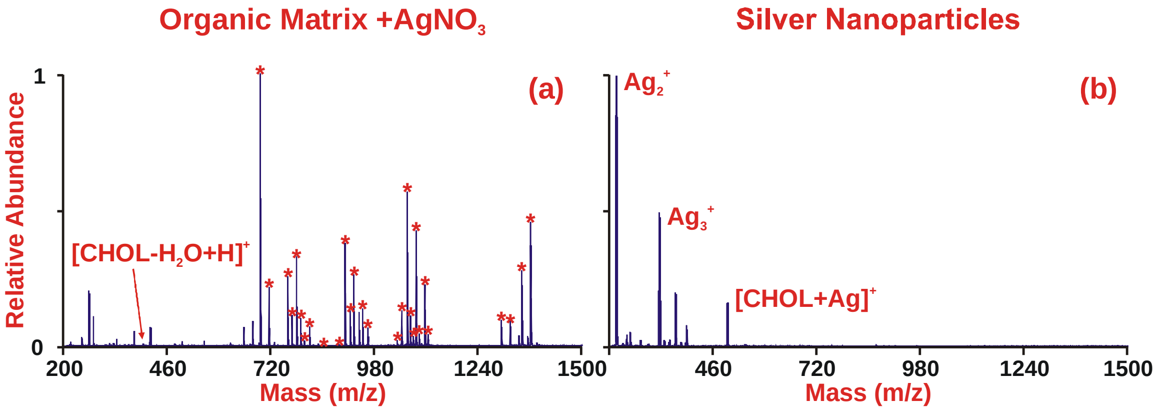

Figure 1

This work demonstrates the benefits of nanomaterials in biological MS and illustrates the potential to provide selective analyte desorption/ionization of low abundance analytes from highly complex samples. That is, by modulating both nanoparticle material and surface chemistry it may be possible to simultaneously impart both analyte pull-down capabilities and enhance analyte ionization. In combination with high throughput imaging MS, these nanomaterial systems have the potential to aid in the developing label free screening assays for a broad range of biologically important compounds.

We are currently incorporating NP LDI chemistries into our imaging MS system, which incorporates beam homogenization optics and digital micro-mirror array (DMA) laser patterning. The beam homogenization optics optimizes the beam profile incident on the DMA, and individual elements of the DMA are addressed by software to be either “on” or “off” state depending on the uploaded pattern. Laser light reflected from individual mirrors in the DMA is focused on the sample plate in a well-defined patterned image. This arrangement provides a rapidly (~16 μs) adjustable (position and/or pattern) ionizing beam for the LDI experiment, and the pattern can be regular or complex shapes of variable dimensions. Our imaging experiments differ from traditional approaches because the user defined laser patterning improves image quality and ion yields. Patterning light also alleviates the inability to probe the areas between laser irradiations (spaces between laser spots). In principle, it is feasible to increase throughput using this optical arrangement because the DMA allows for fast laser movement. By utilizing the DMA and high repetition rate lasers we are currently developing an optical system capable of high throughput imaging MS analysis.

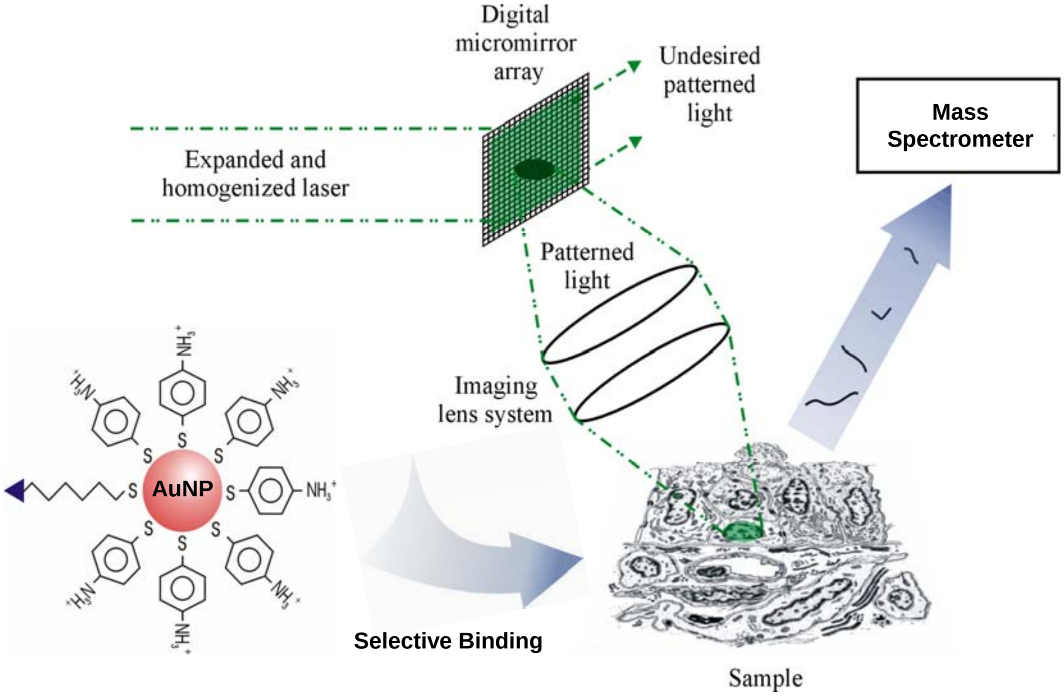

Figure 2

Plasmonic Structures and Assemblies with Tunable Optical Properties

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The goals of the research are to develop and study plasmonic systems with optical properties that may be tailored through organized nanoparticle assembly and control of individual structure fabrication. The approaches focus on the fabrication/assembly and optical characterization of multi-particle assemblies using spatially-controlled surface functionalization methods and well-defined, irregularly-shaped structures using nanosphere template lithography. We are investigating the ability to tune their optical properties, including the surface plasmon resonance wavelength and localized electromagnetic field enhancements. A fundamental understanding of the correlation of the optical properties with metal plasmonic structure shape and assembly will be a basis for tailoring and optimizing these systems for sensing and spectroscopy applications.

We have developed an asymmetric functionalization process for metal nanoparticles.[1] The asymmetrically-functionalized nanoparticles can be used as building blocks in the formation of multiparticle assemblies as shown in Figure 1A and B.[1,2] We are investigating the ability to control the spacing between particles in these assemblies using different types of linkers and by combining the nanoparticles with other materials, such as polymers, for additional organization. For example, we have covalently linked asymmetrically-functionalized gold nanoparticles to polymer pendent groups to form a one-dimensional chain of nanoparticles.[2] Interparticle spacing in the 1-D chains is controlled by the length of the alkylthiol capping molecules used on the gold nanoparticles.[2]

In addition, we are using nanosphere template lithography to fabricate plasmonic structures with unique, tunable optical properties.[3,4] For example, gold crescent-shaped structures (Figure 1C) exhibit multiple, polarization-sensitive plasmon resonances that are tunable from the visible through the infrared. Large electromagnetic field enhancements are expected due the sharpness of the crescent's tips and the ability to bring these sharp tips into close proximity to each other. We are using the crescents as tunable substrates for surface-enhanced infrared absorption spectroscopy.

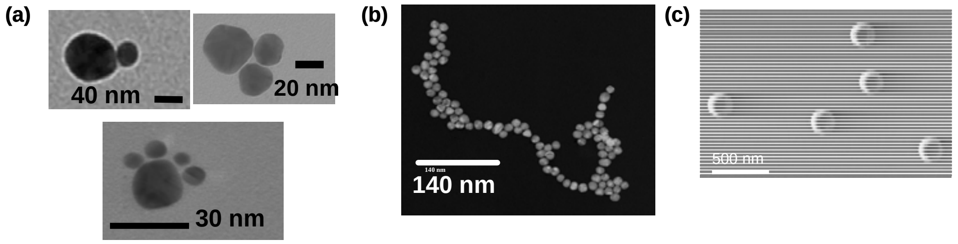

Figure 1. Assemblies of asymmetrically-functionalized gold nanoparticles and structures fabricated using nanosphere template lithography. (a) Transmission electron microscopy (TEM) images of multiparticle assemblies.[1] (b) TEM image of 1-D gold nanoparticle chain using poly(acrylic acid).[2] (c) Scanning electron microscopy image of gold crescents.[3,4]

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Laser Spectroscopy/Imaging at the Nanoscale

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Overall Research Goals: We are integrating second harmonic (SHG) and sum frequency generation (SFG) measurements with nano-scale spatial resolution for creation of images and with femtosecond time-resolved measurements for dynamics. Implementation of efficient computational methodologies that accurately describe laser-matter interactions to aid in the interpretation as well as prediction of experimental results is an additional goal. Advances in nanoscale imaging and spectroscopy will have a profound influence on surface chemical analysis and will provide new fundamental chemical understanding for DOE mission areas.

Significant Achievements in 2006-2008: In earlier efforts we have investigated spatially-correlated atomic force microscope (AFM) topological imaging and fluorescence imaging/spectroscopy. To achieve greater measurement sensitivity and nanoscale spatial resolution for new nonlinear optical spectroscopy experiments, we are assembling an instrument that capitalizes on three enhancements: (1) a total internal reflection (TIR) excitation geometry *via* the microscope objective, (2) sum frequency light collection using a closely coupled microscope objective, and (3) a noble metal coated optical fiber tip that supports plasmon resonances. The latter near-field scanning optical microscope (NSOM) probe serves as a signal enhancement device, as opposed to a collection device. We use electrodynamics calculations to guide the design of the tip used for the SFG experiments to optimize the SFG enhancement. The goal is to engineer the plasmon excitations to be resonant at 650 and 800 nm, two wavelengths of our SFG experiment. The tip structure can be modeled as a truncated, conic shell. Structural characteristics of the shell geometry dictate the frequency of the plasmon resonances, as well as the spatial variation and magnitude of field enhancements. Field enhancements of up to 10,000 have been computed.

We have modified a Nanonics Imaging Ltd. NSOM instrument to be compatible with our inverted fluorescence microscope stage. The NSOM employs a bent, tapered fiber optic tip. The tip is essentially a cantilever design and operates in a tapping mode. The distal end of the tip fiber optic exits the stage to either a light source or a single photon counting detector to provide a means for either light delivery or collection, respectively. The NSOM design in the tip vicinity is particularly unobstructed for flexibility in focusing laser beams onto the sample. We have recorded spatially-correlated images corresponding to two-photon fluorescence from (S)-(-)-1-(4-nitrophenyl)-2-pyrrolidine methanol (NPP) crystallites and Raman scattering data from a polycrystalline diamond thin film using this apparatus.

Some preliminary data that demonstrate tip enhancement are shown in Figure 1. Gold nano-octahedra (60-nm edges) on a glass slide were imaged *via* their emission light as a Si AFM tip was rastered over the sample. The geometry of this experiment is similar to that of our planned SFG experiments. Argon ion laser light (514 nm) excited the sample in a TIR geometry, and the emission was collected using the same objective and spectrally filtered before detection using an imaging CCD camera. The left panel shows the AFM data for a single octahedron. The right panel was constructed by binning the diffraction limited fluorescence image of the octahedron and plotting the binned optical signal intensity as a function of the tip raster coordinates. The octahedron apex image in the right panel is significantly beyond the diffraction limit and is smaller than the AFM image of the overall particle. The optical image also exhibits interference fringes at a larger scale. The apex image was created by collecting light during the entire oscillation period of the scanning tip; this effect averages the enhancement factor, that only is large when the tip is very close to the particle. We will use a gated CCD camera to eliminate this problem.

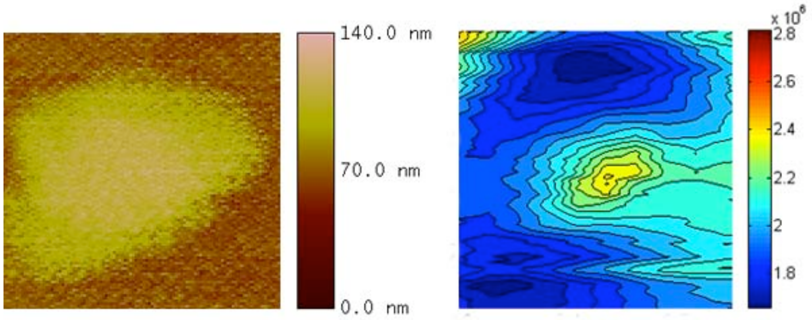

Figure 1. Correlated AFM (left) and optical (right) images for a gold nano-octahedron. (Both panels 250x250 nm.)

These examples represent our initial progress toward tip-enhanced imaging of nanoparticles via nonlinear optical phenomena.

<u>Science Objectives for 2008-2009</u>:

- We will demonstrate vibrational images of molecules adsorbed on individual nanoparticles based on infrared/visible surface sum frequency generation.
- The environmental chamber associated with our NSOM will be implemented to allow us to examine nanoparticles exposed to controlled environments to investigate chemical reactions at nanoparticle surfaces.
- We will extend these studies to include dynamical measurements through the use of variable time delays between SFG pulses.

<u>References to work supported by this project 2006-2008</u>:

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Real-Time Observation of Interfacial Binding and Reactivity with Optical Ring Resonators

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The goal of this research is to develop a robust, label-free signal transduction modality using CMOS-fabricated, silicon photonics to monitor molecular binding, partitioning, and reactivity at the solid-liquid interface.

The presence of a surface can significantly alter the kinetics of molecular interactions compared to analogous processes in which all components are freely diffusing in solution. We are developing microfabricated, semiconductor optical cavities that are exquisitely sensitive to changes in the surface refractive index to probe these differences. Localization of molecules near the surface due to binding or partitioning leads to a measurable change in the optical properties of the cavity. In this way, surface reactions can be monitored without the need for any spectroscopic or radioactive label. To date we have observed, in real-time, molecular mono- and multilayer deposition and subsequent covalent modification of these molecular films with small molecules (<150 amu). We are further developing this general transduction methodology for the evaluation of molecular partitioning and interfacial chemical reactivity as well as a range of applications related to chemical and biological detection.

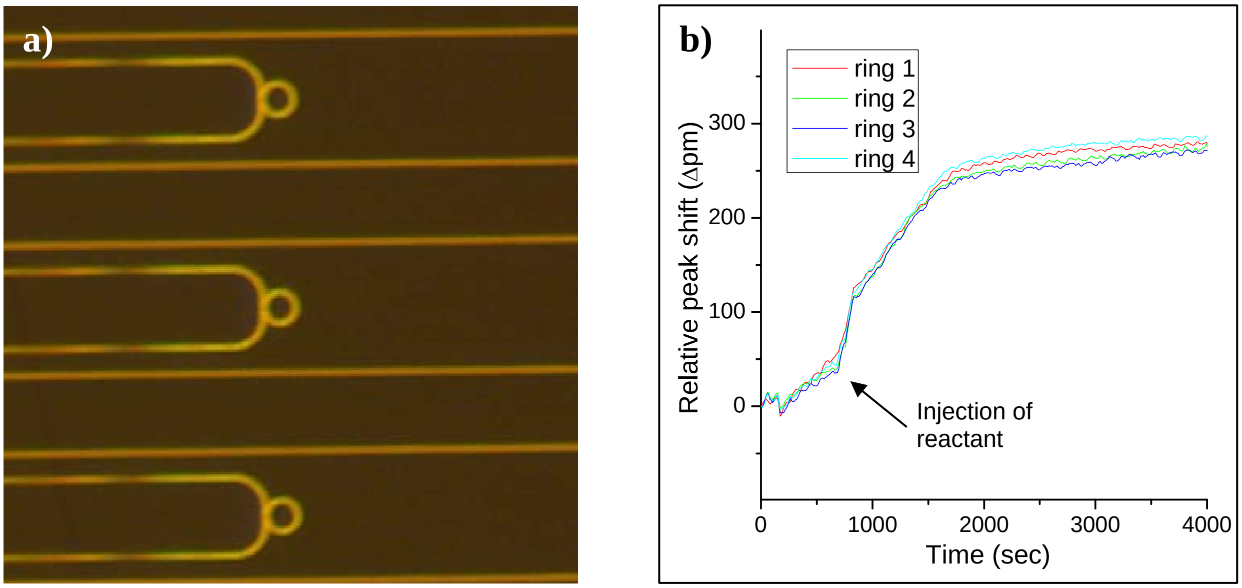

Figure 1. (a) An optical micrograph of three Si photonic ring resonators that are optically interrogated by adjacent waveguides. **(b)** The addition reaction of a ~150 amu molecule covalently linking to an organic thin film can be monitored in real time by measuring the frequency shift in the cavity modes of a ring resonator.

Analytical Spectroscopy Methods for Studying Liquid/Solid Interfaces

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Overall research goals: The goals of this research are development of surface-sensitive spectroscopy and spectroscopic imaging methods for investigating chemical structure and reactions at liquid/solid interfaces. These spectroscopic and imaging tools are leading to understanding and control of interfacial chemistry that impacts both analytical methods (chemical separations and sensors) and environmental transport and remediation (metal-ion complexation, adsorption interactions). We are developing surface-enhanced Raman spectroscopy and fluorescence and Raman microscopy capable of detecting sub-monolayer molecular coverages at liquid/solid interfaces. We are studying the binding of molecules and metal-ions to immobilized ligands and effects of surface structure and electric fields on these interactions.

Significant achievements in 2006-2008: A major goal of the DOE project has been to develop surface-enhanced Raman spectroscopy (SERS) for monitoring the binding of metal ions and molecules to ligands immobilized on metal surfaces. Surface potentials that are present at liquid/solid interfaces influence the interfacial activity of ions and, therefore, the reactions of immobilized ligands with ions from solution. To study these effects, the ligand p-([8-hydroxyquinoline]azo)benzenethiol (SHQ) was synthesized and immobilized on SERS-active electrode surfaces. Metal-ion binding to this ligand shows a potential dependence that originates not only from modulation of metal-ion activity at the interface, but also from electrochemical control over a tautomerization equilibrium of SHQ, where a potential step of ~400 mV can be used to "switch" between two tautomeric forms of the ligand [1]. The potential-dependent switching is consistent with a large difference in the dipole moments of the two tautomers estimated by DFT calculations. The results suggest a new paradigm for potential control over interfacial reactions based on modulating the tautomerization of immobilized species to produce electrically switchable surface properties. SERS was also used to study adsorption equilibria and kinetics of surfactants at hydrophobic surfaces in contact with aqueous solutions [2]. A hydrophobic surface, with stable and reproducible SERS activity, was produced by binding gold colloids to an amine-terminated glass slide and then modifying the gold particles with octadecyltrimethoxysilane producing a C18-modified, hydrophobic surface. *In situ* SERS-detected adsorption of the cationic surfactant cetylpyridinium chloride (CPC) from aqueous solution to this surface was found to follow a Frumkin isotherm. Interactions between the charged head groups could be detected in frequency shifts in the symmetric ring breathing mode, consistent with an interfacial surfactant environment similar to a CPC micelle. Rates of surfactant adsorption were determined by time-resolved SERS measurements, and found to be much slower than diffusion-controlled, indicating a significant kinetic barrier to adsorption. Desorption kinetics were heterogeneous, consistent with the spectroscopic results showing changes in interfacial environment with surface coverage.

A recent goal for this project is the imaging of adsorption, interfacial binding, and molecular diffusion as single-molecule events at the liquid/solid interface. As a step toward that goal, we have developed control over the binding site density of reactive ligands on surfaces [3] by diluting surface amine groups in self-assembled and cross-linked monolayers on glass prepared from solutions containing very low concentrations of 3-aminopropyltriethoxysilane and higher concentrations of 2-cyanoethyltriethoxysilane. The surface amine sites are suitable for attaching labels and ligands by reaction with succinimidyl-ester reagents. Labeling the amine sites with fluorescent molecules and imaging the single molecules with fluorescence microscopy provides a means of determining the density of amine sites on the surface. Imaging of these samples demonstrated quantitative control and chemical conversion of binding sites at very low ($<10^{-7}$) fractions of a monolayer. In a related development, the group has begun imaging diffusion of adsorbed molecules at liquid/solid interfaces [4]. The trajectories of individual molecular motions combined with simultaneous measurements of the fluorescence spot size of the moving molecules gives a detailed picture of the diffusion process (see Figure 1).

<u>Science objectives for 2008-2009</u>:

- Confocal-Raman microscopy imaging of individual C18-silica particles in contact aqueous solution with be used to characterize the interfacial environment of reversed-phase chromatographic materials.
- The surface diffusion dynamics of molecules adsorbed to C18-modified silica surfaces will be studied to differentiate between continuous and hopping diffusion mechanisms at the aqueous solution interface.
- Investigate the effects of applied potentials on the equilibria and kinetics of binding of ionic species to surface-immobilized ligands.

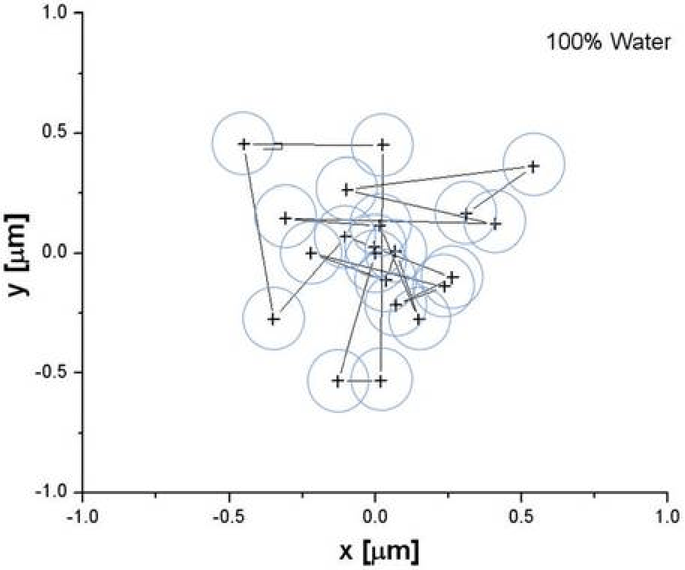

Figure 1. Diffusional trajectory of DiI on C18-modified silica surface in contact with water (30 ms time steps).

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Laser-Material Interactions (ablation) for Chemical Analysis

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

Significant achievements in 2006-2008: The research program continued to study and understand fundamental mechanisms related to particle formation using modeling and experimental measurements, understanding femtosecond laser ablation for producing aerosols ideally suitable for ICP-MS, and the use of near-field optics for achieving sub-micron spatial scale ablation. Pump-probe time-resolved imaging results have shown the time window in which particles nucleate and condense. A detailed theoretical analysis have been conducted which provided in-depth understanding of nanoparticle formation mechanisms after laser ablation (Figure 1). It was found that for ablation in helium, the characteristic particle size is ~10nm. For ablation in argon, the characteristic particle size was about three times larger (~30nm). It was determined that the change in the particle size distribution resulted from the difference in the thermal conductivity of the background gases. Background gases with higher thermal conductivity (e.g. helium) caused faster cooling rate of the laser induced vapor plume and reduced the subsequent particle size distribution.

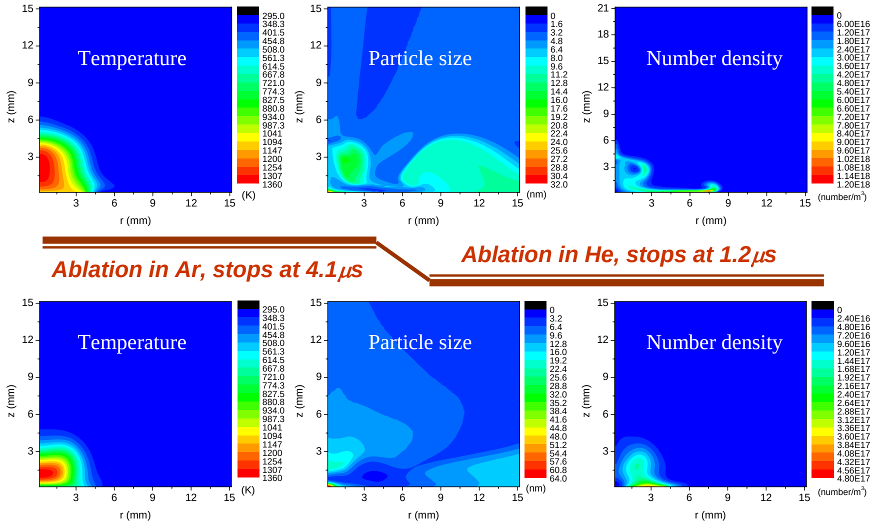

Figure 1. The simulated temperature, particle size, and number density distributions for ablation in argon and helium

The critical issue in achieving nanoscale laser ablation using near field scanning optical microscope (NSOM) tips is to efficiently couple light energy through a fiber tapered to a diameter of several hundred nanometers. Different nano patterns have been generated with the NSOM with multiple femtosecond laser pulses in different background gases. It was demonstrated that, under the present experimental conditions, significant energy was transferred from the NSOM tip to the silicon wafer causing patterns to be generated on the sample surface (Figure 3). The patterns changed from nano protrusions to nano craters when the background gas was changed from air to argon. Two major mechanisms were attributed to be responsible for this dramatic change; namely, nano oxidation and nano laser ablation.

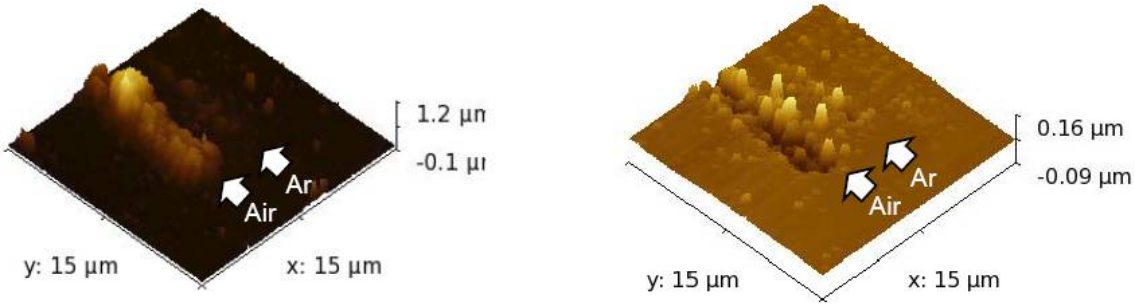

Figure 3. Nano patterns with in air and argon (a) before dipping in HF solution (b) after dipping in HF solution

Science objectives for 2008-2009:

1. Model nanoparticle formation processes with supporting measurements.
2. Establish experimental and theoretical understanding of femtosecond ablation ICP-MS.
3. Expand laser ablation into the nanoscale spatial region.

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Laser-Material Interactions Relevant to Analytic Spectroscopy of Wide Band Gap Materials

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

Significant achievements in 2006-2008: In collaboration with Kenichi Kimura (NPB, Japan), we have completed mass-selected, time-of-flight measurements of negative alkali ions from single crystal alkali halides (NaCl, KCl, KBr, LiF) during 248-nm laser irradiation (KrF excimer) at pulse energies well below the threshold for optical damage and plume formation. As shown in Fig. 1 for KCl, the negative and positive alkali arrival times virtually coincide. Detailed studies of KCl and KBr show no evidence for negative halogen ions, despite the presence of slow neutral halogen atoms (with high electron affinities). Substantial electron densities are observed in the region occupied by the positive ions, with low densities elsewhere. We attribute negative ion formation to double electron attachment to positive alkali ions in the first microseconds after the laser pulse. The low electron fluxes experienced by the slower neutral particles strongly hinder electron attachment to these species, despite favorable energetics.

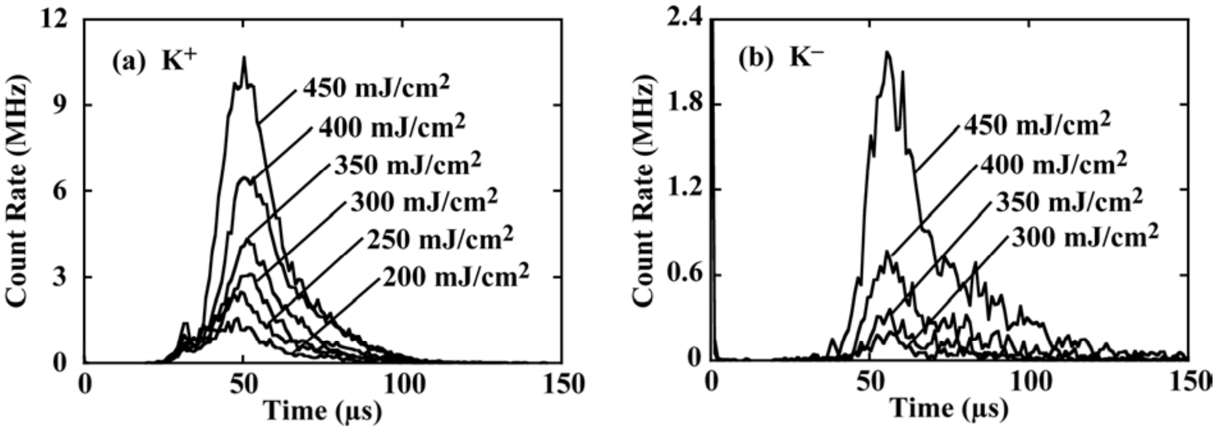

Figure 1. Time of flight signals of the positive (left) and negative (right) K ions from KCl for several fluences at 248 nm.

We have recently completed a study of particle emission from UV-grade fused silica during 157-nm irradiation (F_2-excimer) at fluences below the threshold for optical damage. Consistent with ion emissions from a variety of ionic materials, ions from fused silica are both energetic and depend strongly on surface treatments that affect the density of surface defects. The repulsive forces responsible for positive ion ejection (Si^+, O^+) appear to have both (chemical) antibonding and (physical) electrostatic components. Importantly, the accompanying neutral emissions from fused silica apparently involve strained bonds, but not pre-existing point defects.

We have also completed parallel studies of particle emission from polytetrafluorethylene [$(C_2F_4)_N$—PTFE] and polyvinylidene fluoride [$(CH_2CF_2)_N$—PVDF] during 157-nm irradiation at fluences normally employed for rapid etching. The neutral emissions from PTFE are primarily $(CF_2)_N$ fragments of backbone bond scission, and the emission intensities are relatively consistent from pulse-to-pulse. In contract, PVDF shows dramatic pulse-to-pulse variations in emission intensity. Photoinduced bond-breaking in PVDF is largely confined to side chains to yield neutral HF. Concurrent backbone bond conjugation gradually increases laser absorption. Sporadic bursts of emission (with a wide variety of neutral products) are interspersed with periods of weak HF emission. In both PTFE and PVDF, electron attachment (often dissociative) yields a variety of negative ions. Although 157-nm photons are strongly absorbed in both materials and produce rapid etching, polymer chemistry has important effects on etching behavior.

Science objectives for 2008-2009

- Characterize VUV and UV absorption by transient defects during laser irradiation by *in situ* spectrophotometry. The source of a reported transient absorption in CaF_2 (an important VUV optical material) at 157 nm is currently unknown, for instance.
- Improve characterization and modeling of electron-ion and electron-neutral interactions in weak plasmas produced by pulsed UV and VUV lasers. These interactions often depend on particle mass and thus can affect the transport of charged particles for chemical analysis.
- Compare the role of defects on particle emission and etching from alkali halides using pulsed excimer lasers at photon energies above and below the material bandgap. This work will be performed in collaboration with Stefano Orlando (CNR, Italy).
- Characterize role of step- and kink-like defects on laser-induced, monolayer etching of single crystal ZnO using *ex situ* atomic force microscopy. This work will be performed in collaboration with Lynn Boatner (ORNL) and Wayne Hess (PNL).

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Ion-Surface Interactions in Mass Spectrometry

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

Significant achievements in 2006-2008:.

First detailed studies of the formation of gas-phase peptide radical cations demonstrated that the competition between the electron and proton transfer (ET and PT) in dissociation of metal(III)-salen-peptide complexes is controlled by the redox properties of the metal-saen core, the mode of binding of the peptide ligand in the complex, and the difference in entropy effects associated with these pathways. Fragmentation of radical cations is dominated by bond cleavages that are remote from the initial position of the radical site and is adequately described using statistical theories. Comparison between the dissociation patterns obtained for the $M^{+\bullet}$, $[M-2H]^{-\bullet}$ and $[M+H]^{2+\bullet}$ peptide ions provides clear evidence that charge-remote radical-driven fragmentation processes play an important role in the dissociation of odd-electron peptide ions.

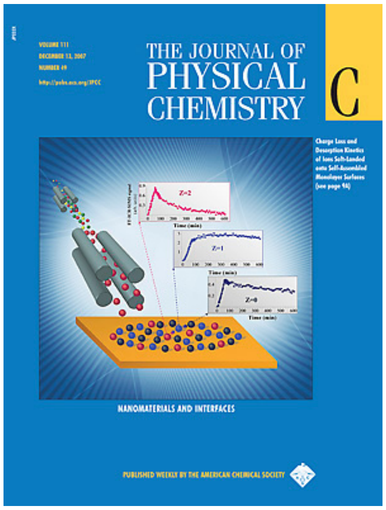

Figure 1 Charge loss and desorption kinetics of ions soft-landed onto self-assembled monolayer surfaces.

Systematic studies of factors that affect ion soft-landing (SL) onto inert self-assembled monolayer (SAM) surfaces demonstrated that intact peptide ions are deposited on FSAM surfaces even at high kinetic energies (at least up to 150 eV) and that ions retain at least one proton after SL. Recently we completed the first detailed study of the kinetics of desorption and charge reduction following SL of doubly protonated model peptide onto the FSAM surface. This study utilized an in-line 8 keV Cs^+ ion gun that allowed us to interrogate the surface both during the ion deposition and after the deposition was finished. We obtained unique kinetics signatures for doubly protonated, singly protonated and neutral peptides retained on the surface. Our results were rationalized using a relatively simple kinetic model that incorporates charge reduction and thermal desorption of ions and neutral peptide molecules from the surface.

Science objectives for 2008-2009:

- Continue studying dissociation of peptide radical cations with an objective to understand the effect of the charge and the radical on the energetics, dynamics and mechanisms of fragmentation of complex ions;
- Explore the effect of the charge state on the energetics of dissociation of non-covalent complexes;
- Continue studying charge reduction and desorption kinetics following soft-landing of complex ions on model substrates.

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Nanostructured substrates and imaging applications of soft laser desorption ionization

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Overall research goals: Soft laser desorption ionization (SLDI) continues to enhance mass spectrometry by broadening its possible applications. Our three main research goals for the current grant period are to explore SLDI from nano- and mesoscopic structures, to better understand the fundamentals of SLDI at atmospheric pressure and to develop new molecular imaging methods preferably at atmospheric pressure.

Significant achievements in 2006-2008:

SLDI from nano- and mesoscopic structures

Nanomaterials and mesostructures, such as laser-induced silicon microcolumn arrays (LISMA), offer a new matrix-free platform for the SLDI of biomolecules. The morphology and surface chemistry of LISMA depends on the processing environment and the laser parameters. Column diameters, lengths, and periodicity are a function of processing conditions (processing medium, laser pulse energy, pulse length, angle of incidence, etc.). Ion yields from the various surfaces were dramatically affected by the pH of the processing environment, indicating a strong influence of the OH-terminated sites on the silicon surface. Structure specific fragmentation of the produced ions primarily depends on their internal energy. To gain insight into the internal energy of ions laser desorbed from native LISMAs and LISMAs derivatized through silane chemistry, the cations of eight benzyl-substituted benzylpyridinium salts were used as thermometer ions (TI). On both native and perfluorophenyl-derivatized surfaces, TIs showed no change in their internal energy over a wide range of laser fluences. While the survival yields for these preformed ions were stable, results on peptides indicated fluence dependent fragmentation. These results point to a different fragmentation mechanism for peptides mediated by hydrogen radicals formed through the recombination of protons.

Fundamentals of SLDI at atmospheric pressure

Atmospheric pressure laser ionization sources promise greater versatility and reduced need for sample preparation compared to their vacuum-based counterparts. At atmospheric pressure, mid-IR laser ablation proceeds through two consecutive stages. Initially, non-equilibrium surface evaporation takes place. That is followed by a phase explosion of the superheated subsurface layer. We introduced a fluid dynamics model for water-rich target ablation with mid-infrared laser pulses at atmospheric pressure in the presence of phase explosion. Calculations were performed for the ablation of water by Q-switched Er:YAG laser pulses at various fluence levels below and above the onset of phase explosion. The remarkable validity of the predicted dynamics was quantitatively assessed by comparison with experimental data.

New molecular imaging methods at atmospheric pressure

Interaction of light and matter has long served as the basis of probing and modifying physical and chemical properties of materials. Recent biomedical applications focus on the mid-infrared (mid-IR) region to couple the laser energy into samples through absorption by the native water. For example, mass spectrometry (MS), relying on atmospheric pressure mid-IR matrix-assisted laser desorption ionization, takes advantage of the small amount of ions in the laser plume. In mid-IR laser ablation, owing to the recoil pressure buildup in the sample, most of the material is expelled in the form of neutral molecules, clusters, and particulates. To enhance ion production, we intercept this plume with a cloud of charged droplets to post-ionize them for MS. As a result, laser ablation electrospray ionization (LAESI) can directly probe the molecular makeup of water rich targets with superior ion yield and dramatically extended mass range (up to 66,500 amu). LAESI also enables two and three dimensional imaging of live tissues (see Figure 1). Fast imaging of the plume-plume interaction reveals the mechanistic aspects of LAESI.

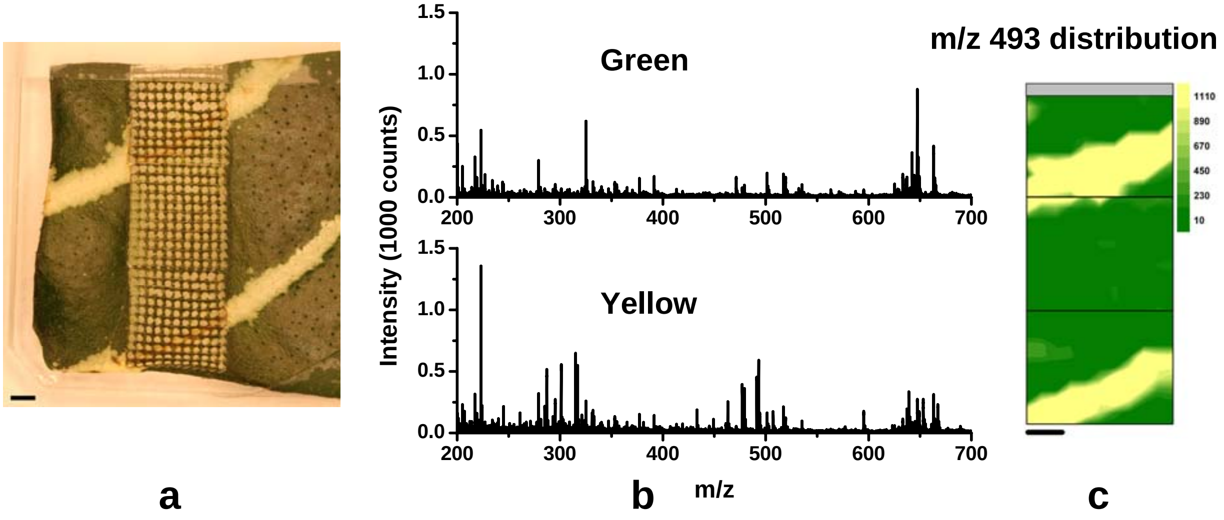

Figure 1. Molecular composition of a variegated zebra plant (*Aphelandra squarrosa*) leaf was probed with LAESI-MS while rastering the surface with a focused infrared laser beam. a) Optical image of the live tissue ablated in 350 µm circular areas. b) Mass spectra indicated that the *m/z* 493 ion was only present in the yellow sectors and c) its molecular distribution was in good agreement with the optical pattern. The scale bars correspond to 1 mm.

Science objectives for 2008-2009:

- Ion yields from LISMAs exhibit a dramatic dependence on the angle of incidence of the desorption laser. Understanding this phenomenon is thought to be essential to uncover the mechanism of SLDI from LISMAs. We plan to combine these studies with internal energy measurements for the desorbed ions.
- Based on the combination of depth profiling and lateral imaging, three-dimensional molecular imaging will be developed. The spatial resolution will be improved to ultimately achieve cell-by-cell analysis.

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Measuring ion currents carried by ionic liquids in nanopores of well-defined geometry and surface chemistry

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Overall research goals: The main focus of our research is experimental investigation of ionic currents carried by room temperature ionic liquids through nanopores of known geometry and surface chemistry. Numerous ionic liquids have been characterized in terms of their *bulk* ionic conductivities[1]. However, studies of currents carried by ionic liquids through restricted geometries such as nanopores have not been performed yet. Transport properties of ionic liquids in nanopores, and interactions of ionic liquids with charged surfaces are important for applications of ionic liquids in fuel cells as well as in separation and extraction processes with ionic liquids supported membranes. The specific goals of the research are: (i) to determine ion current carried by ionic liquids through single nanopores of known geometry and surface chemistry, and (ii) to study interactions of ionic liquids with charged surfaces of nanopores. The second part of the project allows us to study the range of electrostatic interactions in ionic liquids. Rationale: In order to achieve these goals, we prepare single pores with diameters between 2 nm and 1 micrometer having positive surface charges, negative surface charges, and neutral pore walls. These pores are prepared by the track-etching technique in which the Siwy group specializes. Using single-pore membranes gives us a unique insight into physical and chemical phenomena occurring in one nanopore without averaging effects resulting from transport through many pores.

Significant achievements in 2006-2008.

Fabrication of nanopores. The Siwy group specializes in preparation of nanopores of controlled geometry and surface chemistry. The diameter of the nanopores is tailored between 2 nanometers up to hundreds of nanometers. The nanopores are prepared in polymer films by the track-etching technique. This technique is based on irradiating the material with energetic heavy ions (e.g. Au, Xe, U) of total kinetic energy ≅ 2.2 GeV, and its subsequent chemical etching. The irradiation step is done at the Gesellschaft fuer Schwerionenforschung (GSI) in Darmstadt, Germany. We primarily work with samples irradiated with *single heavy ions* that caused the formation of a local, nanometer size zone of damaged material, the so-called track. This single track, after chemical etching, leads to the formation of a single pore. The samples are etched at UCI to desired shaped and sizes. We prepare mostly cylindrical nanopores, tapered-cone pores, and double-cone (hour-glass shaped) pores. The geometry of the pores is determined by the conditions of the chemical etching step. Figure 1 shows the procedure that leads to preparation of conical pores in polyethtlene terephthalate films (PET).

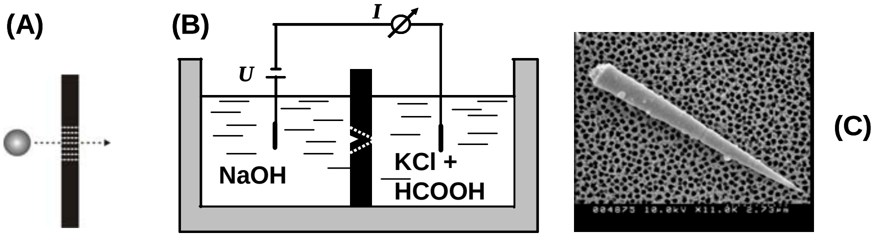

Figure 1. Preparation of PET membranes with single conical pores. (A) Irradiation of a polymer foil with a single swift heavy ion; (B) Experimental set-up used for one-sided etching, which leads to the formation of conical pores; (C) 'Negative' of a conical nanopore obtained by electroless plating with gold of a single conical nanopore in PET.

The Siwy group also specializes in studying transport of ions through these pores as a function of their diameter and surface charge[2]. For example we have found that a conical nanopore with homogenous negative surface charges is cation selective and rectifies the cation flux from the small opening to the big opening of the pore (Fig. 2A). We have also patterned the surface charge so that there is a zone with positive surface charges in contact with a zone with negative surface charges. Such a device was found to behave like a diode (Fig. 2A). Rectifying properties of these systems is possible due to interactions of ions with the charged pore walls. The presence of the ion current rectification points therefore to the existence of electrostatic interactions having range equal at least to the pore diameter.

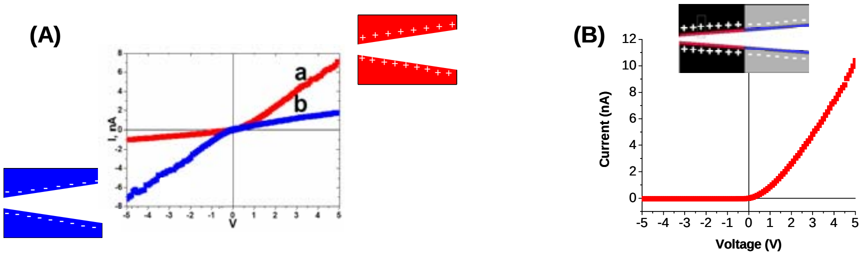

Figure 2. Transport properties of single conical nanopores with (A) homogeneous surface charges as shown in the insets, and (B) with surface pattern. The current-voltage curves were recorded in 0.1 M KCl, pH 5.5. Small opening of these pores was smaller than 5 nm [Ref. 2].

<u>Measurements of ion current carried by ionic liquids through single nanopores.</u>

In order to study transport properties of ionic liquids we have used single-pore membranes. In this way, we can obtain information on nanoscale phenomena occurring in one pore, without the averaging coming from transport through many pores. We have studied so far ionic liquids in single conical nanopores. A tapered cone geometry is superior to a cylindrical shape due to the lower resistance offered by a tapered-cone. Using these nanopores we can probe nanoscale processes while still enjoying high, easy to measure ionic fluxes. Additionally, by studying the transport properties through conical nanopores we can check the existence of ion current rectification, which would give us information on the range of electrostatic interactions in ionic liquids.

Figure 3 shows our first measurements of ion currents carried by ionic liquids through single conical nanopores. Our measurements indicate that the conductivity of ionic liquids in pores with diameter less than 20 nm is smaller than the bulk values of ionic conductivities. So far we have looked at transport properties of trihexyltetradecylphosphonium bromide, and 1-butyl-3-methylimidazolium methyl sulfate. As the next step we will look at ion current of the ionic liquids through nanopores of various surface charges.

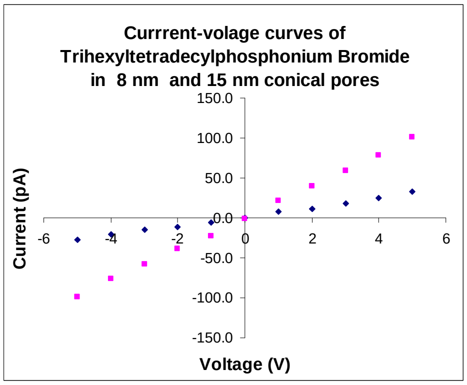

Figure 3. Ion current carried by the ionic liquid trihexyltetradecylphosphonium bromide through a single conical nanopore with diameter of 8 nm (the blue squares) and 15 nm (the pink squares). The ionic conductivity of this ionic liquid in the 8 nanometer pore is three times smaller than its conductivity in the 15 nm pore.

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Molecular Aspects of Transport in Thin Films of Controlled Architecture

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Overall research goals. The ability to control molecular transport is pertinent to a wide variety of energy-related technologies and problems, including membrane separations, environmental remediation and uptake of biological materials, *e.g.*, pathogens, in the ambient. Central to realizing active control over molecular transport is the ability to move molecules over nanometer dimensions with high precision, selectivity, and temporal control -- a capability that would enable advances on both fundamental and technological problems. Our approach to controlling molecular transport combines actively controlled molecular assemblies with transport in confined geometries, *e.g.*, the nanoscale channels of a nanocapillary array membrane (NCAM). The broad goals of this research are to understand transport in these structures sufficiently that they can be exploited to accomplish separations and manipulations which cannot be achieved on the macroscale.

Significant Achievements 2006-8. *Single Nanopore Transport*. We studied the ability of NCAMs to control the transfer of fluid voxels from one microchannel to the other through a nanochannel under rest, injection and recovery by varying the applied potential bias. Numerical simulations based on coupled Poisson-Nernst-Planck and Stokes equations demonstrate that the physical behavior is dominated by ion accumulation/depletion effects at the micro-nano junctions. Ions accumulate at the positive micro-nano interface, while depletion is observed at the other micro-nano junction region (Fig. 1). The key characteristic feature is the observation of a biphasic current recovery after ion injection. The presence of a two-phase recovery, which is unmistakable in the experimental data, is directly linked to the ion depleted region.

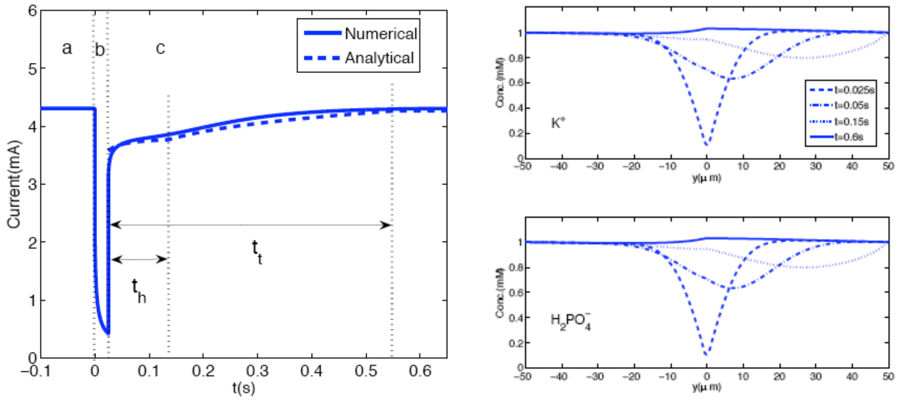

Figure 1. (*Left*) Ionic current vs time when the system is positively biased. (a) current during the rest stage, (b) current during the injection stage, and (c) current during the recovery stage. (*Right*) Ion concentration along the central line of the source channel during the recovery stage. Note that the recovery stage starts from t = 25 ms. (*Top*) cation concentration. (*Bottom*) anion concentration.

Sandwich Nanopore Kinetics. This portion of the project centers on the creation of a known population of surface immobilized species on the interior wall of a nanopore, created by FIB (30 keV Ga^+ ion) milling of a polymer membrane (10 μm thick) consisting of a ~ 2 μm thick layer of a copolymer of methyl methacrylate and glycidyl methacrylate (PMMA-GMA) sandwiched between two thicker (~3 μm) layers of PMMA. To test the activity of the immobilized HRP, a preliminary experiment was performed in which enzyme was immobilized on one wall of a rectangular microfluidic channel. The immobilized enzyme was then exposed to a combination of H_2O_2 and amplex red, a fluorogenic dye that is converted to the highly fluorescent product resorufin upon oxidation. Reaction kinetics were characterized by a Michaelis-Menten model, the immobilized HRP exhibiting very high activity, (v_{max} ~ 1.3 $\mu M\ s^{-1}$) compared to the free-solution value (v_{max} ~ 0.032 $\mu M\ s^{-1}$).

Specific Objectives for 2008-09. We will extend our simulation results by characterizing electrokinetic transport in single nanofluidic channels by *mapping the structural and dynamic features of molecules that determine hindered electrokinetic translocation velocities*. We plan to do this by correlating optical and electrical translocation measurements. We will also extend our efforts at single nanopore kinetics measurements through *assays for ligand binding kinetics and energetics that are sensitive to the intrapore binding events.*

Publications Acknowledging DOE BES Support – 2006-8

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Energetics of Nanomaterials

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Postdocs and students: A, Levchenko, F. Xu. P. Zhang,

Collaborators: Alex Kolesnikov (Argonne), Ricardo Castro (FEI, Sao Paulo, Brazil)

Overall research goals: Using specialized and unique calorimetric techniques, we measure heat capacities, enthalpies of formation and hydration and surface energies of nanoparticles. We combine these thermodynamic studies with inelastic neutron scattering and structural studies to understand chemical bonding and the state of water in nanoparticle systems.

Significant achievements in 2006-2008: We have established the following:

- Crossovers in phase stability at the nanoscale are a general phenomenon, arising from the competition of phase transformation and surface energies.
- At fixed composition, the surface energy decreases as the metastability of a phase increases, regardless of volume relations.
- Oxyhydroxides have lower surface energies than oxides.
- Hydrated surfaces have lower surface energies than anhydrous surfaces.
- TiO_2 nanoparticles do not have a higher heat capacity than bulk when water content is taken into account.
- For ZnO, the measured surface energy increases in the order nanoparticles, nanorods, nanoneedles, reflecting differences in the predominant surfaces exposed.
- Water is bound to nanoparticles with a variety of energies; the most strongly bound water with energies in excess of 100kJ, suggestive of dissociation to hydroxyl species on the surface.
- The heat capacity of tightly bound water on TiO_2 nanoparticle surfaces is less than that of ice, and measured C_p is consistent with that computed from the vibrational density of states calculated from neutron studies.
- A new and general synthetic method for nanoparticles has been developed at BYU.

Science objectives for 2008-2009

- Work on SnO_2 and SnO_2-TiO_2 systems.
- Work on CoO-ZnO
- Measure interfacial as well as surface energies directly by calorimetry
- Further understanding of hydration effects and the role of water in nanoparticle stability.

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Chemical Interactions Between Protein Molecules and Polymer Materials

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Collaborators: Dr. James (Chip) Kilduff, Civil and Environmental Engineering, RPI

Overall research goals: The overall research goal was to develop and test protein adhesion resistant membranes (i.e. surfaces that exhibit minimal adhesive energy *and* minimal amounts of protein adsorption) and to determine protein-substrate adhesion and protein conformational stability at synthetic membrane interfaces.

Significant achievements in 2006-2008: During this period, we have combined *biophysical methods* and *surface science approaches* to achieve the goal of producing protein adhesive resistant surfaces for filtration of bioprocessing fluids. As planned, we have (i) developed and demonstrate the reversible conversion of a photo-grafted, photo-responsive, polymeric synthetic membrane surface from polar to nonpolar character[1], (ii) demonstrated that heterogeneous polymeric surfaces (i.e. surface wettability and surface roughness) accelerate protein precipitation by increasing the local concentration of protein molecules[2], and (iii) changed the rheological properties (rigidity) of adsorbed poly(L-lysine) (PLL) layers through the addition of different anions[3].

Details of the chemical structure, the protein adsorption characteristics and interfacial properties and the photo-responsive polymeric synthetic membrane, in the two optical configurations are summarized in Fig. 1. Exposing a model protein (hormone insulin)

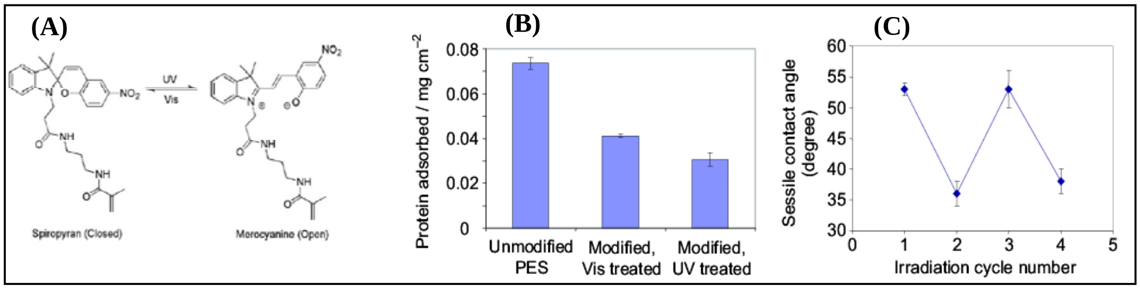

Figure. 1. Schematic of graft polymerization and switching of Rensselaer's patented photografting process in which a synthetic poly(ether sulfone) (PES) ultrafiltration membrane (photo sensitive polymer) is first dipped into a vinyl (spiropyran) monomer solution (1% w/v) in ethyl acetate for 1 h and then exposed to 300-nm UV irradiation to induce grafting and polymerization. (A) The chemical structure of the vinyl spiropyrans in two configurations ("closed" with visible light and "open" with 254-nm UV light) as a function of UV and Vis irradiation. (B) Adsorption of BSA in PBS (10 mm; pH 7.4) at 22±1ºC for 1 h on the as-received PES membrane and on modified PES membranes with grafted vinyl spiropyran in the "closed" and "open" configuration. (C) Surface wettability changes as measured by the sessile contact angle of the grafted PES membrane with a water droplet after alternating exposure to 254-nm UV light (1 h) and visible light (5 min) versus cycle number. (Taken from Ref. 1)

to five commercial synthetic membranes during precipitation, we show that both chemistry and surface roughness speed up the process probably due to heterogeneous reaction at the surfaces[2]. Hydrophobic surfaces are more effective than hydrophilic ones. In a third sub-project, we demonstrate that by exchanging anions (Br^{-1} with SO_4^{-2} and back to Br^{-1}) attached to an adsorbed polycationic layer of poly(L-lysine) (PLL), the rigidity of the layer was reversibly increased and decreased (Fig. 2)[3].

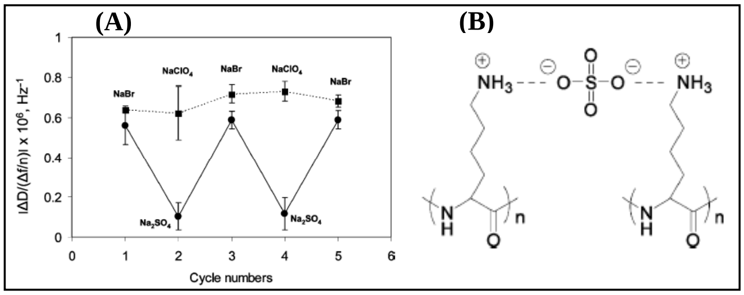

Figure 2. (A) The $|\Delta D/(\Delta f/n)|$ ratio of an adsorbed layer obtained after washing with DI water. Change in frequency was normalized with the overtone number (n=7). Exchange of Br^{-1} with SO_4^{-2} ions resulted in a decrease in the $|\Delta D/(\Delta f/n)|$ ratio while the reverse increased the $|\Delta D/(\Delta f/n)|$ ratio almost back to its initial value. The decrease in $|\Delta D/(\Delta f/n)|$ ratio due to exchanging the Br^{-1} with SO_4^{-2} ions indicates an increase in rigidity of the adsorbed layer (λ and –). Exchanging the Br- with ClO_4^- ions did not cause a significant change in the rigidity of the adsorbed PLL layer (ν and ---). (B) Binding of SO_4^{-2} anions with the ammonium groups of poly-lysine (PLL). (Taken from Ref 3).

Specific objectives for 2008: Although funding for this project ends in a few months, we have submitted a new proposal involving high throughput methods to synthesize and test 100s of novel surfaces in parallel. The goal for the remaining period is to evaluate our best novel membrane filtration surfaces obtained with this new method.

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Patents

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P2. "Coiled membrane filtration system", European Patent #: EPO0784502, Date of filing: March 7th 2007.
P3. UV assisted grafting of PES and PSF membranes", (with M. Taniguchi and J. Pieracci), Canadian patent 2,422,738, issued June 26, 2007.

Nanostructured Hybrid Materials for Advanced Membrane Separations

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Dr. Anita Hill, CSIRO, Melbourne, Australia

Overall research goals: The research objectives are to prepare new polymer-based materials and explore their gas separation properties, increase understanding of fundamental transport phenomena in polymers and polymer-based composites, and explore new materials design strategies to molecularly tailor materials with interesting gas separation properties. The research has focused on fundamental materials science related to CO_2 separations.

Significant achievements in 2006-2008: Within a polymer film, free-volume elements such as pores and channels typically have a wide range of sizes and topologies. This broad range of free-volume element sizes compromises a polymer's ability to perform molecular separations. During the past year, we discovered a new process to prepare polymers of controlled free volume distribution, so that we can prepare polymer films with narrow free volume element distributions and free volume element sizes appropriate for gas separations. This new process leads to molecular transport and separation performance that surpasses the limits of conventional polymers. For example, one member of this family of polybenzoxazoles has CO_2 permeability of approximately 1600 Barrer and a CO_2/CH_4 selectivity of approximately 45 under mixed gas conditions. The unusual microstructure in these materials can be systematically tailored by thermally driven polymer segment rearrangement. Free-volume topologies can be tailored by controlling the degree of rearrangement, flexibility of the original chain, and inclusion of small templating molecules. We have probed the free volume distribution in these materials using positron annihilation lifetime spectroscopy and small angle X-ray scattering. Many fundamental questions remain regarding the details of polymer molecule rearrangment during the thermal conversion process that leads to the formation of high free volume, highly permeable and highly selective structures, and our future efforts will focus on better understanding the linkage between the molecular structure of these materials and their transport properties.

The vast majority of literature data on gas solubility, diffusivity, and permeability in polymers is based on single gas measurements (i.e., measuring the properties of one gas at a time in polymers). However, all separations applications inherently involve mixtures of gases dissolving and diffusing through polymers. Therefore, we have been studying the solubility, diffusivity and permeability of gas mixtures in polymers of interest for separation applications. In solubility, we have observed synergistic effects (where the presence of one gas dissolved in a polymer enhances the solubility of a second gas) as well as antagonistic effects (where the presence of one gas markedly decreases the solubility of a second gas). These effects can be modeled, using available solution thermodynamic models, and our studies are providing some of the first tests and validations of such models. As might be expected, as gas solubility in polymers changes due to such mixture effects, there are also corresponding changes in mixture diffusion coefficients, and both the solubility and diffusivity effects bear upon the observed gas permeability in mixtures. Our initial studies have focused on polymers for removal of higher hydrocarbons from natural gas, and we use n-butane/methane mixtures as a model system for this separation. In poly(dimethyl siloxane) (PDMS), a rubbery polymer, we observe a 30% increase in methane solubility in the polymer in the presence of n-butane. This effect can be quantitatively correlated using the Krichevsky model, which has been applied to polymer systems for the first time in our work. In contrast, in a glassy polymer, poly(1-trimethylsilyl-1-propyne), the competition for nonequilibrium excess volume results in a decrease in methane solubility by a factor of approximately 6 in the presence of n-butane. This effect can be described using the dual mode sorption model. Further studies are needed to test and extend models of diffusion of gas mixtures in polymers.

Science objectives for 2008-2009(style=Stand alone text heading):

- Pursue further studies of mixed gas sorption and permeation in polar polyethers suitable for CO_2 separations in order to expand our fundamental knowledge of mixture sorption and diffusion properties of polymers.
- Pursue more in-depth studies of thermally rearranged polymers to develop a fundamental understanding of the molecular basis for their high permeability and high selectivity.
- Complete fundamental structure/property studies in crosslinked rubbery polymers that are of interest for acid gas separations.

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Zeolitic Imidazolate Frameworks and their Applications to Clean Energy

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Overall research goals: The research objectives are to develop a high-throughput protocol to the point of synthetic utility in the chemistry of zeolitic imidazolate frameworks (ZIFs); and thereby providing opportunities for addressing important technological problems such as the selective carbon dioxide capture.

Significant achievements in 2006-2008: Zeolitic imidazolate frameworks (ZIFs) are a new class of porous crystalline materials with structures based on zeolite-like tetrahedral networks in which transition metals (Zn, Co) replace T atoms (e.g. Si, Al, P) and imidazolate linkers replace oxygen bridges. A striking feature of ZIF chemistry is that link-link interactions rather than structure directing agents (SDAs), commonly used for zeolites, play a determining role in the synthesis of a given structure.

A high-throughput protocol was developed for the chemistry of ZIFs. The strategy of systematically varying linker substituents has led to many ZIF materials of known and predicted zeolite topologies and that are of exceptional chemical and thermal stability. Twenty five different ZIF crystals were synthesized from only 9600 micro-reactions of either zinc (II)/cobalt (II) and imidazolate/imidazolate-type linkers. All the ZIF structures have tetrahedral frameworks: 10 have two different links (hetero-links), 16 are new compositions and structures, and 5 have topologies heretofore unobserved in zeolite science. Members of a selection of these ZIFs (termed ZIF-68, 69 and 70) have high thermal stability (up to 390 °C) and chemical stability in refluxing organic and aqueous media. Their frameworks have high porosity (surface area up to 1970 meters squared per gram) and they exhibit unusual selectivity for carbon dioxide capture from CO_2/CO mixtures and extraordinary capacity for storing carbon dioxide (one liter of ZIF-69 can hold 83 liters of carbon dioxide at 273 Kelvin under ambient pressure).

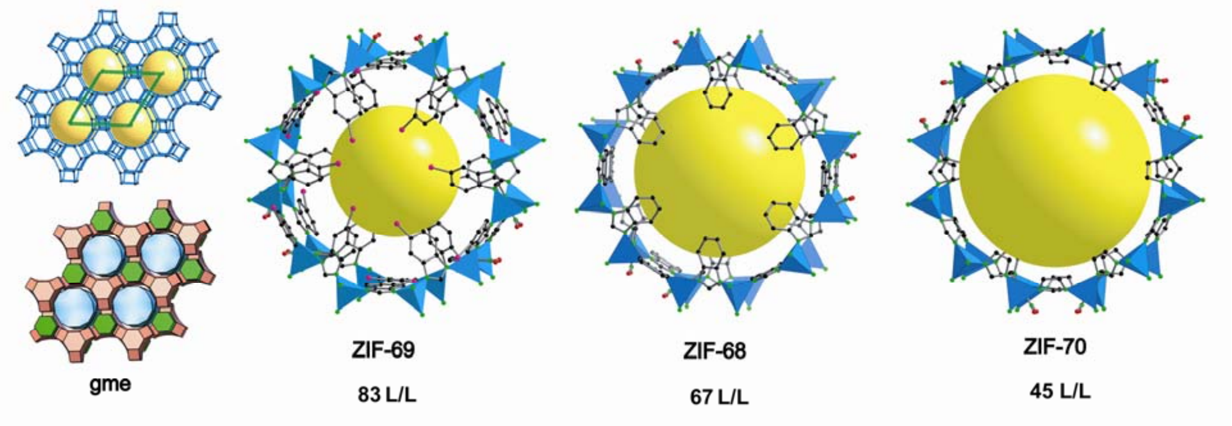

Figure 1. Three ZIF crystals (ZIF-68, ZIF-69 and ZIF-70). First row has the nets (blue line and black dot drawings) shown stacked on top of the tiles representing the subdivision of space (variously colored polyhedral shapes) in the net followed by the crystal structures of ZIFs corresponding to each of the nets. The largest cage in each ZIF is shown with ZnN4 tetrahedra in blue. The yellow ball is placed in the structure for clarity and to indicate space, in the cage. H atoms have been omitted (IM and IM-type links are shown as stick and ball: C, black; N, green; O, red; Cl, pink). The topology and the amount of CO_2 uptake by each of these ZIFs have also been specified.

Science objectives for 2008-2009:

- The high throughput synthetic protocol will be used to discover new ZIFs and MOFs. This will be complemented by theoretical calculations and structural studies of the same complexes with X-ray single crystal diffraction.
- Experiments will continue to measure the gas separation properties of ZIFs for methane (CH_4) form carbon dioxide (CO_2) for natural gas separation.

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Molecular Insights from Polarization-Dependent Nonlinear Optical Measurements

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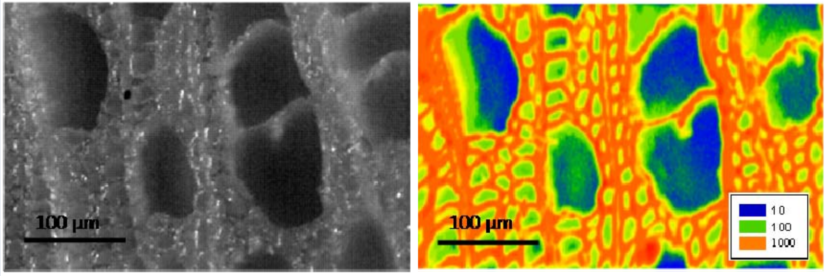
The increasing availability of turnkey ultrafast laser sources has ushered a new era in nonlinear optics, enabling more detailed analysis of surface films and the rapid expansion of nonlinear optical microscopy. The coherence of nonlinear optical processes provides rich information within the polarization dependence of the measurements, directly linked to local structure and orientation. As just one example, surface second harmonic generation has been shown to be ~10 orders of magnitude more sensitive to chirality than conventional absorbance circular dichroism. The goals of our research program have been centered on the development of new tools for acquiring and interpreting precise polarization-dependent nonlinear optical (NLO) measurements emphasizing the role of chirality. One outcome of these studies was the experimental confirmation of a predictive model for relating the macroscopic chiral response back to molecular structure and orientation.

More recently, we have shifted our focus to the development of new applications designed to take advantage of NLO polarization effects and chirality. Targeted applications include combining detailed NLO polarization analysis with molecular modeling to quantify structural changes induced in oriented biopolymer assemblies with an initial focus on cellulose, fundamental studies into surface and bulk nucleation of chiral molecular crystals, the sensitive detection of defects in chiral crystals, and early detection of protein crystallization.



Bright field (left) and SHG (right) images of curly aspen, microtomed across the grain (in collaboration with Richard Meilan, Purdue University).

Science objectives:

- Perform fundamental studies of structural changes within cellulose upon pretreatment and enzymatic degradation to assist in the development and refinement of biofuels processing derived from cellusosic feedstocks (collaborators: Michael Ladisch and Nathan Mosier, Purdue University).
- Develop new beam-scanning approaches for confocal microscopy optimized for nonlinear optical and multi-photon imaging.
- Develop instrumentation for two-photon absorption microscopy targeting *in situ* protein secondary structure determination.
- Perform fundamental studies into crystal nucleation in solution and at solid/liquid interfaces detected by SHG microscopy.

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Ultrafast Imaging of Photosynthetic Solar Energy Flow

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Overall research goals: The goal of this program is to image solar energy flow both at the molecular and nanometer scales in arrays of light-harvesting proteins in natural photosynthetic membranes, and in laboratory-produced 2D and 3D crystalline arrays of isolated photosynthetic proteins. Ultrafast transient laser spectroscopy is combined with nanophotonics techniques for the control and imaging of light at the nanometer scale. This work is directed at resolving the design principles that underlie Nature's remarkable hierarchical architectures for solar energy conversion, and in establishing principles for the design of molecular-based biomimetic systems.

Significant achievements in 2007-2008: During the start-up period of this project, work was directed at resolving ultrafast solar energy pathways at both the molecular and nanometer scales.

Imaging at the Molecular Scale. We applied 150 femtosecond time-resolved transient absorbance spectroscopy to study the primary electron transfer processes in single reaction center crystals from *Rhodobacter sphaeroides*. These are the first ultrafast studies on crystallographically characterized reaction center microcrystals. Reaction center crystals were grown with and without the carotenoid cofactor, and in three different crystallographic space groups. Ultrafast transient crystal spectra were found to exhibit strong polarization dependencies that varied with the crystalline space group, and differed markedly from transient spectra measured for reactions centers in solution. Polarized ground-state and transient excited-state spectra were correlated with cofactor transition moment projections calculated from x-ray coordinates. This analysis demonstrated that polarized excitation aligned along different crystal axes offers the unique opportunity to selectively excite otherwise degenerate optical transitions of individual cofactors within the reaction center. This relieves a major stumbling block that has prevented resolution of the function of individual cofactors within individual photosynthetic proteins. For example, we found that markedly different excited-state reaction pathways are initiated in reaction centers depending upon whether polarized excitation was aligned along the Q_y band of the bacteriochlorophyll, termed B_L that bridges the gap between the bacteriochlorophyll dimer, P, and the primary electron acceptor bacteriopheophytin, H_L, or aligned

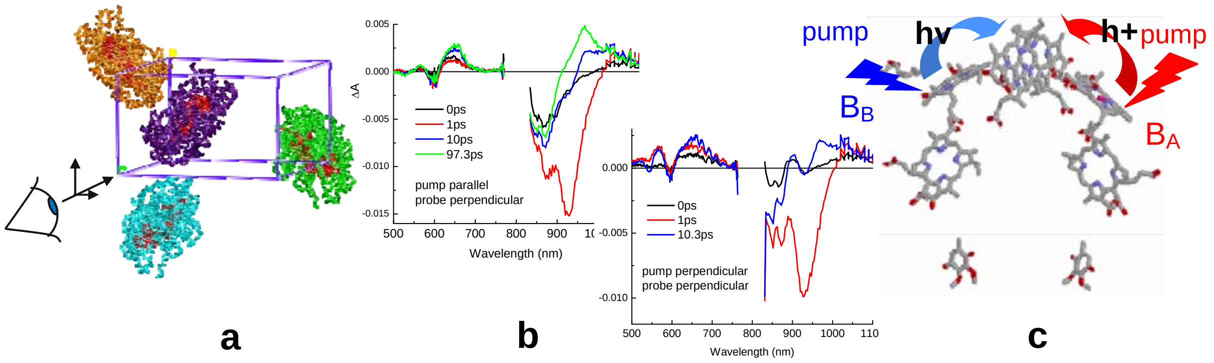

Figure 1. Ultrafast transient absorption measurements in reaction center single crystals. (a) Reaction center orientation in the $P2_12_12_1$ crystals; (b) transient spectra using parallel and perpendicular 810 nm pump orientations, fixed perpendicular probe orientation; (c) cofactor specific excited-state pathways.

along the Q_y transition of the bacteriochlorophyll, B_M, that bridges the gap between P and inactive bacteriopheophytin, H_M. Excitation of B_L was found to lead to the normal charge separation between P and H_L while excitation of B_M and possibly the higher exciton state of P was found to produce a different set of transient photochemistry that included energy transfer to P and charge separation along the normally inactive B-branch. Furthermore, electron transfer from P to the acceptor H_L was found to be slower in crystals than solution, with reaction times varying in the range 7-10ps in different crystals compared to the 5 ps reaction time for quinone-reduced reaction centers in solution. These are the first ultrafast studies in reaction center microcrystals, and provide the opportunity to make direct, quantitative correlation between photosynthetic function and reaction center atomic structure.

Imaging at the Nanometer Scale. Atomic force microscopy (AFM) and initial far-field confocal optical characterization were carried out on intact photosynthetic membranes from photosynthetic bacteria (*Blastochloris viridis* and *R. sphaeroides*) that contained reaction centers and only one of the two bacterial light-harvesting complexes, and on 2D arrays of isolated 22 nm diameter, disk-shape trimeric Photosystem I complexes isolated from the cyanobacterium *S. leopoliensis.* AFM showed that the *R. sphaeroides* chromatophore membrane spheres absorbed to mica surfaces from solution, and formed flattened double membrane layer thick discs composed of tightly packed regular arrays of reaction centers uniformly surrounded by circular light-harvesting complexes. Tightly packed PSI 2D arrays were made by drying a thick film on mica and washing off loosely bound complexes. AFM showed the resulting PSI array to have a stepped topography composed of molecular stacks with heights ranging from 1 to 3 complexes. Fluorescence spectra showed highly structured emission. Both the *R. sphaeroides* membrane disks and the PSI 2D arrays offer the opportunity to spatially image light energy transfer through photosynthetic architectures on the nanometer scale.

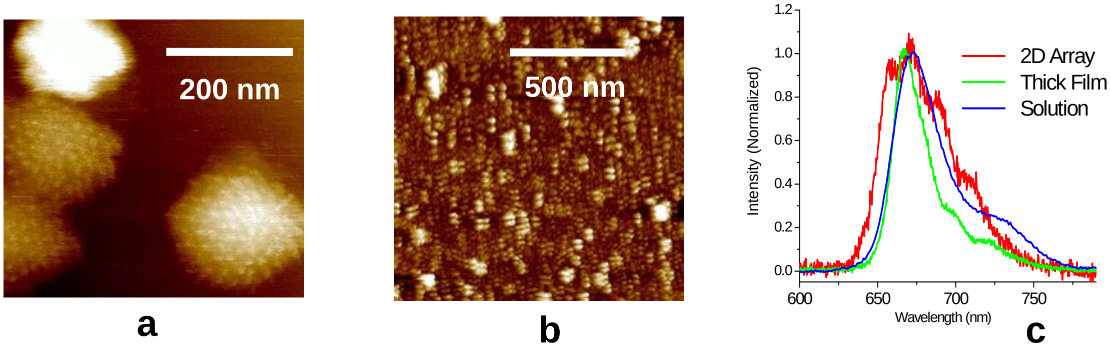

Figure 2. AFM images of natural bacterial photosynthetic chromatorphore membranes (a) and of a monolayer film of isolated cyanobacteria PSI complexes. Confocal microscope measurements of fluorescence from PSI in multilayer and monolayer films and solution (c).

Science objectives for 2008-2009:

- Correlate energy and electron transfer pathways to photosynthetic protein atomic structures by measuring ground and ultrafast excited-state optical absorption analyses of single 3D crystals of reaction center and reaction center-light harvesting complexes.
- Spatially resolved light energy transfer paths in natural photosynthetic membranes and artificial 2D arrays of isolated photosynthetic proteins using near-field scanning optical microscopy (NSOM) using spatially-localized, metal nanoparticle, plasmon excitation.
- Develop ultrafast, time-resolved NSOM techniques for combined temporal and spatial resolution of solar energy flow through natural photosynthetic membranes and artificial 2D arrays of isolated photosynthetic proteins.

Chemical Imaging with Cluster Ion Beams and Lasers

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Overall research goals: The research objectives are to evaluate the efficacy of using laser-based and synchrotron-based photoionization schemes for soft ionization of molecules sputtered from surfaces with a focused C_{60}^{+} primary ion beam, and to utilize these ions for submicron mass spectrometry-based chemical imaging experiments. This new instrumentation is to be utilized in a number of studies aimed at determining the chemical composition of aerosol particles associated with the environment, and will emphasize the study of single biological cells to provide insight into the mechanism of how algae produce biofuels.

Significant achievements in 2007-2008: We have been quite surprised to find that mid-infrared fs laser pulses dramatically reduce the amount of photofragmentation typically observed using competing photoionization schemes, thereby increasing the overall sensitivity for detecting sputtered neutral molecules. To achieve these results, an ultrafast optical parametric amplifier (TOPAS) was successfully integrated into an existing fs laser system to produce mid-IR fs laser pulses within a wavelength range of 1150-2650 nm (Figure 1). We are proposing that the reduced fragmentation and increased sensitivity are attributed to the onset of strong field ionization of the sputtered molecules as opposed to multiphoton absorption at lower wavelengths. Preliminary data of a quite spectacular nature suggest that photofragmentation may be further reduced with further increases in wavelength (Figure 1, right panel). These results promise to resolve a longstanding sensitivity issue pursued by many groups over the last 15 years.

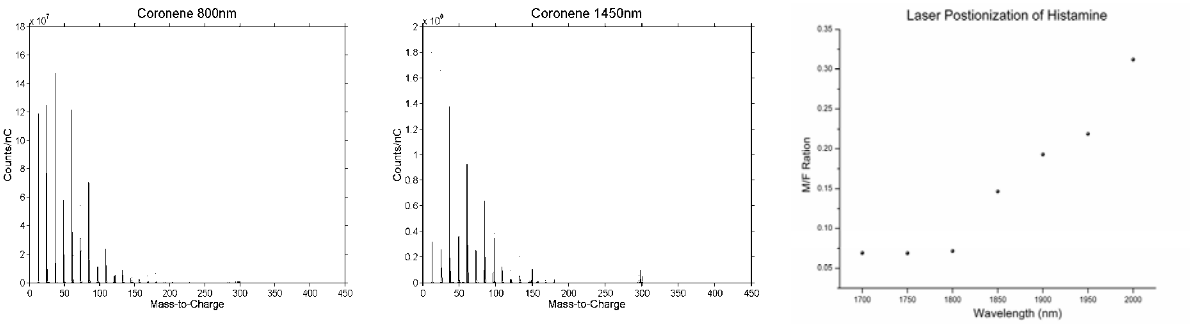

Figure 1 Spectrum of coronene taken with an 800 nm fs source (left). Typical coronene spectrum taken with a TOPAS source at 1450 nm (middle). Wavelength study of histamine molecules showing an increase in molecular ion to fragment ion ratio with respect to increased wavelength (right).

As a consequence, the TOPAS mid-IR system, in combination with the use of the C_{60} probe, has proven to be a powerful tool for pushing imaging mass spectrometry to much greater capabilities. The first high resolution laser post-ionization molecular ion images were taken of a patterned vapor deposited film of adenine (Figure 2). Due to reduced fragmentation, chemical images mapped for the adenine molecular ion were obtained with enough contrast to easily resolve sub-µm-sized features in the film. Furthermore, the first laser post-ionization depth profiles of a molecular species were obtained using the TOPAS system (Figure 2, right panel). When compared with SIMS depth

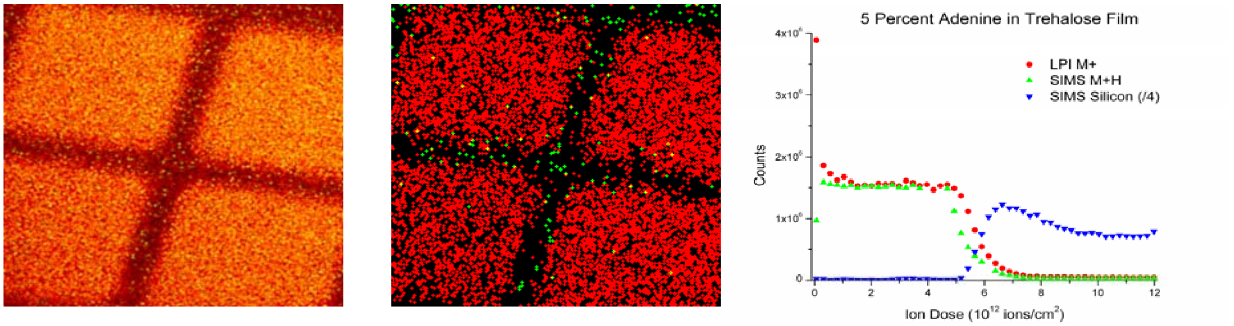

Figure 2. (left) Total laser-induced ion image taken over a 200x200 μm^2 field of view. (middle) Mass selected image; adenine (m/z 135) in red and silicon (m/z 28) in green. (right) Molecular depth profile of 5 percent adenine in a trehalose film; laser-induced in red, SIMS in green, substrate in blue.

profiles of the same sample, the laser post-ionization depth profiles allow one to investigate the influence of ionization effects at both the surface and the interface regions of the profiles.

Science objectives for 2008-2009:

- Investigate photofragmentation dependence of biomolecules on molecular properties, wavelength, and peak power with mid-infrared femtosecond laser pulses.

- Implement new laser technology into providing 3-dimensional chemical images of bioparticles.

- Begin high resolution chemical imaging experiments on environmental particulates and on single cell associated with organic molecule producing algae.

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FEMTOSECOND KERR-GATED FLUORESCENCE MICROSCOPY

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Single-molecule (SM) and single nanoparticle spectroscopy provides insights into hidden inhomogenieties and complex distributions that are not discernible in ensemble measurements yet are often crucial in determining the overall behavior of the system of interest. Among the various techniques, time-resolved single-molecule microscopy is especially powerful as it allows one to probe the spatial, temporal and spectral inhomogeneieties. At present, its most common implementation, the scanning confocal time correlated single photon counting (TCSPC) microscopy is limited to monitoring one object at a time with maximum resolution of 20 ps. In wide-field epifluorescence mode the temporal resolution is achieved by the use of intensified CCD cameras which currently limited to 80 ps. Advanced scanning streak cameras can produce 2D images with time resolution of 20 ps, at a cost that is prohibitive to most individual laboratories. In order to bridge the time domains accessible to ultrafast pump-probe techniques in the bulk and to single molecule fluorescence microscopy, we have constructed a Kerr-gated microscope capable of collecting nearly diffraction limited 2D fluorescence images of sensitized films, nanowires and molecules with 100 fs time resolution, *i.e.* at least 200-times better than the current limit.

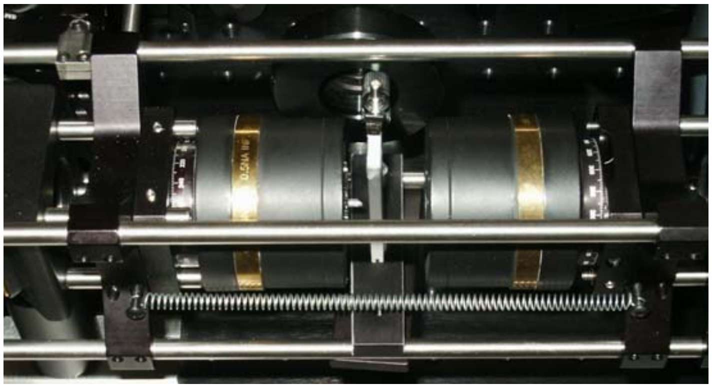

Figure 1. The Kerr-gate assembly consisting of Cassegrainian objectives, Kerr medium, polarizers and the injection mirror.

Kerr gating relies on transient birefringence induced by a light pulse in a nonlinear medium placed between crossed polarizers. The collected emission light passes through the Kerr shutter only when the gating pulse is incident upon the Kerr medium. The transmitted light is detected by a CCD camera, resulting in nearly single photon sensitivity. By delaying the gating pulse with respect to the excitation pulse in the same fashion as in pump-probe experiments, the time evolution of the imaged object, *I(x,y;t)*, can be followed and the corresponding emission decays can be assembled. The microscope can be also configured in a spectrally dispersed mode

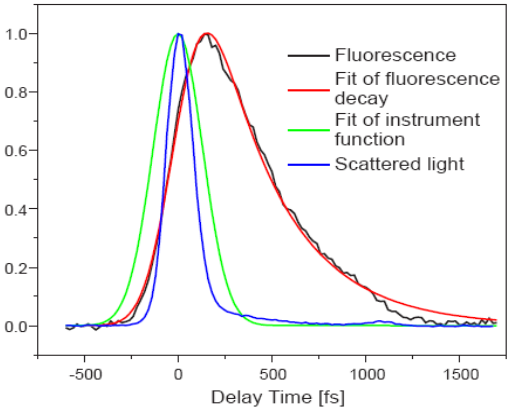

Figure 2. Benchmark time resolved fluorescence of β-carotene, τ = 160 fs.

and function as an ultrafast fluorescence spectrometer. Examples of preliminary results obtained both in the spectroscopy and imaging modes are shown in Fig. 2, 3 and 4.

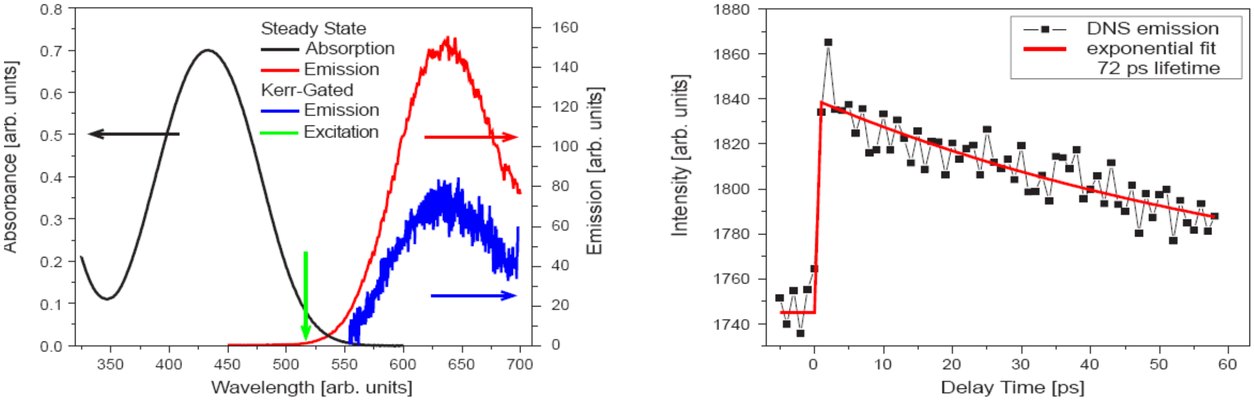

Figure 3. A Kerr-gated spectrum and the fluorescence decay of the 4-dimethylamino-4'-nitrostilbene (DNS) in tetrahydrofuran.

The current FWHM time resolution obtained with 20 fs excitation and 60 fs gate pulses while employing fused silica as the Kerr medium is 110 fs. The 'on-off' contrast of the Kerr gate is sufficient to perform measurements on fluorophores with emission lifetimes as long as 100 ps. Transmittances of 5%, 47% and 54% were obtained with quartz, benzene and benzene saturated with naphthalene as the respective Kerr media. The highest obtained transmittance corresponds to a 95^0 phase shift between the slow and fast components of the polarization.

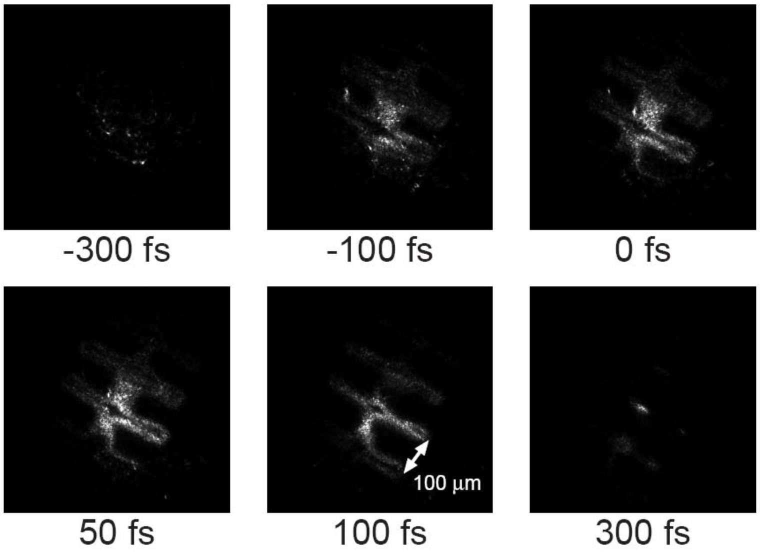

Figure 4. Time resolved reflection image of an etched glass surface. The instrumental response function is 130 fs.

Femtosecond Kerr-gated Wide-field Fluorescence Microscopy, L. Gundlach, P. Piotrowiak, *Opt. Lett.. 2008* submitted*.*

Novel Setup for Time-resolved Fluorescence Microscopy, L. Gundlach, P. Piotrowiak, *Proc. SPIE 6643*, 66430E1-E7, 2007**.**

Inhomogeneity of Electron Injection Rates in Dye-Sensitized TiO_2: Comparison of the Mesoporous Film and Single Nanoparticle Behavior Bell, T. D. M.; Pagba, C.; Myahkostupov, M.; Hofkens, J.; Piotrowiak, P. *J. Phys. Chem. B.*; 2006; 110, 25314-25321.

Small-Angle and High-Energy X-ray Scattering Studies in Catalysis and Gas Storage

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In the study of catalytic reactions, small-angle X-ray scattering (SAXS) for high surface area catalytic materials and for flat substrates grazing incidence SAXS (GISAXS) can provide both *ex-situ* and *in-situ* information on cluster size, shape and inter-particle distance (APS beamline 12-ID). The ability to compare the two classes of materials validates the formation of identical structures on the two support morphologies. GISAXS can also give depth profile information, and the aspect ratio (height/diameter) of a cluster can be calculated from the GISAXS data to obtain the interfacial energy. GISAXS is ideal for *in-situ* studies since it is very sensitive to surface species and there is less parasitic scattering resulting from the substrate compared to a conventional direct-transmission SAXS experiment. GISAXS has been used to study the thermal stability and reactivity of Pt, Au and Ag clusters deposited on a variety of surfaces with insightful results.[1] One example is the partial oxidation of olefins to alkyl oxides where it has been found that the size and shape of catalytic size-selected nano particles is important. ASAXS refers to the extension of standard SAXS experiments in which the energy of the probing X-rays is tuned near the absorption edge of an element in the sample. This method overcomes the problem of separating the scattering of clusters from that of the support. For the first time anomalous GISAXS has been obtained on metal clusters on surfaces and has provided significant insight into the structure of very small metal clusters on surfaces.[2]

SAXS and high-energy wide angle scattering with pair distribution function (PDF) analysis is being used to better understand the fundamental changes in coal structure when pressurized with CO_2 and to model carbon sequestration. PDF provides atom-atom correlations out to at least 2 nm. SAXS has been used to study coal porosity. A large-scale molecular model for a high rank coal, Pocahontas, with and without CO_2-induced swelling has been developed and used to better understand the complex scattering data.

The PDF technique provides atom-atom correlations over distances that this molecular model should fairly represent (APS beamline 11-ID-B).[3] The PDF data have been obtained for all of the Argonne coals including the Pocahontas coal (APCS 5). The PDF calculated from the coal model and the results give a fit which is surprisingly good with both position of the peaks and the intensities. Small differences can be due to minerals, which are not present in the model. It is possible for coals with known mineral composition to include the major minerals in the calculated data. The PDF approach has been used to observe hydrogen in framework materials.[4]

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Fundamental Studies of the Inductively Coupled Plasma and Glow Discharge as Analytical Sources

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

Significant achievements in 2006-2008: *Developed a warning indicator and correction methodology for matrix interferences in Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES)*: The presence of matrix interferences, without the awareness and subsequent correction by an analyst, will lead to an analytical error. Therefore, it is crucial to have indictors that can successfully flag the presence of a matrix effect so immediate remedial work can be undertaken. Matrix effects in ICP–AES can be broadly divided into three categories: spectral interferences, sample-introduction-related and plasma-related. Although there are ways to flag the presence of each category of matrix interferences, there is currently no unified method to flag the presence of all three categories. Recently, we developed a novel and more universal methodology that can flag inaccuracy in the analytical results caused by the presence of interferences from any of the three major matrix-effect categories, in a real-time fashion during an analysis. This simple all-in-one indicator is based on the fact that plasma behavior and excitation conditions are heterogeneous along the ICP vertical axis. As a result, the relative magnitude and even the direction of the change in emission intensity caused by a matrix effect are not constant, but are functions of observation height in the plasma. Since the determined concentration of an analyte in a sample is proportional to the measured intensity, any change in matrix effects or system drift along the vertical profile will similarly shift the determined concentration, allowing the drift or interference to be detected. The theoretical basis of this novel matrix-effect indicator and its effectiveness has been evaluated. In the case that the analytical inaccuracies are caused by plasma-related matrix interferences, a novel on-line method has been developed to determine the spatial location in the plasma at which such interferences are eliminated (i.e., the so-called matrix-effect cross-over point) for accurate analytical measurements.

Characterization of a pulsed radiofrequency Glow Discharge (GD) for three-dimensional elemental surface imaging: There is a continuing growth in interest to employ GDs for elemental analysis. Unlike the ICP, the GD is ordinarily employed to analyze solid samples directly. Moreover, it can do so in a depth-resolved fashion, because sample layers are eroded sequentially by means of cathodic sputtering. Previously, we have focused on characterizing the effect of cell pressure and the electrical characteristics of the glow-discharge pulse on the temporal behavior of all fundamental plasma parameters (electron number density, electron temperature, and gas-kinetic temperature). Here, we emphasize the development and optimization of a GD for three-dimensional surface imaging. We found that two-dimensional spatial images of the glow discharge above a sample surface can yield lateral resolution if the power to the GD is pulsed. When a GD is powered in a pulsed fashion, the erosion rate of a sample surface is reduced, so atomic layers can be examined with even greater depth resolution. Further, sample heating is reduced. Ranges of gas flows, pulse frequencies, pulse potentials, pulse widths, and pressures were explored to determine their effect on spatial resolution and were related to atom transport in the glow discharge cell. The obtainable resolution under optimized discharge conditions and with the use of gated detection was found to be as good as 100 µm. This work has also been extended to the analysis of non-conductive samples. For such samples, it is necessary to use a radio-frequency (RF) powered discharge rather than one operated at DC. Our first application of this new approach was to the examination of blots such as those produced in the two-dimensional chromatographic separation of proteins on gels. In this first example, proteins separated by such a gel and recorded on a blotting membrane were stained with both silver and colloidal gold and the resulting spots imaged by a pulsed RFGD-imaging system. Spatial resolution was found to be more than adequate for imaging such separated proteins. Several alternative sample types were also examined, including photographic film and fiberglass substrates.

Characterization of an electrolyte–solution glow discharge: We also investigated a new type of GD in which the cathode is not a solid sample but rather an electrolyte-containing solution. This so-called ELCAD (ELectrolyte as CAthode Discharge) has been described and applied by others, but has not before been fundamentally characterized. Initially, we investigated the emission intensities and vertical distributions of analytes and background species in this discharge, and compared them to the vertical distribution of ion excitation and rotational temperatures. Here, the study was expanded to emphasize the role of ion and electron populations in the ELCAD. Stark broadening of the hydrogen-beta line was utilized to measure spatially resolved electron number densities (n_e), which were found to be on the order of 10^{14} cm^{-3}. These values of n_e are much higher than those in the reduced-pressure conventional GD and approach those found in the ICP. A number of consequences of these fundamental findings apply directly to practical analyses with the ELCAD and were investigated experimentally. First, the n_e was found to be relatively insensitive to current applied to the ELCAD, a behavior that is different than in low-pressure GDs. Second, the relatively high n_e found in the ELCAD suggests that calibration curves obtained with it should not be subject to non-linearity from concentration-dependent degrees of ionization such as are commonly found in measurements with chemical flames. Also, the higher n_e reduces interference problems caused by easily ionized elements (e.g., the alkali metals) as in chemical flames. Third, because the ELCAD possesses a lower thermal temperature than the ICP, it is not surprising that it exhibits a greater level of interelement interference. Indeed, vaporization-based interferences seem to be about the same in the ELCAD as are commonly found in chemical flame atomic spectrometry. Fortunately, commonly used techniques to reduce interferences in flame atomic spectrometry (e.g., La as analyte releasing reagent) apply equally well to ELCAD. Lastly, some analytical figures of merit were evaluated. For example, when coupled with flow injection, the ELCAD can analyze 25-μL sample volumes at a rate of 1000 samples/hour with detection limits ranging from 5 pg (0.2 ppb) for Li to 6 ng (270 ppb) for Hg.

Science objectives for 2008-2009:

- Excitation and ionization processes and interference effects in the ICP will continue to be investigated. Emphases will be on applicability of the developed matrix-effect flagging indicator and correction methodology on ICPs with axial viewing mode. Also, the hypothesis that matrix effects in the normal analytical zone of the plasma are due to Penning ionization will be studied by radial mapping of the excited-argon population and analyte excited states.
- The effect of adding small amounts of foreign gases (e.g., H_2, N_2, etc.) on the GD fundamental (i.e., temperature and n_e), emission (e.g., excitation via charge transfer mechanism), sputtering characteristics and the associated effect on obtained spatial resolution will be studied.

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Vibrational Spectroscopy of Chromatographic Interfaces

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Overall research goals: The overarching research objective of this work is to better understand the chemistry of chromatographically-relevant interfaces at the molecular level. Specific efforts are directed along three independent lines of inquiry: 1) further elucidation of the mechanistic details of analyte retention in reversed-phase liquid chromatography (RPLC) through characterization of alkylsilane stationary phase conformational order; 2) determination of mobile phase interfacial structure and composition through the analysis of residual mobile phase films formed by forced dewetting; and 3) analysis of the size dependence of chromatographically-relevant surface modification chemistry within the pores of porous silica support materials by systematic investigation of ordered arrays of silica nanoparticles of differing sizes.

Significant achievements in 2006-2008: The analysis of high surface coverage docosylsilane (C22) stationary phases by Raman spectroscopy has shown for the first time a correlation between stationary phase conformational order, and hence, solvation of the stationary phase, and either the Gibbs free energy change for infinite dilution of these solvents in hexadecane (ΔG_{HD}^{o}) or the solvent parameter log K_{ow}. Several common polar (water, methanol, acetonitrile) and nonpolar (benzene, toluene, chloroform) solvents confer a state of conformational order on the stationary phase that correlates with ΔG_{HD}^{o}, while conformational order in a series of aromatic solvents is linearly dependent on log K_{ow}. In general, polar solvents actually increase slightly the conformational order of these C22 stationary phases, while nonpolar solvents decrease conformational order. This behavior suggests solvation by partitioning of nonpolar solvents into the alkyl chains of the stationary phase.

A novel method for spectroscopic characterization of interfacial mobile phase solvent structure based on analysis of residual films of nm-scale thickness formed by forced dewetting has been developed and used to characterize the structure of water at silica surfaces as a function of pH. A layered structure comprised of an ultrathin silica layer supported on a reflective gold substrate through a gold oxide layer has been developed to allow IR reflectance-absorbance spectroscopy (IRRAS) to be used to probe silica surface chemistry. Comparison of spectra from the residual films in the v(OH) region with the IRRAS spectrum simulated for isotropic water indicates that the interfacial water structure differs considerably from that of isotropic bulk water and that the structure is dependent on solution pH. Populations of water that are either in an ice-like environment or are weakly hydrogen-bonded and/or monomeric are observed in ~ 5-nm thick residual water layers at all pH values, with relative amounts of these components dependent on pH. Initial studies of mobile phase solvent structure in residual films of methanol/water mixtures on octadecylsilane-modified silica surfaces also indicate unique interfacial structure and composition compared to the bulk liquid.

Methods to create ordered arrays of silica nanoparticles (NPs) with diameters < 100 nm have been explored, and quasi-ordered arrays several layers thick have been fabricated from NPs of 38, 50 and 80 nm dia. Challenges that have prevented previous fabrication of *ordered* arrays of this size regime NP include adequate control of NP size dispersity and mitigating capillary forces that lead to random, not ordered, aggregation of particles. SEM images show close-packed, relatively uniform packing of sub 100-nm NPs that are monodisperse to within <12%; FFT analysis of the images shows evidence for hexagonal packed structures, albeit with relatively short coherence lengths. Figure 1 shows a sample SEM and its FFT for an array of 50 nm NPs. Spectroscopic studies on surface modification within pores of these NP arrays are underway.

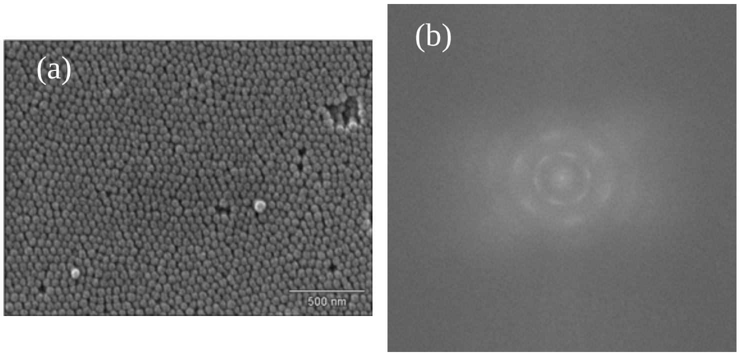

Figure 1. (a) SEM of array of 50 (± 6) nm diameter silica nanoparticles assembled onto silicon substrate with thermally-grown silica overlayer; (b) FFT of SEM image .

Science objectives for 2008-2009:

- Complete Raman spectroscopy studies of horizontally-polymerized alkylsilane stationary phases prepared with varying ratios of C18 and C1 in the presence of common solvents.
- Complete IRRAS studies of residual films of the mobile phase solvent systems of methanol/water, acetonitrile/water, methanol/tetrahdryofuran/water, and acetonitrile/tetrahydrofuran/water formed by forced dewetting on octadecylsilane stationary phases prepared by traditional routes and by horizontal polymerization with .
- Complete ATR-FTIR and micro-Raman spectroscopic studies on pore size dependence of alkylsilane surface modification for alkylsilanes of differing chain length using ordered arrays of sub-100-nm silica NPs.

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6. Z. Liao, J.E. Pemberton, *Anal. Chem.* **2008**, in press. “Structure-Function Relationships in High-Density Docosylsilane Stationary Phases by Raman Spectroscopy and Comparison to Octadecylsilane Stationary Phases: Effects of Common Solvents.”
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8. Y. Huang, J.E. Pemberton, *Chem. Mater.*, submitted. “The Self-Assembly of Sub-100 nm Silica Particles: A Comparison Study of Particles Made by the Modified Stöber and Reverse Micelle Methods.”
9. P. Macech, J.E. Pemberton, *J. Electroanal. Chem.*, submitted. “Passivation of Microelectrode Array Defects in Ultrathin Silica Films Immobilized on Gold Substrates.”
10. Z. Liao, J.E. Pemberton, *Anal. Chem.*, submitted. “Alkylsilane Stationary Phases with Controllable Surface Coverage using n-Alcohol Displaceable Surface Templates: Effects of Alcohol Chain Length.”
11. P. Macech, J.E. Pemberton, *Langmuir*, in preparation. “IRRAS of Residual Water Films Formed by Forced Dewetting on Silica as a Function of pH.”
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Abstract: DOE BES Chemical Science, Geosciences, and Biosciences Division workshop

Flickering semiconductor nanowires

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Over the last 10 years, there has been significant interest in understanding emission intermittency within colloidal quantum dots (QDs). This is a phenomenon whereby the emission of individual QDs turns "on" and "off" in a sequential manner under continuous laser illumination. Even more interestingly, such "blinking" has been observed in a diverse array of other systems such as fluorescent dye molecules, fluorescent proteins, light harvesting complexes, porous silicon, nanorods and more recently semiconductor nanowires (NWs). In fact, blinking appears to be a near universal phenomenon at the single molecule level. Apart from the existence of blinking, what has been even more surprising has been the existence of unusual, yet common, power law blinking kinetics in single molecule, quantum dot, nanorod and nanowire trajectories. The existence of such ubiquitous distributed kinetics would then suggest a universal explanation for single molecule emission intermittency.

Our current studies have focused on understanding the physical origin of emission flickering in solution grown semiconductor NWs. Recently we have found that one can spatially modulate the NW emission as well as its intensity using external electric fields. This has led us to speculate the role excess surface charges play in causing, not only apparent spectral diffusion, but also emission flickering. Direct single NW and NW bundle electrophoresis experiments have shown the existence (and number) of such surface charges. This has since led us to discover that one can deliberately control the NW emission through electrical biases when wires are placed directly onto a conductive substrate. The interest in these studies is then that colloidal quantum dots and nanorods are known to possess analogous surface charges. As a consequence, the lessons learned with NWs may have applicability towards addressing the broader problem of emission intermittency in other systems.

Nanoparticle-Enhanced Capillary Electrophoresis

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These research objectives aim to elucidate the mechanism of nanoparticle-assisted separations in capillary and microchip electrophoresis experiments by systematically varying both nanoparticle and separation attributes.

The inclusion of nanoparticles in capillary electrophoresis experiments have been shown to improve detection of analytes, facilitate the separation of nanoparticles themselves, and dramatically improve the resolution of target analytes. Despite these advances, surprisingly little research has been performed that correlates separation performance to nanoparticle attributes such as aspect ratio, composition, size, surface chemistry, and zeta potential. Our research advances have focused on three classes of experiments: (1) synthesis and characterization of monodisperse nanoparticles (gold and silica), (2) characterization and optimization of ligand exchange reactions to vary the surface chemistry on the nanomaterials, and (3) investigation of how these nanoparticles impact the capillary electrophoresis separation of three neurotransmitters, catechol, dopamine, and epinephrine.

In an effort to investigate the mechanism of nanoparticle-enhanced separations, a high degree of control over nanoparticle dimension is vital for thorough and consistent results. As a result, sspherical gold nanoparticles were investigated because they are straight-forward to synthesize and their surface chemistry is easy to modify. As shown in Figure 1 (left panel), we have achieved a high degree of control over the synthesis of gold nanoparticles (diameter = 12±1 nm).

When added to the sample matrix, nanoparticles that are in their native form (surface chemistry = citrate) do have an impact on the migration times and resolution of the targeted analytes using capillary electrophoresis and UV detection. It is important to note two things. First, this response is extremely small. The migration times of the analytes varying by only ±3 s for all nanoparticle concentrations studied. Second, in contrast to previously published work; these data indicate that nanoparticles ***both increased*** the mobility and resolution of the targeted analytes at high nanoparticle concentrations and ***decreased*** the mobility of the targeted analytes (observed previously) at low nanoparticle concentrations (Figure 1, center, right).

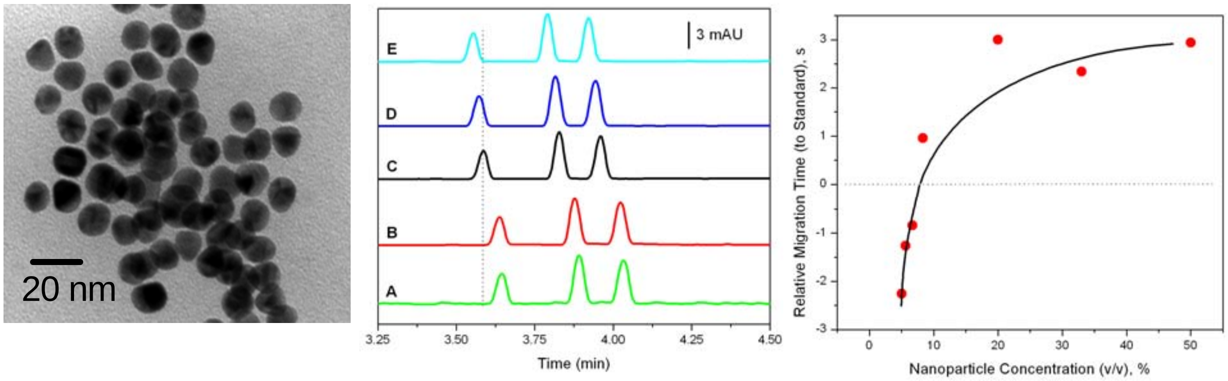

Figure 1. (Left) Transmission electron micrograph images of gold nanoparticles (12±1 nm diameters). (Center) Effects of varying nanoparticle concentration on the separation of a mixture of aromatic compounds. Electropherograms that demonstrate both decreased and increased mobility of target species. (A) 50%, (B) 33%, (C) 0%, (D) 6.7%, and (E) 5% (v/v) of gold nanoparticles in the sample matrix. The dotted line is included for a reference point. Separation voltage = 30 kV. Injection pressure = 0.5 psi for 5 s. Detection wavelength = 214 nm. (Right) Trends demonstrating the migration time of p-hydroxybenzoic acid both decreases at low nanoparticle concentrations and increases at high nanoparticle concentrations relative to its mobility in the absence of nanoparticles. The black is not a fit to the data, but is meant to guide the eye. The dotted line marks the location of the mobility when no nanoparticles are present.

A Fundamental Study of Transient Electrokinetic Effects within a Microfluidic Device incorporating a Nanoporous Membrane

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Overall research goals: The objective of this project is to establish a fundamental understanding of the effect of membrane ion-permselectivity on electrokinetic concentration enrichment in microfluidic membrane-based filtering units and to evaluate the performance of different membranes varying in their ion-permselectivity.

Significant achievements in 2006-2008: Membranes integrated within microfluidic systems have been shown to be useful for a number of analytical tasks, including: sample preparation, volume measurement, sample injection, and separation. On-chip concentration enrichment often is a crucial step in these applications, due to the limited number of analyte molecules present in the very small fluidic volumes. Through the use of experiments and computer simulations, we have studied how mass and charge transports are affected by the presence of nanoporous hydrogel membranes contained within microfluidic channels.

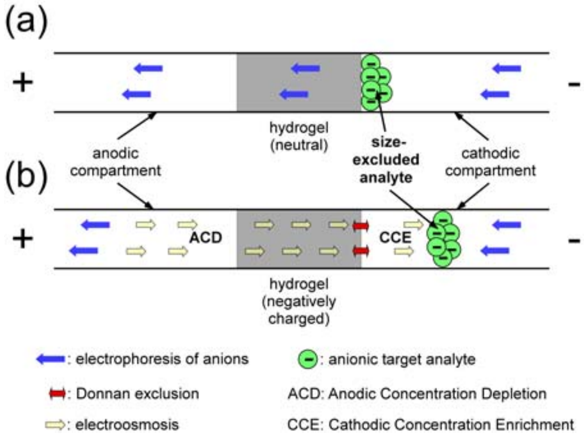

Figure 1.Concentration enrichment scheme with (a) neutral, and (b) anionic hydrogel membrane.

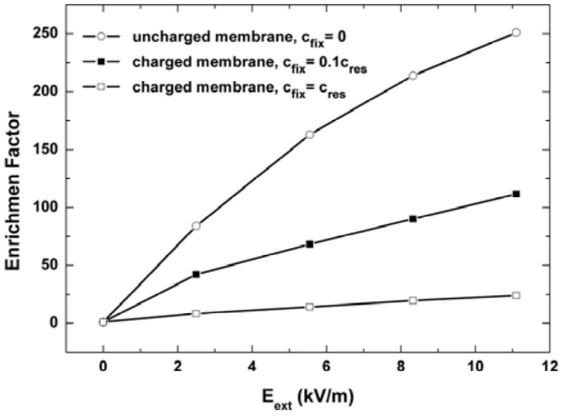

Figure 2. Steady-state enrichment factors as a function of the applied electrical field strength (E_{ext}) for uncharged ($c_{fix} = 0$), weakly charged ($c_{fix} = 0.1c_{res}$), and highly charged ($c_{fix} = c_{res}$) membranes.

Our approach is illustrated in Figure 1. The hydrogel membrane is fabricated within the fluidic channel using lithographic methods. The size of the membrane, as well as its net charge and average pore diameter, can be controlled, and hence it is possible to compare simulations and experiments directly. An uncharged membrane (Figure 1a) acts as a simple physical barrier to electrophoretic transport of charged analytes which are size-excluded from the membrane pores, resulting in concentration enrichment at the membrane-bulk solution interface. If the walls of the membrane nanopores bear fixed charges (Figure 1b), these matrices can be used for tailoring trans-membrane mass and charge transport through their ion-permselectivity. The presence of fixed charges on the internal and external surface of the membrane gives rise to a Donnan electrical potential at the macroscopic membrane boundaries which reflects counterion enrichment and co-ion exclusion by the charged membrane at electrochemical equilibrium. For instance, as an electrical field is applied to a negatively charged membrane the transport of electrical current is accomplished nearly exclusively by the counterions (cations). The transport number of the counterion (or the sum of the transport numbers of all counterionic species) is nearly unity, i.e., the fractional electrical current carried by the counterions within the membrane phase is much larger than the corresponding value within the bulk liquid phases. As a consequence, ion concentration gradients result at the membrane-solution interfaces: enriched and depleted concentration polarization (CP) zones form in the bulk, quiescent solutions adjacent to the cathodic and anodic interfaces of the cation-selective membrane, respectively. The efficiency of analyte concentration enrichment with a charged membrane then is strongly influenced by the actual intensity of CP. In addition, electroosmotic flow in the microfluidic system plays an important role in determining the location of the analyte enrichment zone. While studying the functionality of nanoporous membranes differing in their ion-permselectivity for analyte concentration enrichment (Figure 2), CP was identified as an undesired side effect with the anionic hydrogels: it reduces the local electrical field strength driving concentration enrichment of negatively charged analytes at/close to the cathodic hydrogel plug-microchannel solution interface, thus lowering the concentration enrichment efficiency. In principle, this effect can be compensated by applying (much) higher field strengths across a (highly) charged compared with a neutral membrane. However, the corresponding field strengths may limit device performance and scalability due to Joule heating and complex (electro)-hydrodynamic phenomena originating in the anodic depleted CP zone under nonequilibrium conditions.

Science objectives for 2008-2009:

- We are working towards simplifying the electrokinetic concentration enrichment technique for charged analytes by incorporating a thin (~100 nm thick) bipolar electrode within the microfluidic channel.
- We will establish the fundamentals of this concentration enrichment approach based on a single bipolar electrode with electrochemical experiments and computer simulations.
- Once the electrokinetic behavior of the system is characterized, we will begin optimizing the approach for efficient concentration enrichment and further integration into lab-on-a-chip analytical systems.

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Chemistry and Microphysics of Small Particles

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

Significant achievements in 2006-2008: This project proceeded along three parallel pathways: 1) development of SPLAT II; an ultra-sensitive, high-precision instrument for multidimensional characterization of individual aerosol particles in real-time; 2) study of the chemistry and microphysics of size-selected nanoparticles; 3) development and application of novel data analysis and visualization approaches.

With SPLAT II, our 2nd generation single particle mass spectrometer, we had established unparalleled detection sensitivity, precision, and temporal resolution. SPLAT II provides 2 orders of magnitude higher sensitivity to small particles and a factor of 10 increase in temporal resolution over the previous instrument. With SPLAT II we demonstrated significant improvements in mass spectral quality by the use of an IR laser for particle evaporation followed by a time-delayed UV ionization.

We developed a novel method for real-time identification of particle asphericity and applied it to a number of particle systems, including secondary organic aerosol (SOA) particles. These high precision measurements yielded the first determination of the shape and density of SOA particles formed by oxidation of α-pinene. This method was also used to study the properties of particles in metastable states, far from equilibrium.

Investigation of behavior of aspherical particles in different flow regimes yielded the first measurements of dynamic shape factors in the free molecular regime for model systems of agglomerates of spheres and a number of particle system of atmospheric importance. An extension of this work resulted in the development of a new method to identify particle asymmetry in real-time and the ability to separate particles on the basis of their shapes. In addition, morphologies of the several nanoparticles systems were probed in series of "depth-profiling" experiments.

These tools and methodology were successfully applied to simultaneously measure in real-time the size, composition, shape, fractal dimension, and hygroscopicity of individual particles, not only providing information on the multitude of individual particles properties, but addressing the critical question of how these properties relate to each other and their effect on particle chemical reactivity.

Simultaneous measurements of density, hygroscopicity, shape, and composition of size-selected particle coated with organic surfactants revealed complex behavior, which can not be modeled by commonly used approaches. On the basis of these observations we have developed a new empirical approach, which uses concentration dependent surfactant density.

To take full advantage of the vast amounts of detailed multi-dimensional data that SPLAT II produces in addition to our data mining and visualization software, SpectraMiner, we had developed a beta version of a program called ClusterSculptor. It uses a novel, expert-steered data classification approach to provide comprehensive and intuitive visual framework to aid scientists in data classification. In effect, it overcomes the limitation of statistics by offering the scientist the ability to insert his/hers scientific expert knowledge into the data classification.

Science objectives for 2008-2009:

- Conduct studies of the effect of surface active organic molecules on the reactive and non-reactive uptake by hygroscopic particles. Investigate effect of surfactant oxidation by OH and O_3 on properties and behavior of surfactant coated particles.
- Quantify the chemical and microphysical transformations of soot nanoaggregates as a result of their interaction with sulfuric acid, nitric acid, ozone, and water. Measure the impact of PAHs, unburned fuel components, and inorganic compounds, often co-produced with the soot, on these transformations.
- Investigate the effect of size, internal composition, shape and morphology on particle hygroscopicity, CCN and IN activity.
- Continue development and application of ClusterSculptor, expert-driven data classification.

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Electron Transfer, Proton Transfer, and Metal Ion Transfer in Gas-Phase Ion/Ion Reactions

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

Significant achievements in 2006-2008:

Ion/ion Electron Transfer. We have made significant progress in our systematic studies of the fundamental aspects associated with electron transfer ion/ion reactions. One important issue that we examined was the role of the nature of the cationic charge site in the electron transfer to multiply protonated polypeptides. Several competing channels are associated with reactions of this type, including proton transfer, electron transfer with prompt dissociation, and electron transfer without dissociation. For the species that fragment, there is a competition between a variety of dissociation channels. We examined a series of model cations to probe the role of arginine, lysine, histidine, and a fixed charge derivative on the partitioning of products among the competing reaction channels. This work was highly informative and showed that the nature of the charge site plays a very important role in determining the outcome of the ion/ion reaction. The results have important implications regarding the underlying mechanisms as well as practical application of this type of chemistry for structural characterization of polypeptides. We also have obtained extensive data for the role of net charge on the partitioning among the various channels. We anticipate that this work will also be an important contribution to the fundamental understanding of both electron transfer ion/ion reactions and electron capture dissociation. We have also examined deuterated and methylated polypeptides to address specific mechanistic questions and anticipate that these works will be submitted for publication in the upcoming budget period.

Metal Ion Insertion/Removal. We completed an extensive study on the competition between electron transfer and metal transfer in the ion/ion reactions of transition metal-containing cations and multiply deprotonated oligonucleotides. We found that the recombination energy of the cation plays a major role in determining the extent to which metal transfer and electron transfer compete. The results are consistent with a Landau-Zener based model that we have developed for these kinds of reactions. What we have learned will be particularly useful in selecting reagent cations to effect chemistries that we desire. For example, both the oligonucleotide radical anions produced via electron transfer and the metal-containing oligonucleotide anions produced via metal ion transfer show fragmentation behaviors that are distinct both from one another and from the deprotonated species. This chemistry, therefore, provides new options for the structural characterization of this class of oligomers. We are currently examining the reactions of the same suite of reagents with multiply deprotonated peptides. The initial results indicate very similar trends. We are also following our studies with gold cationized species, with particular emphasis on sulfur-containing polymeric ions.

Charge Inversion. We recently submitted a paper describing our work to date in examining the characteristics of reagent ions for maximizing the net charge of an analyte ion subjected to an ion/ion charge inversion reaction. We are currently drafting a manuscript on the tendency for some analyte species to form adducts with charge inversion reagents. We hope to have that work submitted by summer. We have extended the work to examine the role of reagent ion identity on the charge inversion efficiency. This has been a more difficult value to measure but we have developed an approach that at least allows for a relative measure of efficiency so that reagent ions can be compared with one another. This is the kind of information we need to test our current models for charge inversion.

Science objectives for 2008-2009:

- We will complete the collection of data associated with the study of the charge-state dependent partitioning of ion/ion reaction products associated with common electron transfer reagents. Specifically, the study is aimed at identifying the fundamental factors that govern the competition between proton transfer, electron transfer (with and without dissociation), and the various fragmentation channels that contribute to the product ion spectrum.

- We will determine the fragmentation mechanisms associated with Au(I) and Au(III) cationized polypeptide ions. Model systems that contain a disulfide linkage, those that contain methionine and cysteine but no disulfide linkages, as well as peptides devoid of sulfur will be examined.

- We will establish ion/ion reactions that give rise to anions with radical sites and explore the dissociation chemistries of such species. We will also pursue the formation of cations with radical sites via ion/ion reactions.

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Self-Assembly of Polyelectrolyte Structures in Solution

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Overall research goals: The goal of this project is to understand the molecular-level processes controlling the self-assembly of nanoscale structures from polyelectrolytes in solution. Specific research goals have centered on understanding the interplay of forces leading to self-assembly in solution, and to investigating the effects of macromolecular structure on the formation of multilayer membranes from anionic and cationic polyelectrolytes.

Significant achievements in 2006-2008: In the initial stages of this project poly(cyclohexadiene) was identified as an important test compound for understanding self assembly, in that it has a different backbone structure but relatively similar chain size as compared with widely-studied polystyrene. The flexibility of chemistry and supramolecular architecture are indicated in Figure 1. Studies of aggregation in solution (reference 1 below) indicated much stronger self-assembly in poly(cyclohexadiene sulfonate) (PCHDS) than in poly(styrene sulfonate) (PSS). This aggregation behavior has been linked with the slightly stiffer backbone structure in PCHDS as compared with PSS, resulting in less intra-chain charge bridging interactions and more interchain aggregation.

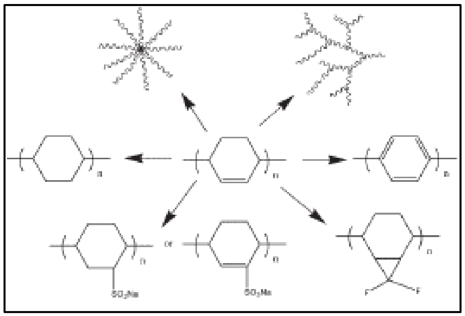

Figure 1. Chemical and architectural variability in polymers based on cyclohexadiene. (Reference 6)

This self-assembly can lead to aggregation into nanoscale (e.g., colloidal) structures in solution; films of varying thickness and composition on interfaces; and under controlled conditions to tailored membrane assemblies for separations applications. After the initial studies of self-assembly in solution, experimental efforts have centered on incorporating PCHDS into a bound multilayer membrane structure with poly (allyl amine hydrochloride) (PAAH) using variants of published approaches for incorporating other polyanions (e.g., PSS). We have found that the relatively low solubility and high self-aggregation of PCHDS, particularly in aqueous solutions with added salt, effectively inhibits the formation of consistent multilayer structures. Investigations of the resulting multilayer structures by ellipsometry, SEM, and STEM indicate inconsistent film thickness formation, and significant "nodular" appearance of the films, indicating the deposition of aggregates rather than molecularly-dispersed PCHDS within the films.

Further insight into the mechanism of self-assembly and the effects of added salt in solution have been obtained from molecular simulation. Working with model short-chain (8-mers) of PSS enabled calculation of local cation environment around sulfonate sites while accounting for solvation interactions using fully-detailed molecular water models. The lithium PSS with no salt added showed strong tendency toward ion association at modest concentrations in solution (Figure 2 and reference 3). Adding salts with higher-charged cations did not fully replace the lithium near the sulfonate sites, but effectively strengthened 'bridging' structures where polyvalent cations are partially charge-neutralized by sulfonate ions on separate polyanions. This simulation has given additional insight into both general effects with respect to cation charge, and specific effects related to cation solvation versus counterion condensation (e.g., Ba^{2+}).

We expected to base further understanding of the detailed mechanisms of competitive interactions between polyanions and solvent molecules in cation solvation on detailed studies of the local cation environment by neutron diffraction with isotopic substitution. Toward that end, significant contributions have been made to the design and performance goals of the Nanoscale Ordered Materials Diffractometer (NOMAD, reference 2) and experiments on local structures in carbon-containing fluids (CO_2, CS_2) were carried out as precursors for understanding backbone structures in polyelectrolytes. Through detailed data analysis and additional interferometry experiments it was found that the scattering length difference between ^{12}C and ^{13}C is smaller than expected, and that these carbon-difference experiments are not feasible (reference 4).

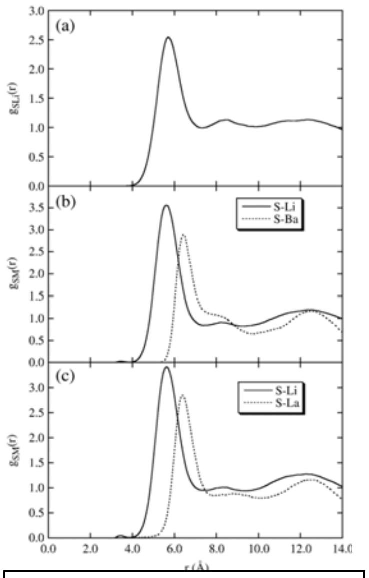

Figure 2. Radial distribution functions for counterion condensation in PSS. (Reference 3)

Science objectives for 2008-2009

This project is scheduled for completion in FY 2008.

- Complete analysis of experimental multilayer membrane synthesis work for publication.
- Complete simulation studies in progress on interactions of anionic ionomers and counterions in solution interacting with a fixed, charged hydrophobic surface (graphene), indicating the effect of fluid-solid interactions on multilayer membrane formation processes.
- Establish capabilities for neutron scattering studies and simulations of solvation effects in anion separations.

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Suspended lipid bilayers for membrane protein separations

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Overall research goals: The research objectives are to understand how the nanoscale structure of suspended lipid bilayers controls the diffusion coefficients of membrane-bound species, and to design materials with fast diffusion of membrane bound species.

Significant achievements in 2005-2008: We have made the first medium that allows for reproducible mobility of transmembrane proteins. We have a plan to improve this medium further to enable the first separations of functional transmembrane proteins. The significance is that this will provide a new separation tool to further the understanding biological cells. Transmembrane proteins are the active constituents in biological and biomimetic solar energy production.

The principle is illustrated in Figure 1. A POPC lipid bilayer, under certain conditions, suspends over a monolayer of silica nanoparticles. Transmembrane proteins normally cannot diffuse or electromigrate in supported lipid bilayers on planar surfaces because they contact the support. This new design reduces contact between the transmembrane proteins and the support.

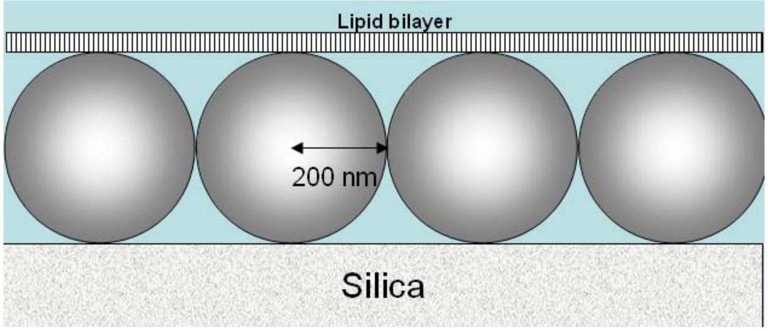

Figure 1. Silica nanoparticles of 200 nm in radius form an ordered monolayer on silica. The lipid bilayer is suspended above the nanoparticles.

Choosing larger vesicles allows the bilayer to form over the particles, as is drawn in Figure 1. Choosing small unilamellar vesicles causes the entire three-dimensional surface area of the nanoparticles to be coated with lipid bilayer. While this might have uses, such a material would not be promising for separations of transmembrane proteins. This control is an important advance.

We had previously made a material enabling diffusion of a transmembrane protein (human delta-opioid receptor) by supporting a bilayer on a very flat brush layer of polyacrylamide, made by atom-transfer radical polymerization. The diffusion coefficient depended so sharply on the thickness of the polymer brush that it was impractical for eventual application. The bilayer of Figure 1, by contrast, gave easily reproducible behavior in the diffusion of the same transmembrane protein. We found that that the diffusion was slower and only 25% of the transmembrane proteins were mobile. The fundamental study of diffusion in these nanoscale systems is revealing that the mobility and mobile fraction could be improved.

To study diffusion in the suspended lipid bilayer of Figure 1, labeled lipids were introduced into the bilayer and their diffusion was probed by fluorescence recovery after photobleaching (FRAP). The experiments revealed that the diffusion coefficient is three-fold slower compared to the same bilayers on planar silica. Curiously, the fluorescence is two-fold brighter. These observations are consistent with the bilayer warping over the top of the silica layer to give more surface area, causing a higher brightness but a longer contour distance for diffusion. If this interpretation is correct, it points to a means of speeding diffusion, which is critical to practical separations.

This interpretation of bilayer warping was tested by adding cholesterol to the bilayer. Cholesterol normally slows down diffusion by making the bilayer stiffer. We reasoned that cholesterol would have offsetting effects on the diffusion coefficient for the system of Figure 1 because stiffness would reduce contour length but increase the friction coefficient. We added varying amounts of cholesterol, and indeed, the results showed that the diffusion coefficient is much less sensitive to cholesterol content for the bilayers of Figure 1 compared to bilayers on planar silica. The results are summarized in Figure 2.

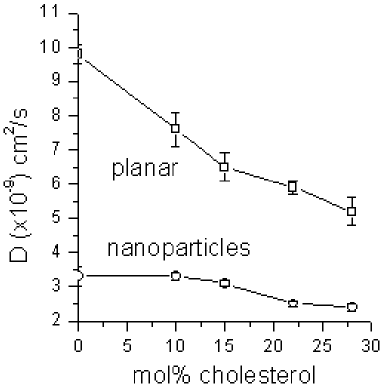

Figure 2. The diffusion coefficient of labelled lipids in planar bilayers vs. bilayers supported on silica nanoparticles.

These results show a flattened dependence on cholesterol content when nanoparticles are used as the support. This is an exciting result because it indicates that a new design to create flatter bilayers will greatly increase mobility. These designs are currently under investigation.

Science objectives for 2008-2009(style=Stand alone text heading):

- To reduce bilayer curvature, the tops of the nanoparticles will be made to have a hydrophobic surface, with the rest of the nanoparticle pegylated. This will reduce curvature by forcing the bilayer to contact the silica nanoparticles only on the very tops of the silica nanoparticles.
- AFM topography and phase measurements will be used to study the extent of the hydrophobic capping monolayer. Bilayer curvature with and without hydrophobic patterning will be studied using DiI as a membrane probe.
- Diffusion of labeled lipids and transmembrane proteins will be investigated to determine the mobile fraction and the mobilities of these species in the novel medium.

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Ion Production and Transport in Atmospheric Pressure Ion Source Mass Spectrometers

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

Significant achievements in 2006-2008: **Plasma source mass spectrometry.** We are conducting parallel computational and experimental efforts to characterize ion production and transport in inductively coupled plasma mass spectrometers (ICP-MS). We continue to model the flow of plasma through the vacuum interface of the ICP-MS by means of the Direct Simulation Monte Carlo Algorithm (DSMC). Recent work has focused on the first expansion stage.

With reasonable assumptions about the way that the expanding gas interacts with the surface of the skimmer, the skimmer triggers a secondary shock structure at the skimmer tip (as shown in the temperature contour plot shown in Fig. 1a). This leads to a re-expansion into the skimmer instead of ideal skimming and agrees with earlier experimental measurements from our lab (Fig. 1b).

We have also added the physical effect of the ambipolar electric field in the nozzle and into the expansion region to model the velocity-separation of ions and neutrals. Calculated argon velocities are obtained from the neutral gas simulation. Calculated calcium velocities are obtained by assuming that the calcium ions are acted upon by collisions with the argon and by the ambipolar electric field

$$E = -\frac{1}{en_e}\nabla p_e.$$

The calculations of the effect of the ambipolar electric field are being directly compared to experimental measurements of argon atom and calcium ion velocities based on Doppler shifts in fluorescence excitation spectra.

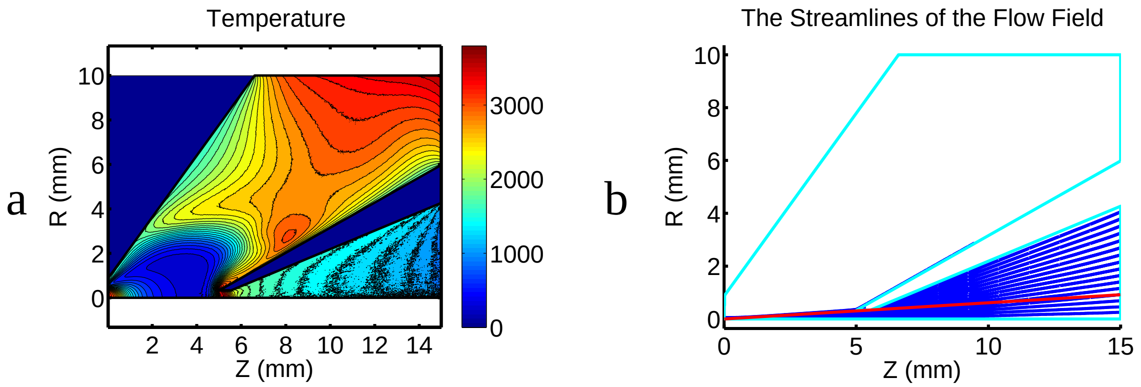

Figure 1. (a) Temperature contours in the first vacuum stage of an ICP-MS showing the formation of a secondary shock at the tip of the skimmer cone. (b) Flow streamlines showing secondary expansion downstream from the skimmer tip.

We have experimentally examined the effects of the sampling cone on the plasma in an ICP-MS using planar laser-induced fluorescence imaging. The images, examples of which are included in Fig. 2, show that there is a precipitous drop in ion density immediately upstream from the sampling cone that exceeds what would be predicted in a simple fluid dynamics model of the sampling process. Farther upstream ion densities are enhanced by the insertion of the cone, an effect that we attribute to a disruption and slowing of the overall flow from the plasma torch caused by the insertion of the cone.

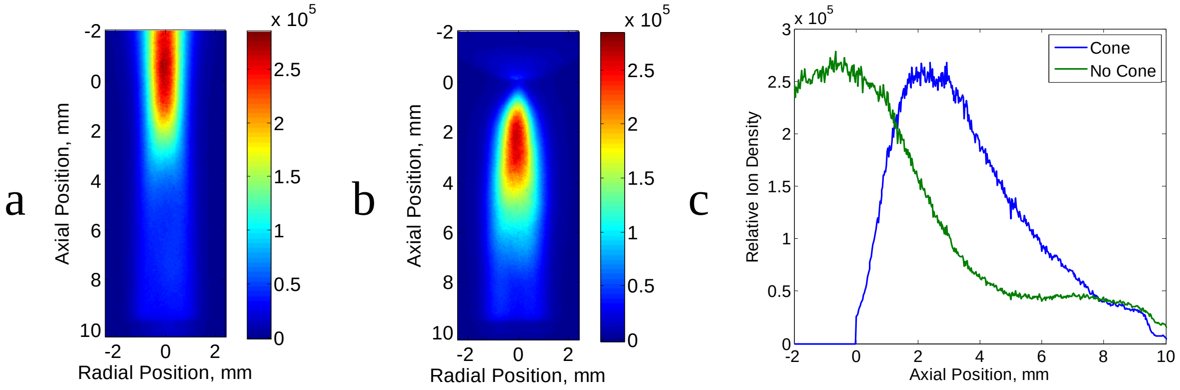

Figure 2. (a) Relative barium ion densities in the absence of a sampling cone. (b) Relative barium ion densities in the presence of a sampling cone. (c) Centerline traces (r = 0) from parts a and b.

Ambient ionization techniques. We have developed an instrumental system that allows us to simultaneously monitor removal of ions from a surface by fluorescence microscopy and record mass spectra of those ions.

Science objectives for 2008-2009

- Use Monte Carlo simulations to study the effects of skimmer cone geometry and placement on shock formation and skimming efficiency. Incorporate trace atoms into the simulation.
- Experimentally measure ion and neutral flow through the skimmer cone of an ICP-MS. Refine experimental studies of space charge effects in the second stage of the vacuum interface.
- Compare ion distributions produced by laser ablation sample introduction with those produced by solution nebulization. Examine the effects of helium as a nebulizer gas.
- Generate clear pictures of sample removal from surfaces by ambient ionization techniques.

References to work supported by this project 2006-2008

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Sampling, Ionization, and Energy Transfer Phenomena in Mass Spectrometry

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Overall research goals: The overarching goal of the present research portfolio is to further the understanding of fundamental chemical and physicochemical processes influencing diverse and complex chemistries observed with and that take place within mass spectrometry (MS). Within that framework, the current aim of the research program is to understand, advance, and create means to transfer chemical species at atmospheric pressure from complex matrices in the condensed-phase (solid or liquid) to the gas-phase without loss of information, particularly in the context of analyte sampling and chemical imaging at the micrometer and nanometer scale.

Significant achievements in 2006-2008: We provided a new understanding of the physical properties for the desorption electrospray ionization (DESI) impact plume, viz., that the desorption/ionization effectiveness within the impact plume region under typical conditions was not uniform. It was shown that the solvent/gas jet plume forms an elliptical region on the surface, with most effective desorption/ionization obtained from a smaller elliptical area within the larger impact region. We also showed that analyte accessibility to this area is limited by solvent and gas flow out of the desorption/ionization region when the analyte is on a surface for which it has little affinity. Chemical processes leading to the production of reactive oxygen species in the DESI spray plume and resulting in oxidation of specific analyte compounds also were noted and described.

We have begun investigation of a new concept, tip-enhanced, near-field atmospheric pressure laser desorption/ionization mass spectrometry (AP-LDI-MS), as a unique probe for nanoscale chemical imaging. The key scientific question to be addressed in these studies is whether the implementation of near-field optics can obviate the inherent resolution limits imposed by diffraction in conventional laser-based desorption/ionization, while retaining the capability for acquiring chemical information (mass, structure, and gas-phase reactivity, etc.) via MS.

A controlled-current, two-electrode electrochemical cell was developed to control the electrochemical reactions of analytes in an ES emitter; the control demonstrated has been impossible to achieve with a conventional ES emitter. The cell contains a porous flow-through working electrode with high surface area and multiple auxiliary electrodes with small total surface area. The cell system provides the ability to control the extent of analyte oxidation in positive ion mode in the ES emitter by simply setting the magnitude and polarity of the current at the working electrode. In addition, this cell provides the ability to effectively reduce analytes in positive ion mode and to oxidize analytes in negative ion mode.

Our general moment theory for radio-frequency ion traps (based on transformation of the Boltzmann equation) was expanded to include ion-molecule reactions for both atomic and molecular ions and neutrals. The theory indicates that ion-neutral reaction rate coefficients determined in traps are indeed equivalent to high-temperature, thermal rate coefficients measured in a conventionally heated apparatus; the appropriate reaction temperatures can be determined from ion trap operating parameters and solutions to either our two-temperature or multi-temperature differential equations.

Electrochemically initiated homogeneous reactions using a bulk-loaded nano-ES device were investigated as a means to enhance analyte identification in ESI-MS. Quantitative tagging of thiol groups by benzoquinone generated from hydroquinone by the inherent electrochemistry of electrospray was achieved. Mass shifts obtained in the addition reaction were used to determine number of thiol groups and helped more confidently identify the analyte of interest. We also demonstrated for the first time that a novel polymer film modification of a regular metal emitter electrode could prevent analyte electrolysis by the inherent electrochemistry of the ESI source by acting as a surface-tethered redox buffer.

Science objectives for 2008-2009:

- The fundamental aspects and viability of tip-enhanced, near-field AP-LDI-MS for nanoscale chemical imaging will be investigated.
- We will continue on identifying the fundamental physical phenomena that occur in DESI at the macroscale and microscale, as well as on the chemical processes in those size regimes.
- Ways to prevent analyte electrochemistry in bulk-loaded nanospray emitters will be investigated.
- Experiments will be performed that aim at verifying one aspect of our previously developed moment theory for ion traps, viz., that thermal ion-neutral reaction rate coefficients appropriate to elevated temperatures in the absence of electric fields can be extracted from low temperature measurements (at high fields) in ion traps.

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Shock Waves in Thermal Diffusion

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Overall research goals: An objective of the research carried out here has been to investigate the fundamental properties of the Ludwig-Soret effect, which is a separation method based on thermal gradients. In particular, research has focused on what the author considers the most fundamental problem in the field, namely, the thermal diffusion of a binary mixture in a linear temperature gradient. A second goal of the research has been to study laser generation of bubbles. The transient grating method has been chosen for experiments with impulsively and quasi-continuously generated bubbles in solution. Experiments have been carried out showing significantly different behavior of the dynamics of bubble motion for different paths of generation.

Significant achievements in 2006-2008: We have made progress in determining the evolution of concentrations in a mixture of two chemical species in a linear temperature field. Three approaches have been explored. First, the linearized Ludwig-Soret problem can be solved with mass diffusion included using Laplace transforms. The solutions are rigorously valid for small values of the density fraction of one species, which translates, in general, to early times after initiating the temperature gradient. The second method uses numerical integration of the nonlinear equations to give an exact solution to the nonlinear equation that includes the effects of mass diffusion. It is this result that is used to compare theory and experiment, and which permits the extraction of the thermal parameters. Third, an analytical solution has been obtained for the nonlinear problem that shows the presence of a pair of shock fronts. Shock waves are considered to be discontinuities in state variables that propagate in time. The shocks found here are related to the commonly known fluid shocks, as found following explosions or associated with supersonic flight, only in that they obey analogous conservation laws. The shocks found here describe only the slow motion of the separation of two components of a mixture.

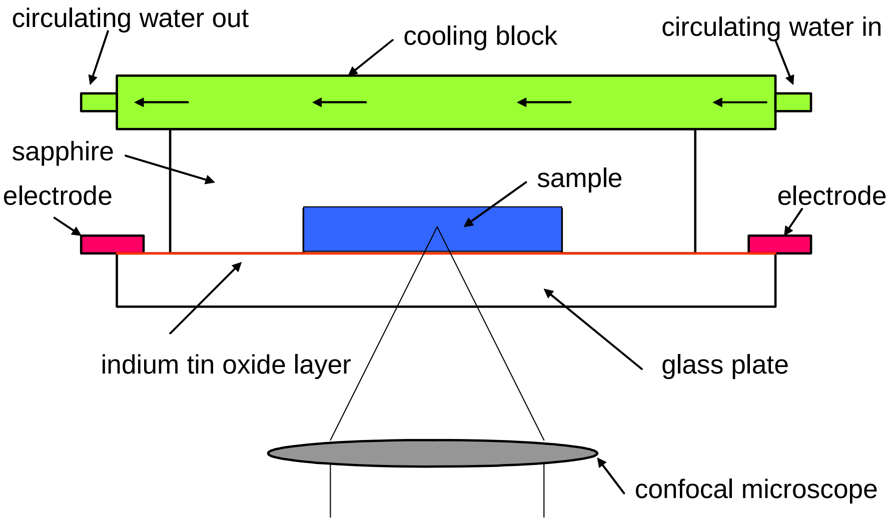

Figure 1. Schematic drawing of the cell used for generating a linear thermal gradient. The hot surface is provided by the electrically heated indium tin oxide coating on a piece of glass; a cold surface is maintained by circulating water through a cooling block. Current is fed from a power supply to the electrodes.

We have also introduced a new method of observing the Ludwig-Soret effect in a linear temperature field. Our method, as shown in Fig. 1, relies on production of a large thermal gradient by using a piece of glass coated with indium tin oxide through which a current is passed. The cell for the Ludwig-Soret effect is formed between the indium tin oxide glass and a piece of sapphire which has a section 100 micron deep ground from its bottom surface. The upper surface of the sapphire piece is cooled with flowing water from a temperature controlled refrigeration unit. The small size of the cell permits the production of very large thermal gradients using temperature differences between the top surface of the sapphire and the indium tin oxide heater of only a few degrees. Experiments have been done with silica particles specially labeled with fluorescent dyes in water. The measurements are carried out using a confocal microscope that images the concentration of the particles (which owing to their size are treated as a fluid) through fluorescence. Scans of the confocal microscope are carried out at intervals of tens of minutes.

Experiments have also been carried out on laser generation of gas bubbles at the sites of particles and through photochemical reaction. The production of the bubbles can be described as impulsive in the case of colloidal Pt suspensions and adiabatic for the chemical reaction. The impulsive production of bubbles, depending on the chemical system, can result in vapor that rapidly condenses rapidly, or permanent gas, which remains on a long time scale compared with the period of the grating. The complicated time dependence of the diffracted light in the transient grating experiments is explained by combinations of the linear photoacoustic effect, a nonlinear photoacoustic effect, and diffraction by a sinusoidal distribution of scattering centers in space.

Science objectives for 2008-2009(style=Stand alone text heading):

- Experiments will focus on gathering improved data which must be normalized in order to be fit to theory. Convolution procedures will be worked out in order to extract accurate spatial distributions of the components.

- Numerical integration of the exact equations that describe the Ludwig-Soret effect will be carried out to compare theory with experiment. Soret parameters will be determined from the numerical integration results.

- Mathematical methods for determination of the shock velocity will be investigated. The shock velocity is an important parameter in the theory, and can be determined from experiments.

- Transient grating experiments will be investigated for particulate suspensions at different temperatures, with different size particles, and at different laser fluences. Transient grating signals from the picosecond and nanosecond experiments will be compared.

References to work supported by this project 2006-2008:

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Ion Soft Landing for Catalyst Preparation

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Post-doctorals Wen-Ping Peng and Zongxiu Nie
Graduate students Michael Goodwin, Aliah Dugas

Overall research goals: The objective of this proposal is to develop new instrumentation and methodology for the creation of size-specific catalytic particles by (i) electrospray ionization of solutions containing metal salts and support oxides, (ii) mass-selection of particular ions using a non-scanning low frequency two-dimensional ion trap, and (iii) ion soft landing of the mass-selected catalytic particles onto substrates. The surfaces of the resulting materials are to be characterized by mass spectrometry and x-ray photoelectron spectroscopy. They are then to be tested for catalytic activity in a high throughput chamber using mass spectrometric vapor phase analysis**.**

Significant achievements in 2006-2008: 1) **We have designed and built instrumentation needed to soft land mass-analyzed ion beams on surfaces and demonstrated that soft landing can be achieved**. This instrument uses a novel long ion trap which can be operated in a continuous mode (using RF/DC as a mass filter) during ion soft landing and in a discontinuous mode (using mass-selective instability) as a conventional ion trap to record mass spectra. Mass selection can also be achieved via continuous RF/DC isolation using a bent square quadrupole ion guide, as an alternative to the ion trap and as a way of increasing soft landing yields. To test the performance of the RIT as a continuous mass filter, a mixture of crystal violet and reserpine was electrosprayed, and the crystal violet was selected via appropriate RF and DC voltages. Approximately 16ng of crystal violet (m/z 371) was landed onto the surface (Figure 1), while no reserpine (m/z 610) was detect in the landed material. The overall transfer efficiency from solution to surface was ~0.2%. Similar experiments were performed using RF/DC isolation of both arginine and lysine from a mixture using the bent square quadrupole in RF/DC mode. The unconventional continuous mass selection methods utilized maximize soft landing yields, while still allowing the simple acquisition of full mass spectra.

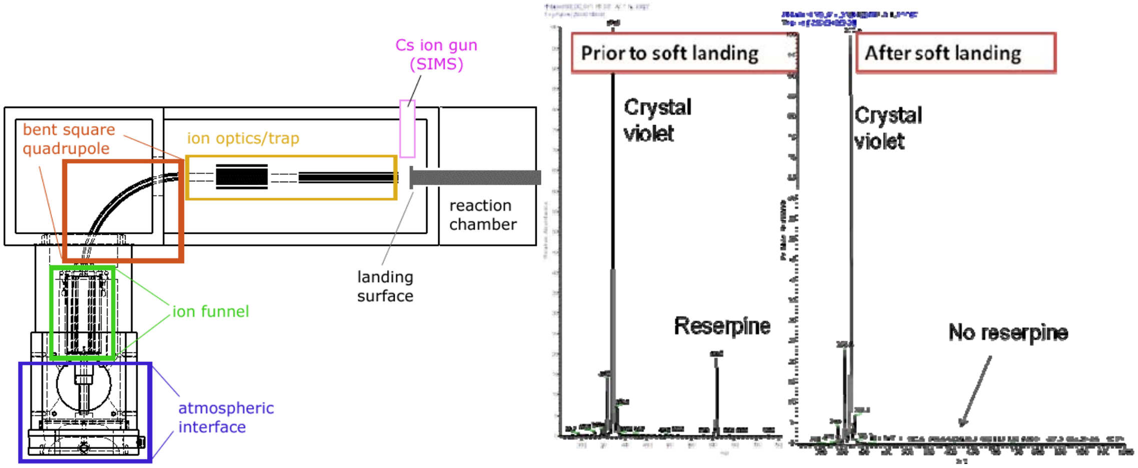

Figure1: (left) Schematic of our soft landing instrument; (right) Nanospray spectrum obtained after rinsing the soft landed surface. Crystal violet (m/z 371) was mass selected from reserpine (m/z 610) using an RIT in RF/DC mode, as evidenced by the lack of a reserpine peak

2) We have developed a new ionization method, atmospheric pressure thermal desorption ionization (APTDI) and shown this to be useful in the characterization of organometallic and inorganic compounds. This method gives high yields of metal-containing cluster ions and is being used as a superior alternative to ESI for the production of the multi-metal atom inorganic clusters needed in this soft landing work. These ions are produced simply by heating appropriate inorganic and organometallic compounds at atmospheric pressure in an inert environment. APTDI appears to have value as a method of characterizing air and moisture sensitive compounds. Because ions are formed under ambient conditions, the method lends itself to scale up (w/o mass analysis, once appropriate conditions for formation of desired ions are established). APTDI has also been used to characterize various catalyst species (including Wilkinson’s, Grubbs’ and Jacobsen’s catalysts).

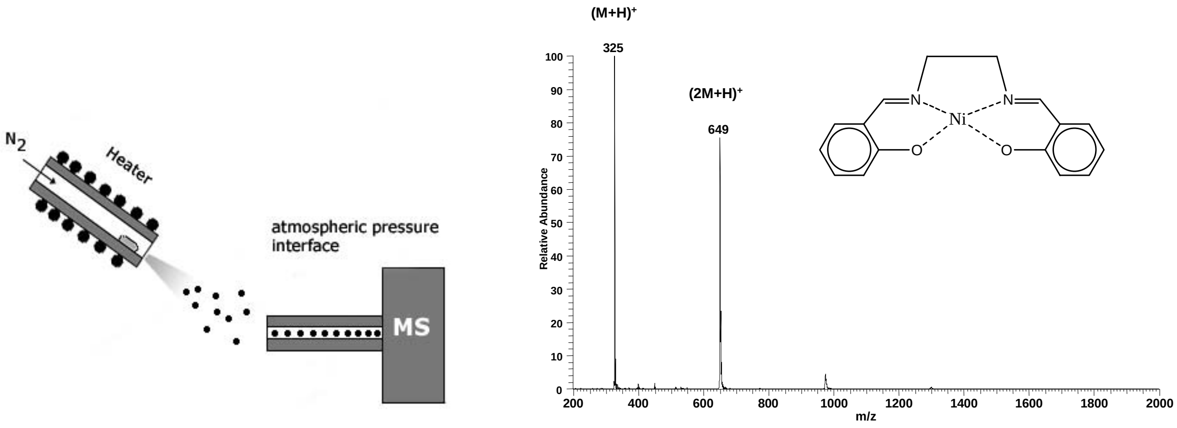

Figure 2: (left) Schematic of the APTDI process; (right) APTDI spectrum obtained from a Ni(salen) sample

3) We have developed a method of removing ions from an ion beam on the basis of their m/z values and transmitting all others. This is a SWIFT-type method and this is the first implementation of such a method for ion beams (all previous implementations are for trapped ions). It is a powerful new capability that should be widely useful.

Science objectives for 2008-2009

- Utilize the APTDI methodology for cluster ion soft landing
- Implement a SIMS source within the vacuum chamber for characterization of the landed surfaces
- Analyze the prepared surfaces by SIMS
- Characterize reactivity of landed materials in the reaction chamber attached to SL instrument

Publications acknowledging this grant

- Wen-Ping Peng, Mike Goodwin, Hao Chen, R. Graham Cooks, Jonathan Wilker, “Thermal Formation of Mixed-Metal Inorganic Clusters at Atmospheric Pressure”, Rapid Commun. Mass Spectrom., 2008, to be submitted.
- Wen-Ping Peng, Mike Goodwin, Zongxiu Nie, R. Graham Cooks, “Development of a New Soft Landing Mass Spectrometer”, Anal. Chem., 2008, to be submitted.
- Q. Song, Mike Goodwin, Zongxiu Nie, R. Graham Cooks, “Waveform Mass Filtering with a Continuous Beam in a Quadrupole Ion Guide”, Int. J. Mass Spectrom. Ion Processes, 2008, to be submitted.
- Mike Goodwin, Zongxiu Nie, Michael Volny, R. Graham Cooks, “Operation of a Rectilinear Ion Trap as a Continuous Mass Filter”, Rapid Communications in Mass Spectrometry, 2008, to be submitted

Patent application

Q. Song, Zheng Ouyang, R. Graham Cooks, “Mass Filtering of Ion Beams using Selected Waveforms” submitted

Adsorption States of Amphipatic Solutes at the Surfaces of Naturally Hydrophobic Minerals

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Hao Du, Ph. D Graduate Student
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Overall research goals: This flotation chemistry research program is motivated by the need to develop improved particle separation processes for the more effective use of energy and mineral resources. The general objective is to improve our understanding of the surface chemistry of selected nonsulfide flotation systems (soluble salts, semi soluble salts, and layered silicates) using surface vibrational spectroscopy (FTIR/IRS and SFVS), atomic force microscopy, and molecular dynamics simulation. The objective of this particular project is to study the adsorption states of selected amphipatic solutes at selected naturally hydrophobic mineral surfaces using molecular dynamics simulation (MDS), in order to provide further information regarding the adsorption mechanisms, and the significance of hydrophobic interactions in the flotation separation process.

Significant achievements in 2006-2008: MDS analysis using the DL_POLY simulation package suggests that due to the absence of electron donor/acceptor sites at naturally hydrophobic mineral surfaces, such as the basal planes of talc and graphite, water molecules interact weakly with the surface atoms, and arrange themselves randomly some distance (~3 Angstrom) from the surface. On the other hand, the exposed oxygen/magnesium/silicon atoms at the talc edge provide abundant hydrogen bonding sites for surface hydration and account for a hydrophilic state at this surface. See Figure 1A and 1B.

It is concluded from MD simulation that the low polarity of the basal planes of talc and graphite explains hydrophobic interactions with nonpolar alkyl chains of selected surfactants which render the basal plane surface hydrophilic. See Figure 1C for example. These MDS results are in agreement with previously reported results which reveal a significant decrease in contact angle when such surfactants are present at sufficient concentration and with other results from soft contact AFM imaging which reveal the formation of surface micelle structures.

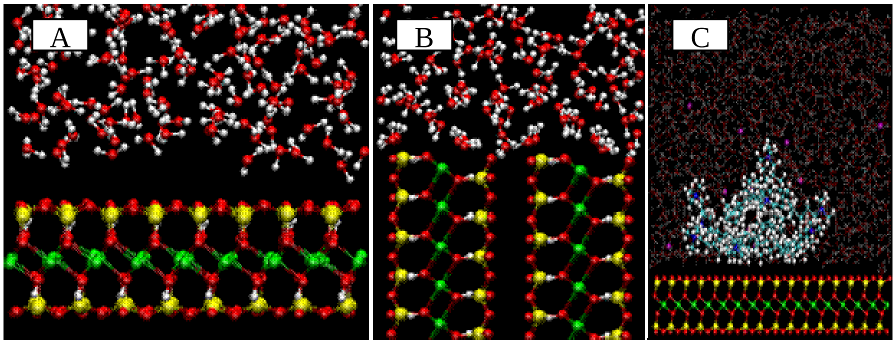

Figure 1. MDS snapshots of water molecules at talc basal plane (A), talc edge (B) surfaces, and adsorbed DTAB molecules at the talc basal plane surface(C). (Red-oxygen atoms, white-hydrogen atoms, blue-nitrogen atoms, purple-bromide atoms, yellow-silicon atoms, green-magnesium atoms, blue-nitrogen atoms, and light blue-carbon atoms.)

Similar MD simulation regarding the adsorption of "dextrin" at selected naturally hydrophobic surfaces such as the basal planes of talc, graphite, and sulfur suggests that hydrophobic interactions between the substrates and the hydrophobic moieties of the dextrin molecule play a significant role in the adsorption processes. At the graphite surface, the "dextrin" molecule reorients to expose as many hydrophobic moieties as possible to the graphite surface while the majority of the dextrin hydroxyl groups hydrogen bond with water molecules by stretching into the bulk aqueous phase and creating a hydrophilic surface state. See Figure 2.

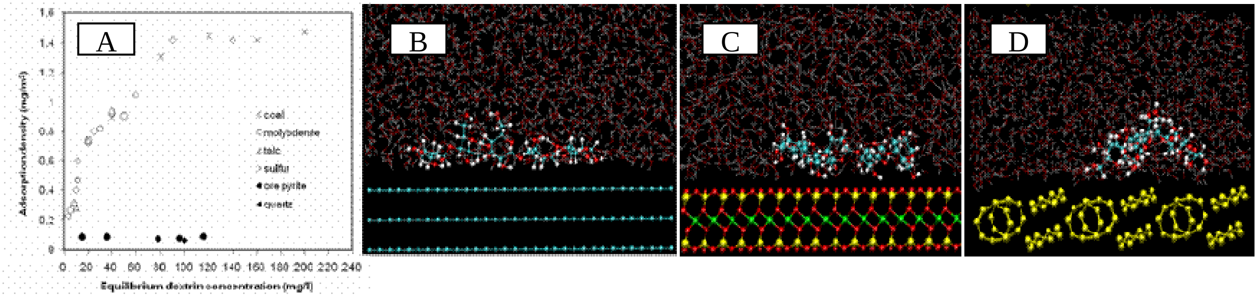

Figure 2. Dextrin adsorption isotherm (A) and MDS snapshots of "dextrin" adsorption states at graphite basal plane (B), talc basal plane (C), and sulphur (D) surfaces (Red-oxygen atoms, white-hydrogen atoms, blue-nitrogen atoms, purple-bromide atoms, yellow-silicon/sulfur atoms, green-magnesium atoms, and light blue-carbon atoms.)

Science objectives for 2008-2009:

- Alkyl amine adsorption at selected oxides surfaces will be examined using SFVS, FTIR as well as MDS and AFM in order to establish surface chemistry conditions for improved flotation separations in the iron and phosphate industries.
- Interfacial chemistry of adsorbed surfactant structures under high shear conditions will be studied using FTIR/IRS and AFM to determine the influence of surface turbulence on the hydrophobic surface state.
- Surface chemistry and surfactant structures at selected alkali halide salts will be studied using MDS, SFVS, and AFM to understand conditions for improved flotation of potash and other soluble salt minerals.

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Photophysics of Organic Semiconductors Probed by a Combination of High Resolution Fluorescence Microscopy and Ion Mobility Mass Spectrometry

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I will discuss our results from probing the fluorescence from single molecules of a new class of oligo(phenylenevinylene) (OPV) molecules, where four OPV "arm" molecules are linked via a single sp3 carbon center (see Figure 1). [1] Our results show that these so called tetrahedral molecules contain multiple chromophores with limited inter-arm coupling, but significant molecular motion about the central carbon. This motion leads to fluctuations in the both the polarizability axis of the molecule and the fluorescence intensity on the timescale of 100 ms to 10 s. The statistics of emitted photons from single tetrahedral molecules have been examined using photon pair correlation spectroscopy (PPCS). [2] The second order correlation function obtained from PPCS is used to quantify the number of chromophores involved in emission. An example of the photon anti-bunching observed using the PPCS technique is shown in Figure 2. These results show that the tetrahedral molecules are able to sustain simultaneous emission from multiple arms.

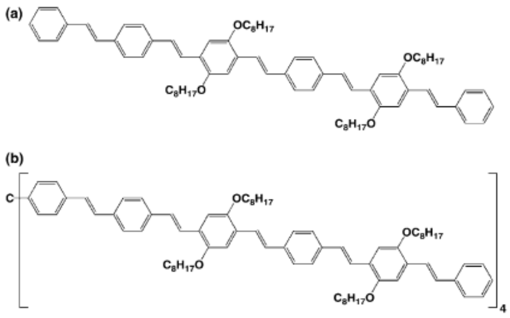

Fig. 1. Structures of OPV (6R-4OC$_8$H$_{17}$) (a) and TOPV (T-6R-4OC$_8$H$_{17}$) (b).

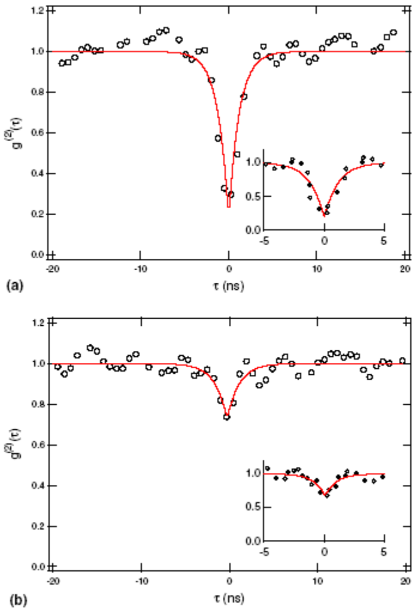

Figure 2. Photon pair coincidence histograms for OPV (a) and TOPV (b). Histograms were produced by averaging coincidence data from 100 molecules (a) and 50 molecules (b). Insets: dip region with coincidence bins set at 470 ps.

We have shown, for the first time, direct comparisons of the detailed structures of the OPV "arm" molecules and their luminescence properties on a single molecule level and in thin films. This data originates from a combination of two powerful diagnostic tools in physical chemistry: gas-phase ion mobility and single molecule fluorescence spectroscopy. [3] The results show that the structures observed in the gas phase are strongly correlated to the categories of molecules observed in the single molecule polarization anisotropy measurements with nearly identical distributions for the two OPV molecules studied. These categories are determined by the number of cis vinylene linkages in the OPV structure and are shown to directly influence the fluorescence intensity, the structure of the tetrahedral molecule and the morphology of films made from these materials. An example of an arrival time distribution with the corresponding isomer structures is presented in Figure 3b. This arrival time distribution is produced from a thin film of OPV's as depicted in the fluorescence image of Figure 3a. The arrival time distribution of Figure 3b is produced by averaging over all of the fluorescence domains shown in Figure 3a. We have seen through spatially-resolved spectroscopy (see Figure 4) that the different domains observed in the fluorescence image exhibit different vibronic structure in their corresponding fluorescence spectrum. [4] We have attributed this difference to a different isomer distribution in a given fluorescence domain. In order to test this hypothesis we have recently begun developing a new apparatus that will allow us to measure the isomer distribution from a specific domain in the image of Figure 3a. In this new apparatus the fluorescence microscope is placed in the source chamber of the ion mobility mass specrtrometer. A fluorescence image (similar to that of Fig. 3a) is acquired and then OPV molecules from a specific fluorescence domain are desorbed from that domain, an arrival time distribution is acquired and the resulting distribution is compare to that obtained by spatial averaging (Fig. 3b). I will discuss our progress in constructing this new machine and present the first data acquired from it.

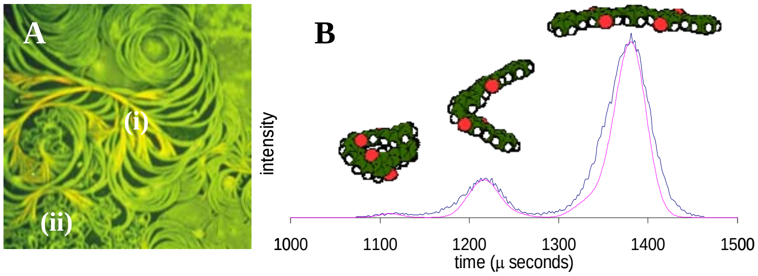

Figure 3: (A) Far-field fluorescence image of an annealed 6OPV film (i) a region exhibiting ribbon-like structure (ii) a region exhibiting amorphous structure(B) Arrival time distribution taken from a laser desorbed film of 5OPV

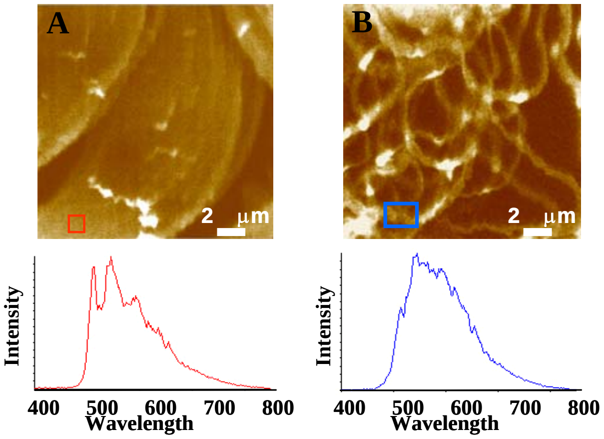

Figure 4: NSOM images and spectra from annealed 6OPV films (A) a "sheet-like" region with fluorescence spectrum from boxed region (B) a "ribbon-like" region with fluorescence spectrum from boxed region

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Studies of Solvation Processes in Supercritical Fluids

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Collaborators: Dr. Gary A. Baker, ORNL

Overall research goals: Our DOE-sponsored research seeks to develop a molecular-level understanding of key phenomena occurring within environmentally friendly solvent systems that are important to the DOE mission. The research is divided into four sub-projects: (i) polymer and junction aggregation phenomena in supercritical fluids (SFs) and ionic liquids (ILs); (ii) dynamics of small flexible molecules and linear polymers in ILs; (iii) interfaces in contact with pure and cosolvent-modified $scCO_2$ and ILs, and (iv) biomolecule dynamics and function in ILs.

Significant achievements in 2006-2008: Our results have been reported previously.[1-12]
Flexible Molecules in ILs. We have studied the dynamics of 1,3-bis-(1-pyrenyl) propane (BPP), 1,3-bis-(1-pyrenyl) dodecane (BPD), and Py-PDMS-Py (a poly(dimethylsiloxane) polymer with the ends tagged with the fluorescent probe pyrene) in 1-butyl-1-methylpyrrolidinium ([C_4mim])-based ionic liquids between 298 and 383 K. The observed "tail" behaviour is significantly different in comparison to their behaviour in pure and CO_2-dilated molecular liquids, and pure supercritical fluids, showing the ability of an IL and temperature to tune the tail dynamics. For example, Py-PDMS-Py in [C_4mim][Tf_2N] shows no evidence for excimer emission in the pure IL at any temperature until 50% v/v toluene is added. An anomalous temperature effect in the 50/50 IL/toluene samples arose from temperature-induced demixing of the toluene from the IL. The Py- residues in Py-PDMS-Py are rich in PDMS at *all* toluene compositions and temperatures, suggesting the Py-PDMS-Py molecules are not well solvated and the Py- tails are buried within PDMS-rich microdomains. Time-resolved fluorescence suggested Py-PDMS-Py aggregates in the IL solution.
IL Solvation at Silica Surfaces. We have explored how [Tf_2N]-based ILs solvate sparingly dansylated controlled pore glass (D-CPG) surfaces and free dansylpropylsulfonamide (DPSA). [C_4mim][Tf_2N] and [C_4mpy][Tf_2N] exhibit dipolarities similar to liquid methanol. [$P(C_6)_3C_{14}$][Tf_2N] exhibits a dipolarity similar to 1-octanol. These ILs do *not* solvate/wet the dansyl groups on the uncapped D-CPG surface as well as the corresponding molecular liquids (methanol and 1-octanol). Cation size plays a leading role in silica wetting by these ILs.
Cosolvent Solvation at Silica Surfaces in Supercritical CO_2. In uncapped D-CPG one can poise the system such that the local concentration of an environmentally less responsible cosolvent (alcohol) in the immediate vicinity of the silica surface can approach 100% even though the bulk solution contains orders-of-magnitude less of this less environmentally responsible cosolvent. In capped C-CPG this surface excess is attenuated.
Proteins in ILs. Biocatalytic reactions can be carried out in IL-based solvent systems, often with improved activity, enantioselectivity, reusability, and/or operational stability. We have investigated the dynamics of a well-known multi-domain protein, human serum albumin (HSA), in IL/water mixtures. Results reveal that the HSA structure is much different in the IL/water mixtures in comparison to aqueous buffer and depends on the water loading, temperature, and IL chemistry.

Science objectives for 2008-2009:

- Determine the density-dependent kinetics for BPP, BPD, and Py-PDMS-Py in the aforementioned IL systems.
- Determine the effect of cosolvent acidity for non-alcohols on the solvation of capped and uncapped D-CPG in cosolvent-modified CO_2 and the remaining ILs.
- Elucidate how IL structure, water loading, and temperature affect model protein dynamics within ILs.

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Fundamentals of Electric Field-Enhanced Multiphase Separations and Analysis

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Dr. Michael T. Harris (Chemical Engineering, Purdue University)
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Overall research goals: The research objectives are to elucidate and understand through theory, simulation, and experiment the dynamics of drop breakup and the physics of finite time singularities that arise during the pinch-off of fluid interfaces. Understanding the effects of surfactants, polymers, and imposed electric fields in such situations is of central importance in the research.

Significant achievements in 2006-2008: We made significant advances in a number of areas involving formation of simple emulsion and double emulsion drops. Among the most exciting of these was using two co-flowing liquids in a concentric tube arrangement to form extremely small drops. We showed by simulation that as the ratio Q_r of the flow rate of the outer liquid (flowing in the big tube) to that of the inner liquid (flowing in the smaller tube) increases, the dynamics changes as shown in figure 1 from (a) slugging to (b) dripping to (c) jetting and finally to (d) tip streaming. Prior to our work, over 50 years of research had led to the incorrect belief that tip streaming cannot occur without surfactants or electric fields. Our simulation results have given rise to a flurry of activity around the world, including experimental confirmation by a Spanish group of our predictions and a recent report of the use of three co-flowing liquids to push drop sizes down to the nanometric scale. We were also invited to write a Nature Physics News and Views piece on account of our work.

We made several notable contributions to the understanding of interface pinch-off in the presence of surfactants and polymers. In Xu et al. (2007), we reported an analytical theory, which is supported by simulations, that shows that in contrast to macroscopic filaments, surfactant can remain in the vicinity of the pinch point when a surfactant-covered microscopic or nanoscopic filament breaks.

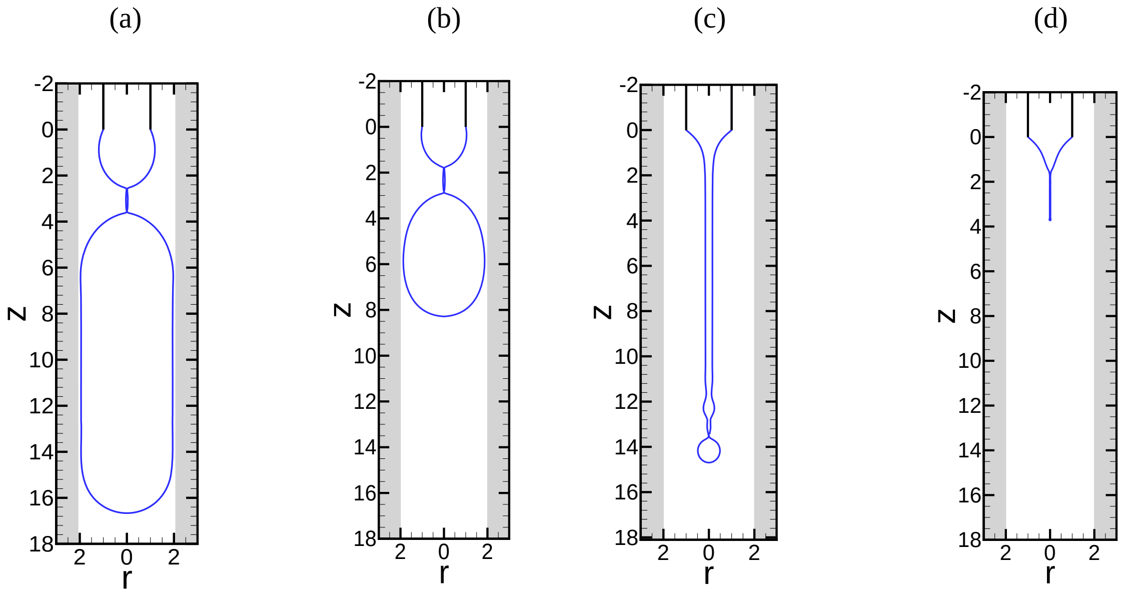

Figure 1. Focusing a liquid emerging from an inner tube by subjecting it to the flow of a faster moving surrounding liquid that is flowing in a concentric tube of larger radius. Here Q_r varies as (a) 0.1, (b) 10, (c) 30, and (d) 35.

Science objectives for 2008-2009:

- Motivated by applications in separations (field-driven extraction), analysis (electrospray mass spectrometry), and energy (drop-wise printing of solar cells), develop a fundamental understanding of electrohydrodynamic (EHD) tip streaming.
- Use simulation and experiment to investigate EHD tip streaming from liquids of finite conductivity.
- Develop scaling laws for the sizes of micro-(nano-)scale drops produced from the breakup of the thin tip streaming jets emitted from liquid cones and the amount of charge carried by these drops.

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Investigation of Transport Mechanisms in Surface Modified Inorganic Membranes

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Overall research goals: The objective of this project is to synthesize, characterize, and investigate the transport mechanisms in surface modified inorganic membranes for a variety of separations including hydrocarbons from light gases and CO_2 from N_2 and H_2.

Significant achievements in 2006-2008: During the past reporting period, we have synthesized and characterized silane modified inorganic membranes that contain nanoscale polymer layers (< 100 nm), polymer brush structures, and membranes that combine polymer layers and polymer brushes. These three structures are shown in Figure 1. Membranes with polymer layers (A) have similar characteristics to rubbery polymer materials, but the very thin polymer layers produce very high permeances. Membranes modified with monochloro silanes produce polymer brush structures (B in Figure 1). These membranes have higher mixed gas selectivities, over 200, for highly interacting gases, such as n-butane over N_2 in the case of alkyl silane modifications, due to competitive adsorption and pore blocking mechanisms. Dual silane modified membranes essentially combine the characteristics of membranes with polymer layers and polymer brushes at a cost of lower permeance. We have observed that adsorbed butane in a dual silane modified membrane can effectively "block" the transport of methane in mixed gas permeation experiments. Mixed gas C_4H_{10}/CH_4 separation factors of 21 to 61 were measured at ambient temperature. Butane/methane separation factors increase as the butane partial pressure in the feed gas increases at 295 K.

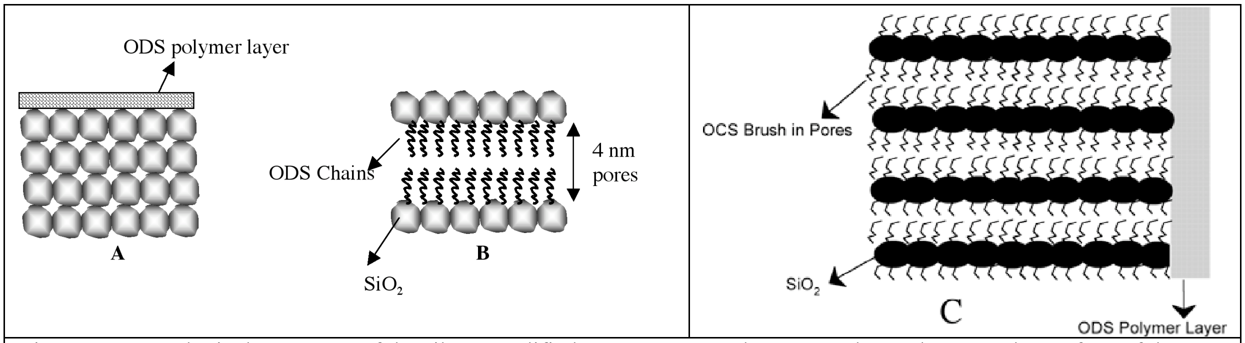

Figure 1. Hypothetical structures of the silane modified Vycor porous glass. A. Polymer layer on the surface of the membrane. B. Polymer brush in the pores, decreasing the pore size. C. Polymer brush and polymer structure in the same substrate (dual silane modification).

In the next phase of this research, we will investigate fundamental transport mechanisms expected to produce reverse selectivity for CO_2 over light gases such as H_2 and N_2. These mechanisms include surface diffusion and pore blocking that are not observed in the solution diffusion mechanism of polymeric membranes. Our synthesis strategy is to produce a polymer brush using monochlorodimethylfluorosilane and acetoxyethyldimethylchlorosilane. When polymerized into structure similar to Figure1A. above, membranes modified using both of these silanes are CO_2 selective.

Science objectives for 2008-2009:

- Prepare **polymer brush** structures on mesoporous substrates such as Vycor glass using monochlorodimethylfluorosilane and acetoxyethyldimethylchlorosilane. Both of these silanes are commercially available.
- Characterize silane modified mesoporous membranes using techniques such as ^{29}Si CP-MAS NMR spectroscopy, AFM, electron microscopy, Raman and FTIR spectroscopy
- Perform pure gas permeation studies with silane modified membranes using penetrants of interest such as CO_2, N_2, H_2, CH_4, and CO as a function of temperature, 243 to 373 K
- Perform sorption studies with the same penetrants as the pure gas permeation studies over the same range of temperature
- Investigate the use of newly developed quantum chemical, density functional methods (vdW-DFT) to model weak van der Waals interactions between CO_2 and silanes used in the surface modification.

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

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

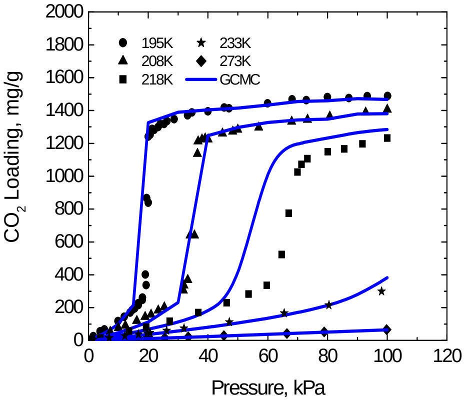

Figure Comparison of GCMC simulations and experimental adsorption isotherms for CO_2 in a representative MOF.

Significant achievements for 2006-2008: a) demonstrated separation of enantiomers (comprising a racemic alcohol) using a post-synthetically chirally modified MOF material, b) observed with two MOFs high selectivities (S > 10) for sorption of carbon dioxide versus methane, c) computationally verified the applicability of the BET method to the problem of measuring the internal surface areas of MOF materials, d) developed methods for creating framework-reduced, metal-ion-doped MOFs and determined that doping greatly enhances hydrogen adsorption, e) developed, validated, and applied to several systems code for quantitatively modeling molecular adsorption in MOFs (see example in figure at right), f) developed a method for separating mixed phases of MOF materials, including mixtures of catenated and non-catenated MOFs.

Science objectives for 2008-2009

- Understand physical basis for highly selective carbon dioxide sorption
- Develop non-interpenetrating framework materials suitable for post-synthetic tailoring and selective sorption
- Computationally identify & model, and experimentally obtain, materials that kinetically separate small molecules

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Synthesis and Analysis of Polymers with High Permeabilities and Perselectivities for Gas Separation Applications

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Overall research goals: To identify fundamental principles to enable preservation of the intrinsic separation properties of solution-processable polymers under aggressive separation conditions. The polyimide family has among the best intrinsic separation properties, and we are establishing relationships between polyimide structure, selective layer thickness, degree of crosslinking, physical aging and resistance to swelling-induced plasticization in our work.

Significant achievements in 2006-2008: Chemical crosslinking, created via ester bonds, extends the range of high permselectivity of polyimides for gas pairs such as CO_2 *vs*. CH_4. This treatment can be applied to high performance asymmetric membranes with 100-200 nm selective layers, thereby enabling purification of trillions of cubic feet of contaminated natural gas (Fig. 1 a). The ultra-thin selective layer of such membranes makes them prone to physical aging, which largely results from the much more rapid diffusive removal of intersegmental unoccupied ("free") volume from thin (e.g. 600 nm) vs. thick (49 µm) chemically identical films as shown by the dramatically larger and more rapid reduction in methane permeability in Fig. 1b for the 600 nm film vs. aging time.

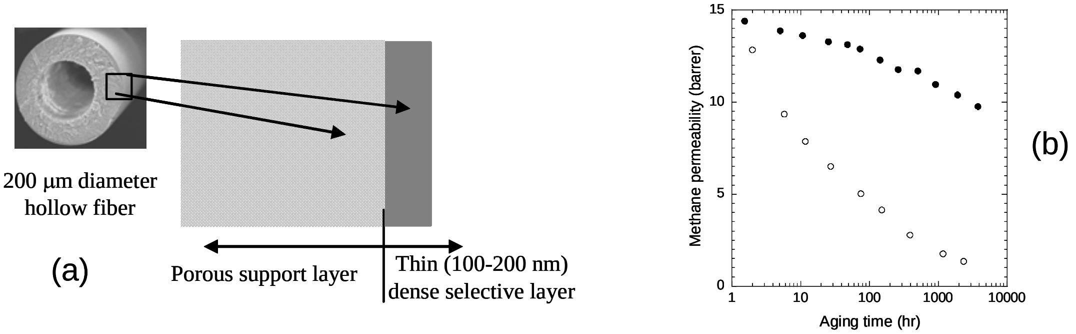

Figure 1.(a) Typical asymmetric hollow fiber membrane with ultrathin selective layer supported on an open cell porous layer, which also has untrafine submicron porous features; (b) Methane permeabilities in 6FDA-DAM:DABA (2:1) crosslinkable films of 49 µm thickness (●) and 600 nm thickness (○).

Our work is probing the effects of the nature of the specific polyimide backbone and different thermal exposure conditions on the response of (i) polyimides *without* the ability to be crosslinked, (ii) polyimides that are capable of being crosslinked (but *are not yet crosslinked*), and (iii) *actual crosslinked samples*. The three above types of samples have been characterized not only using direct sorption and transport properties but also by x-ray scattering and spectroscopic ellipsometry. Results have been analyzed in terms of loss of free volume during aging. The effects of selective layer thicknesses on the above properties have also been probed as functions of time for samples heated above the glass transition temperature (Tg). An interesting effect due to decarboxylation-induced crosslinking of the precursor crosslinkable polymer was shown to provide similar stability to that achieved via the ester crosslinking treatment against swelling-induced loss in properties. While useful for thin *dense films*, heating above Tg may not be viable for the complex asymmetric thin skinned structures shown in Fig. 1a, since the supporting porous layer might densify upon passage above the Tg and destroy the high productivity graded morphology critical to the functioning of such membranes.

Notwithstanding these concerns, the fundamental aging and gas separation properties of crosslinked structures formed via these two quite different approaches is being compared to understand the impact of subtly different approaches to induce crosslinks into a rigid organic glass.

Science objectives for 2008-2009:

- Complete the plasticization-resistance and aging studies using high temperature decarboxylation induced crosslinking for polyimides containing only carboxylic acid groups (i.e. not using diol monoester treatments to crosslink these groups)
- Explore lower temperature (sub-Tg) catalytic esterification crosslinking of monoester-capped carboxylic acid groups in order to minimize morphology disruption in future asymmetric crosslinked membranes for use with aggressive swelling and plasticizing feeds
- Compare intrinsic transport performance, plasticization resistance to aggressive feeds and physical aging tendencies of (i) thick dense films, (ii)thin dense films and (iii)asymmetric samples prepared via high temperature decarboxylation and lower temperature catalytic esterification.
- Continue to study the effects of high-pressure CO_2 conditioning on the free volume of the crosslinkable and crosslinked polymers.

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Exploring New Methods and Materials in the Formation of Selective, High-Flux Membranes for CO_2 Removal

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Overall research goals: The first objective of this work is to examine the utility of atom transfer radical polymerization for growing ultrathin membrane skins containing poly(ethylene glycol) (PEG) side chains. Such membrane skins are attractive for the selective removal of CO_2 from H_2 streams. The second objective is to examine the crystallization of thin films of poly(ethylene glycol methacrylates) and develop new techniques for disrupting crystallization to maintain high gas permeability.

Significant achievements in 2006-2008: Removal of contaminant gases (e.g., CO_2, H_2O and H_2S) from H_2 streams produced by hydrocarbon steam reforming and a subsequent water-gas shift reaction is vital in current methods of H_2 production. PEG-containing membranes are especially attractive for CO_2 removal from H_2 streams because of the high CO_2 solubility in PEG, but such polymers have not been prepared as the ultrathin materials that are needed to achieve practical fluxes. We are developing new methods to grow PEG-containing films as the ultrathin (<50 nm) skins of composite membranes. Atom transfer radical polymerization of poly(ethylene glycol methylether methacrylate) (PEGMEMA) from the surface of a porous membrane support yields a composite membrane with an ultrathin PEGMEMA skin. Our recent synthetic work shows that with an appropriate catalyst, 100 nm-thick PEGMEMA films can be polymerized in less than 30 min. Figure 1 shows the SEM image of a relatively thick PEGMEMA film grown on a porous alumina substrate. Remarkably, these films show a CO_2/H_2 selectivity of 7, which is essentially the selectivity of amorphous PEG.

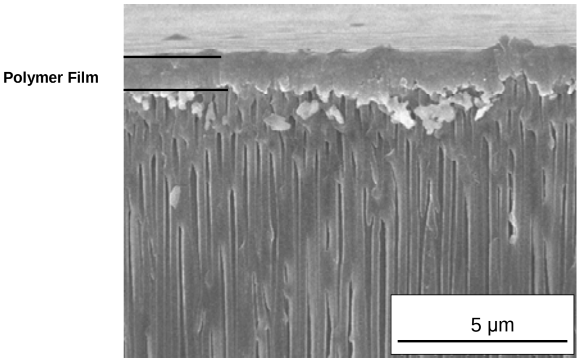

Figure 1. Composite membrane formed by polymerization of PEGMEMA (n=22-23) from porous alumina.

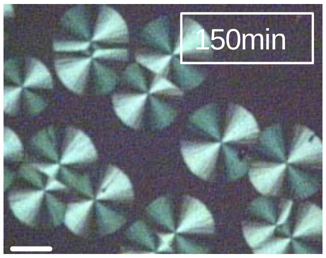

Figure 2. Optical micrograph of spherulites formed in a 240 nm thick PEGMEMA film at 23 °C. The samples are viewed using crossed polarizers, and the scale bar represents 100 μm.

However, membrane permeability rapidly decreases with time because the PEG sidechains, which contain 22 to 23 ethylene oxide repeat units, rapidly crystallize. The image in Figure 2 demonstrates the widespread crystallization of PEGMEMA films that occurs just 150 minutes after exposure to water. Crystalline regions, which are represented by spherulites, are highly impermeable to gases. Although crystallization is reversible and can be removed by immersion of the membrane in water, this is not a practical scenario for membrane use. Thus, future work will focus on further development of the controlled synthesis of PEGMEMA and methods to decrease crystallization.

Science objectives for 2008-2009:

- Efforts will continue to refine the growth of PEGMEMA brushes from surfaces using atom transfer radical polymerization. This will include new methods of attaching initiators to both polymeric and alumina supports.
- Several methods designed to decrease the extent and rate of PEG crystallization will be investigated. These will include incorporation of cross-linkable monomers, inclusion of nanoparticles and salts such as NaF in films, and examination of shorter PEG side chains.
- Membrane permeabilities will be examined over a wide temperature range, as CO_2/H_2 selectivity increases with decreasing temperature. Crystallization will also be examined as a function of temperature.

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Atomic- and Molecular-Resolution Chemical Imaging Tools

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Overall research goals: We are developing new tools that combine the atomic-resolution imaging of scanning tunneling microscopes (STMs) with well-established electronic and vibrational spectroscopies involving photons in the visible (and near-UV) and the vibrational infrared. These will enable us to relate structure and environment with chemical, physical, and optical properties and with function of molecules, supramolecular assemblies, and nanostructures. New (highly automated) methods of data acquisition and analysis yield statistically significant data sets that will be used to determine the key control parameters of properties, spectra and function of the nanostructures and assemblies studied.

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Significant achievements in 2007-2008: We have constructed three high-resolution STMs in which we will measure either absorption or emission of light simultaneously with topography and tunneling spectra. All of these have molecular resolution or better. We have developed new tools for acquiring and analyzing STM data.

We have applied one of these instruments and these new tools to the (first) measurements of the reversible photoisomerization of single tethered azobenzene molecules.[1] These molecules are placed in controlled chemical environments in order to avoid competing effects such as changes in the hybridization of the molecule-surface bond (which would mimic photoisomerization).

Preliminary experiments on assemblies of these functional molecules indicate that the efficiency drops substantially when there is steric hindrance (due to the matrix), or when these molecules are clustered in either one or two dimensions. We will explore this dramatic effect in upcoming work.

We have isolated donor-acceptor triads in self-assembled matrices, and resolved the submolecular structures within these molecules. In upcoming work, we will measure the intrinsic photoconductance of these molecules.

Science objectives for 2008-2009:

- Measure the intrinsic photoconductance of single molecules in well-defined environments that have been measured with molecular resolution.
- Measure the vibrational spectra of single molecules.
- Determine coupling of adjacent and nearby molecules and nanostructures upon photoexcitation in photoisomerization and photoconductance.

References to work supported by this project 2007-2008:

1. A. S. Kumar, T. Ye, T. Takami, B.-C. Yu, A. K. Flatt, J. M. Tour, and P. S. Weiss, Reversible Photo-Switching of Single Molecules in Controlled Nanoscale Environments, *Nano Letters,* in press.

Nanporous Structures for High Speed Size- and Functionality-Selective Chemical Separations

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Overall Research Goals: The primary goal of the work supported during this Grant cycle has been to develop comparatively high surface area nanoparticle and inverse opal structures that can act as support materials for the polymer surface chemistry we have developed in previous cycles. We create and control chemically selective interfaces by growth of discrete molecular layers (ca. 30 Å/layer) of monomeric or polymeric materials onto optically- or electrochemically addressable substrates. The use of nanoparticles is well developed and the formation of inverse opal structures is still in an evolutionary process.

Significant Achievements in 2005 – 2008:

Controlled growth of AuNPs. We have evaluated amines as reducing agents in the formation of gold nanoparticles.[1] We are interested in using AuNPs in chemical sensing devices and as a probe of local environment because of their wide availability and the consequent ability to form controlled-size nanoparticles *in situ* in a variety of environments, including biological systems. The reaction scheme we utilize is:

$$HAuCl_4 + 3\ NR_3 \rightarrow Au^0 + 3\ NR_3^{+\bullet} + H^+ + 4Cl^-$$

We can predict whether or not amines will function as reducing agents in this reaction based on their redox properties. The kinetics of AuNP formation can be understood in terms of Marcus electron transfer theory, where the slower reactions proceed in the inverted region owing to the difference between the Au reduction potential and the amine oxidation potential. For certain amines, after reduction of $HAuCl_4$ a subsequent reaction of the amine radical cation with other reducing agents in solution forms poly(amine)s. These findings point to the utility of amines as reducing agents in AuNP formation and provide information on the conditions under which these reactions proceed.

We have also used poly(allylamine) (PAH) as a reducing agent for the controlled formation of AuNPs.[2] The formation of AuNPs using this water-soluble polymer matrix allows AuNPs to become imbedded in the polymer matrix. The kinetics of AuNP formation are pseudo first-order in [$HAuCl_4$] at room temperature and are controlled by the ratio of reducing agent to $HAuCl_4$. Additionally, at low PAH:$HAuCl_4$ mole ratios, the plasmon resonance wavelength can be controlled through the ratio of the reactants. TEM data demonstrate the relatively narrow size distribution of the AuNPs, and indicate that we have identified a thin film polymer matrix useful for selective chemical sensing, with the selectivity being determined by the surface chemistry we apply to the AuNPs.

Characterizing the viscoelastic properties of polymer films. We have designed and constructed an instrument to measure the viscoelastic properties of monomeric and polymeric monolayers. We use an impedance analyzer to measure the frequency-dependent complex impedance of a quartz crystal microbalance (QCM). The QCM frequency-dependent impedance depends not only on the mass loading of the device (resonance frequency), but also on the viscoelastic properties of the adlayer (resonance lineshape). We use an equivalent circuit model to extract viscosity, density and shear stiffness information on monolayers from the data. Our technique is extremely sensitive to the morphology of the adlayer bound to the QCM. Immersion of monolayer-coated QCMs in selected solvents modifies the adlayer viscoelastic properties substantially.[3]

Sensitive detection of organophosphates/phosphonates using surface-modified AuNPs. We have created a high surface area, chemically selective material for adsorption of organophosphates and organophosphonates (OPPs). Using silica microparticles as a substrate to bind surface-modified gold nanoparticles, we have created a material with a binding constant for the organophosphate diethylchlorophosphate (DECP) of $K \sim 2\text{x}10^6\ M^{-1}$.[4] The binding of OPPs to modified AuNPs appears as a spectral shift in the AuNP plasmon resonance. The sensitivity of this technique is limited by scattering losses in particle suspensions, and much of this sensitivity can be recovered by using solvents with a refractive index close to that of the silica particles.

The Zr-bisphosphonate (ZP) chemistry used to achieve selective adsorption of the OPPs is well understood in both the solid state and for interfaces. It is difficult to quantitate the ZP bond strength because the equilibrium for bond formation lies far to the right, but indirect estimates place it at > 60 kcal/mol under favorable conditions. It is important to consider what other compounds can complex with Zr^{4+} and whether or not Zr^{4+}, once complexed to a surface-bound phosphate, can be displaced by other metal ions. We have found that $Zr(RPO_3)^{2+}$ can form complexes with RSO_3^- and RCO_2^-, but these complexes are weaker than $Zr(RPO_3)_2$. While there may be slight differences in binding efficiency for the different OPPs, binding to Zr^{4+} is sufficiently strong in all cases that we do not observe preferential binding phenomena. Our AuNP-coated silica particles are class-selective rather than compound-specific.

The sensitivity of coated silica particles to OPPs was evaluated using DECP concentrations ranging from 5 nM to 5 mM. The plasmon resonance band maximum of the analyte-exposed silica gel was compared to that of non-exposed silica gel to determine magnitude of the plasmon resonance band shift. At DECP concentrations below 0.5 µM, the plasmon resonance band does not shift outside the spectral resolution of the measurement. For DECP concentrations higher than 0.5 µM the modified AuNP plasmon resonance blue shifts, indicating complexation.

The signal-to-noise ratio (S/N) of the plasmon resonance spectra for silica gel-AuNP suspensions in ethanol is 5.8, with a background of ca. 2.5 absorbance units. This large background is due to scattering losses from the silica particles. Using a solvent system that is better matched to the refractive index of the silica particles reduces the scattering background. The refractive index of silica gel is approximately 1.46, and with DMSO as the solvent, (n = 1.48), we obtain a seven-fold decrease in background signal compared to ethanol (n = 1.36).

References of work supported by this project:

1. Newman, J. D. S.; Blanchard, G. J., Formation of Gold Nanoparticles Using Amine Reducing Agents. *Langmuir* **2006,** 22, (13), 5882-5887.
2. Newman, J. D. S.; Blanchard, G. J., Formation of Gold Nanoparticles Using a Polymeric Amine Reducing Agent. *Journal of Nanoparticle Research* **2007,** 9, 861-868.
3. Newman, J. D. S.; Roberts, J. M.; Blanchard, G. J., Optical Organophosphate/ Phosphonate Sensor Based Upon Gold Nanoparticle Functionalized Quartz. *Analytica Chimica Acta* **2007,** 602, 101-107.
4. Newman, J. D. S.; Roberts, J. M.; Blanchard, G. J., Optical Organophosphate Sensor Based Upon Gold Nanoparticle Functionalized Fumed Silica Gel. *Analytical Chemistry* **2007,** 79, 3448-3454.

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