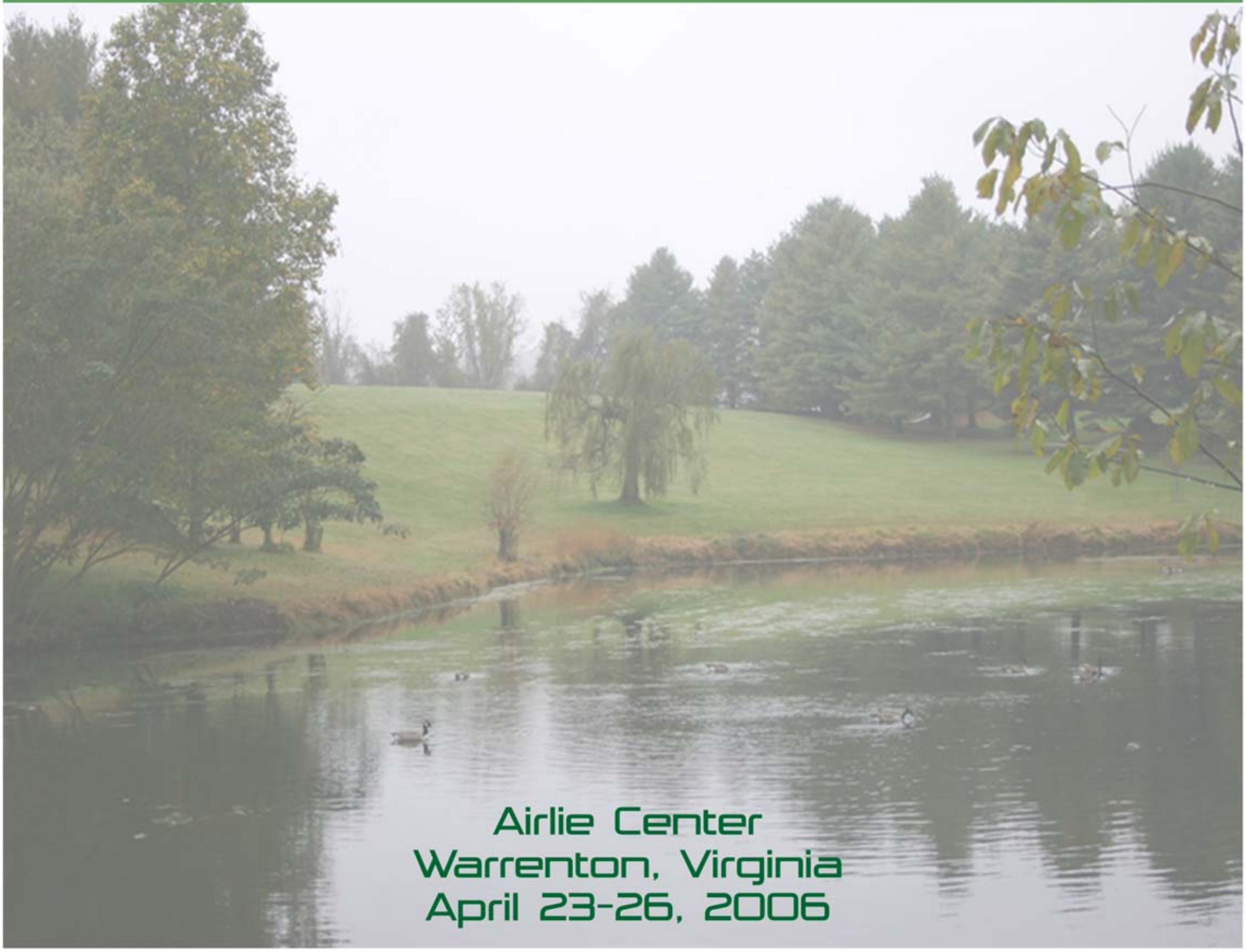
2006 Analysis Research Meeting



Airlie Center
Warrenton, Virginia
April 23-26, 2006

U.S Department of Energy
Office of Basic Energy Sciences

FOREWORD

This abstract booklet provides a record of the 2006 U.S. Department of Energy (DOE) Analysis Contractors' Meeting. 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 keynote talks, oral presentations, and posters; 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 have the privilege of organizing this joint meeting and of serving as the managers for the research program. In carrying out these tasks, we learn from the achievements and share the excitement of the research of the many sponsored scientists and students whose names appear on the papers in the following pages. We also hope that this meeting will enhance your research efforts and will nurture future collaborations and initiatives.

We thank all of the researchers whose dedication and innovation have advanced our research and made this meeting possible and, we hope, productive. We 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 Sophia Kitts and Angie Lester of the Oak Ridge Institute for Science and Education for the technical and logistical features of this meeting.

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Analysis Contractors' Meeting
-Agenda-

Arlie Conference Center
Warrenton, Virginia
April 23-26, 2006

Sunday, April 23

3:00-6:00 p.m.	Registration
6:00 p.m.	Reception at the Pub (No Host)
7:00 p.m.	Dinner
8:00 p.m.	Introductory Remarks: William Millman, DOE Basic Energy Sciences

Session I
Chair: Bob Shaw, Oak Ridge National Laboratory

8:10 p.m.	*Nanoscale Spectroscopy with Optical Antennas* Invited Speaker - Lukas Novotny, University of Rochester

Monday, April 24

7:30 a.m.	Breakfast
8:45 a.m.	Introductory Remarks: William Millman, DOE Basic Energy Sciences

Session II
Chair: Jean Futrell, Pacific Northwest National Laboratory

9:00 a.m.	*Driving Mass Spectrometry Forwards* Invited Speaker - R. Graham Cooks, Purdue University
10:00 a.m.	Break
10:30 a.m.	*Activation and Dissociation of Large Ions in Mass Spectrometry* Julia Laskin, Pacific Northwest National Laboratory
11:00 a.m.	*The Dynamics and Thermodynamics of Gaseous Macro-ions* Scott A. McLuckey, Purdue University
11:30 a.m.	*Understanding the Electrochemistry of the Electrospray Ion Source* Gary J. Van Berkel, Oak Ridge National Laboratory
12:00 p.m.	Lunch
3:00-5:00 p.m.	Poster Session
5:00 p.m.	Reception
6:00 p.m.	Dinner

Session III

Chair: Ben Smith, University of Florida

7:00 p.m.	*Ion Sampling and Transport in Plasma Source Mass Spectrometers* Paul Farnsworth, Brigham Young University
7:30 p.m.	*Fundamental Studies of the Inductively Coupled Plasma and Glow Discharge as Analytical Sources* Gerardo Gamez, Indiana University
8:00 p.m.	*Fundamental Studies of Gold Nanoparticles as MALDI Matrices* David H. Russell, Texas A&M University

Tuesday, April 25

7:30 a.m.	Breakfast

Session IV

Chair: Randall Winans, Argonne National Laboratory

8:30 a.m.	*Fluorescence Labeling of Surface Species (FLOSS) As a Probe of Chemical Composition of Complex Interfaces* Eric Borguet, Temple University
9:00 a.m.	*Spectroscopic Methods to Characterize Adsorption or Binding to Immobilized Ligands* Joel M. Harris, University of Utah
9:30 a.m.	*Laser-Surface Interactions Relevant to Analytic Spectroscopy of Wide Band Gap Materials* J. Thomas Dickinson, Washington State University
10:00 a.m.	Break
10:30 a.m.	*Ion Formation and Fragmentation in UV and IR Soft Laser Desorption Ionization* Akos Vertes, George Washington University
11:00 a.m.	*Laser-Material Interactions (ablation) for Chemical Analysis* Richard E. Russo, Lawrence Berkeley National Laboratory
11:30 a.m.	Lunch

Session V

Chair: Richard E. Russo, Lawrence Berkeley National Laboratory

1:00–2:00 p.m.	*Progress in Chemical Analysis Through Sample Engineering: New Challenges, Opportunities, and Paradigms of 21st Century LIBS* Invited Speaker - Andrzej W. Miziolek, Army Research Laboratory
6:00 p.m.	Dinner

Session VI

Chair: Joel M. Harris, University of Utah

7:15-9:00 p.m.	Opportunities and New Directions in Analysis Research

Wednesday, April 26

7:30 a.m.	Breakfast

Session VII

Chair: Gary J. Van Berkel, Oak Ridge National Laboratories

8:30 a.m.	*Chemistry and Microphysics of Small Particles* Alla Zelenyuk, Pacific Northwest National Laboratory
9:00 a.m.	*A Fundamental Study of Transport within a Single Nanoscopic Channel* Richard M. Crooks, University of Texas at Austin
9:30 a.m.	*Chemical Analysis at Nanodomains: Structure-Function Relationships* Marc D. Porter, Ames Laboratory
10:00 a.m.	Break
10:15 a.m.	*Bidimensional Liquid Chromatography* Georges Guiochon, University of Tennessee
10:45 a.m.	*Experimental Studies of Photoacoustic and Photothermal Effects* Gerald J. Diebold, Brown University
11:15 a.m.	Concluding Remarks: William Millman, DOE Basic Energy Sciences
11:30 a.m.	Lunch (Optional Boxed Lunches Available)

POSTER PRESENTATIONS
Session: Monday, April 24, 3:00-5:00 p.m.

Nanoparticle Imaging at Surfaces
Robert W. Shaw, William B. Whitten, and Kent A. Meyer
Oak Ridge National Laboratory

Modeling and Application of the Laser Induced Plasma
J. D. Winefordner, B. W. Smith, N. Omenetto, and I. B. Gornushkin
University of Florida

Facilitation of Chemical Sciences at BESSRC CAT
Randall E. Winans and Jan P. Hessler
Argonne National Laboratory

Electrochemically-Modulated Separation of Uranium and Plutonium
Douglas C. Duckworth, William J. Clark, Jr., Gary J. Van Berkel, and Debra Bostick
Oak Ridge National Laboratory

Enhancement of the Analytical and Fundamental Utility of Radio-Frequency Ion Trap Mass Spectrometers by Development of a Comprehensive Model
Douglas E. Goeringer, Oak Ridge National Laboratory

Chemical Microscopy of Conjugated Organic Macromolecules
Michael D. Barnes, Paul M. Lahti, D. Venkataraman, Todd Emrick
University of Massachusetts-Amherst
Bobby G. Sumpter
Oak Ridge National Laboratory

Nanoscale Spectroscopy with Optical Antennas

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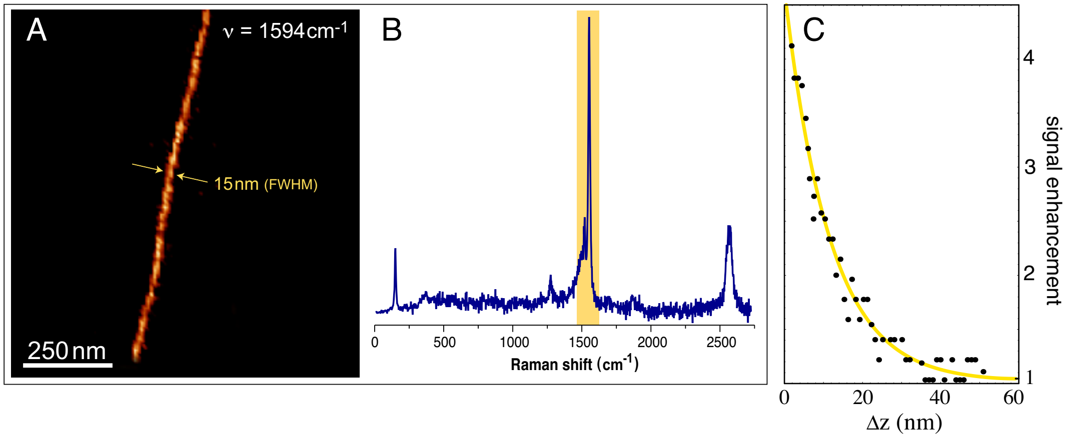
In optics, lenses and mirrors are used to redirect the wavefronts of propagating optical radiation. But because of diffraction, propagating radiation cannot be localized to dimensions much smaller than the optical wavelength. Borrowing concepts developed in the radiowave and microwave regime, we use antennas to localize optical radiation to length-scales much smaller than the wavelength of light. We place a laser-irradiated optical antenna, such as a bare metal tip, a few nanometers above a sample surface in order to establish a localized optical interaction and a spectroscopic response (fluorescence, absorption, Raman scattering, ..). A high-resolution, hyperspectral image of the sample surface is recorded by raster-scanning the antenna pixel-by-pixel over the sample surface and acquiring a spectrum for each image pixel. This type of near-field optical spectroscopy has been applied to map out phonons and excitons in individual single-walled carbon nanotubes (SWNT) with a resolution of 10nm [1]. The method is able to resolve defects in the tube structure as well as interactions with the local environment.

The proximity of the antenna influences the local light-matter interaction and affects the selection rules, the quantum yield, and momentum conservation. Using the fluorescence from a single molecule we are investigating these effects and we characterized the trade-off between fluorescence enhancement and fluorescence quenching as a function of the separation between the antenna and the molecule [2].



Near-field Raman imaging of single-walled carbon nanotubes. The image has been recorded by raster-scanning the sample underneath a laser-irradiated metal tip (antenna) and integrating, for each image pixel, the photon counts that fall into a narrow spectral bandwidth centered around the G-line at $\nu = 1594\,cm^{-1}$ *(indicated by the yellow stripe in B). (B) Raman scattering spectrum recorded on top of the nanotube, (C) Enhancement of the G-line signal as a function of tip-sample distance.*

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[2] P. Anger, P. Bharadwaj, and L. Novotny, “Enhancement and quenching of single molecule fluorescence,” *Phys. Rev. Lett.* **96**, in print (2006).

Driving Mass Spectrometry Forwards

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Summary of presentation

This presentation has three aims. One is to report on particular developments in mass spectrometry at Purdue; the second is to identify features that help drive forward an instrumentally intensive subject like mass spectrometry, and the third is to offer some particular suggestions regarding the impact of the new capabilities of mass spectrometry in fundamental and applied energy science.

Developments/discoveries/instruments

A number of recent discoveries and inventions will be covered. They include new methods of creating ions, new methods of investigating ion chemistry and thermochemistry, and studies on particular chemical systems of importance.

(a) New ionization methods

Desorption electrospray ionization (DESI) is a generally applicable method of ionization of condensed phase samples which operates in the ambient environment at high speed without need for sample preparation. It is applicable to proteins, lipids, alkaloids and small polar and non-polar compounds. The optimization of the experiment and its application to a variety of problems is described. Electrosonic spray ionization (ESSI) is a very gentle variant on electrospray ionization (ESI) and like ESI it is applicable to samples in the solution phase. This experiment can be used to create gas phase protein ions without (immediate) loss of biological activity.

(b) Ion chemistry in the ambient environment

Experiments have been developed in which the reactivity of ions is studied in the ordinary ambient environment. These experiments include thermal evaporation of neutrals followed by ionization and direct sublimation of solids to give organic ions.

(c) Miniature mass spectrometers

Miniature handheld tandem mass spectrometers based on ion trapping in rectilinear ion traps have been built and characterized. These instruments allow in situ air and water analysis for organic constituents.

(d) Thermochemical and chiral determinations

The dissociation of cluster ions provides a readily implemented method of making approximate thermochemical measurements. The procedure is applicable also to the measurement of chiral purity, using suitable chiral reference compounds.

(e) Explosives and drug monitoring

The new miniature instruments and ambient ionization methods allow very rapid analysis of ordinary surfaces for explosives, drugs, pollutant residues and other compounds of interest in forensics and environmental remediation.

(f) Preparative mass spectrometry

Use of gentle ionization methods in conjunction with ion soft landing on surfaces allows preparation of pure materials by mass spectrometry. This has been demonstrated for small and large molecules.

Facilitating features

An important aspect of this presentation is the attempt to delineate factors which facilitate research progress in an instrumentally intensive area like mass spectrometry. The following have been identified as being particularly important: (a) Infrastructure - facilities but more especially personnel- to allow new instrumental ideas to be tested. (b) Opportunities for collaborations across the disciplines. (c) Organizational structures that foster commercialization of ideas. (d) Opportunity for open-ended instrument development.

Opportunities for energy research

Exploring the outer limits of mass spectrometry appears to offer significant advantages in energy research. Basic energy sciences would be positively impacted by the ability to create new types of materials, in ultra-high purity, by new routes as is possible by using mass spectrometry to deliver molecules (or well-defined clusters) to particular positions on surfaces by the process of soft landing. Nanofabrication in 3D by on the micro- to nanoscale is within range. The same methodology could be used to construct and deposit catalyst mimics for high throughput exploration of mechanism and activity as a function of composition and conditions.

The ability to perform mass spectrometry in the ambient environment, without sample preparation, should have enormous impact on the ease and speed of characterization of organics, inorganics and metals. Applications could include searches for energy sources, understanding pollution and its migration patterns, in situ analysis of manufacturing processes aimed at minimizing waste and increasing energy efficiency and remediation activities. These long-standing objectives will become feasible with the availability of miniaturized ambient mass spectrometers.

Activation and Dissociation of Large Ions in Mass Spectrometry

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Collaborators. Jean Futrell, PNNL; Graham Cooks, Purdue University; Ivan Chu (Hong-Kong U); Raphy Levine (Hebrew U); Hai Wang (USC); Paul Mayer (U Ottawa); Richard O'Hair (U Melbourne); Murray Johnston (U Delaware); Bill Hase (Texas Tech).

Overall research goals. The purpose of our research is to achieve a fundamental understanding of the reaction kinetics and dynamics of activating and dissociating complex molecular ions. These processes are the scientific foundation for tandem mass spectrometry, one of the most important analytical methods developed in the last century. Our studies provide fundamental information on the factors that influence collisional activation of complex ions, leading to optimization of ion activation methods for tandem mass spectrometry.

Specific objectives for 2005-2006. (1) Continue studies of the fragmentation energetics and dissociation mechanisms of selected model peptides using RRKM modeling of experimental fragmentation efficiency curves; (2) Conduct first studies of the energetics and dynamics of dissociation of peptide radical cations; (3) Explore what factors affect soft landing of peptide ions on surfaces; (4) Study SID of singly protonated ions generated by MALDI to explore the effect of the size of the ion on dissociation rates.

Significant Achievements:

Energetics and Mechanisms of Peptide Fragmentation

We used dissociation of angiotensin analogs to demonstrate that detailed analysis of time- and energy-resolved SID data (TFEC) can provide a consistent mechanistic description of peptide fragmentation in tandem mass spectrometry. We showed that dissociation of these peptides is dominated by loss of ammonia from the precursor ion followed by proton mobilization resulting in formation of highly excited ion that can access a variety of non-specific dissociation pathways with very high rate constants.

Detailed modeling was used to determine the energetics and dynamics of seven primary dissociation channels protonated leucine enkephalin – a well-studied model peptide commonly used as a "thermometer" ion for characterization of internal excitation of gas phase biomolecules. Comparison with Arrhenius activation energies of the two lowest-energy dissociation channels reported in the literature demonstrated for the first time the reversal of the order of activation energies as compared to threshold energies for dissociation.

Soft-Landing of Peptide Ions onto Self-Assembled Monolayer Surfaces

In collaboration with Graham Cooks's group at Purdue we conducted first systematic study of several factors that affect soft landing of peptide ions on SAM surfaces. Peptide ions are particularly attractive model systems that provide important insights on the behavior of soft landed proteins. Fundamental principles derived from such studies of interaction of protonated peptides with hydrophobic surfaces are relevant to transport of biomolecules through membranes in living organisms. We presented evidence that peptide ions retain at least one proton after SL on FSAM or HSAM surfaces. Quantitative investigation of the effect of the initial kinetic energy of peptide ions on SL demonstrated that in the range of collision energies from 0 to 150 eV SL deposits intact ions on surfaces. Most of our findings were rationalized using the hard-cube model. For example, the decrease of the SL efficiency with increase in collision energy is well reproduced using this model. Lower SL efficiency on the HSAM surface is attributed to somewhat weaker binding of ions to the surface with lower polarizability, while the slow decay of the sputtered signal with time can be rationalized as a slow physisorption of ions from a potential well of ca. 20 kcal/mol dominated by electrostatic forces. We suggested that ions are oriented with their charged residues to the surface to maximize their binding energy. Larger SL efficiencies observed for doubly protonated as compared to singly protonated ions is in good agreement with this model.

First AFM study of surfaces modified by SL utilized atomically flat gold on mica substrates. Two types of small features were observed on the surfaces following SL. The size of the features observed in AFM is consistent with the simple model used to estimate the interaction force between neutral or charged peptide and the AFM tip. Smaller (<1 nm in height) features correspond to neutral peptide molecules while larger spots (~2.5-4 nm high) correspond to adsorbed peptide ions.

Plans for future research on this project. (1) Conduct first studies of energy and entropy effects in dissociation of non-covalent complexes; (2) Continue studying dissociation of peptide radical cations with an objective to understand the effect of the charge on the energetics, dynamics and mechanisms of peptide fragmentation; (3) Study the effect of surface roughness on the energy transfer and the scattering efficiency in ion-surface collisions; (4) Install and test a new in-line Cs^+ gun on our FT-ICR machine and continue studies of the fundamental aspects of soft-landing of peptide ions on a variety of surfaces; (5) Conduct first maximum entropy calculations for quantifying shattering transition in SID.

Publications Acknowledging DOE Support – 2004-06

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2. J. Laskin, K.M. Beck, J.J. Hache, J.H. Futrell "Surface-Induced Dissociation of Ions Produced by Matrix-Assisted Laser Desorption Ionization in a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer" *Anal. Chem.*, **76**, 351-356 (2004)
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11. J. Laskin, T.H. Bailey and J.H. Futrell "Mechanisms of Peptide Fragmentation from Time-and Energy-Resolved Surface-Induced Dissociation Studies: Dissociation of Angiotensin Analogs", Int. J. Mass Spectrom., 249–250 (2006) 462–472
12. J. Laskin "Energy and Entropy Effects in The Gas Phase Dissociation of Peptides and Proteins", in press [Book chapter]
13. Y. Fu, J. Laskin, and L.-S. Wang "Collision Induced Dissociation of [4Fe-4S] Cubane Cluster Complexes: $[Fe_4S_4Cl_{4-x}(SC_2H_5)_x]^{2-/1-}$ (x = 0 - 4), Int. J. Mass Spectrom., in press
14. F. M. Fernandez, V.H. Wysocki, J.H. Futrell and J. Laskin "Protein Identification via Surface-induced Dissociation in an FT-ICR Mass Spectrometer and a Patchwork Sequencing Approach.", J. Am. Soc. Mass Spectrom., in press.
15. J. Laskin "Fragmentation Energetics of Protonated Leucine Enkephalin from Time-and Energy-Resolved Surface-Induced Dissociation Studies", J. Phys. Chem. A, in press.

The Dynamics and Thermodynamics of Gaseous Macro-ions

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Overall research goals: To understand 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. Particular emphasis is being placed on the reactions of oppositely charged ions because the novelty of this chemistry provides rich opportunities for fundamental studies.

Significant Achievements for 2004-2006:

Reactions of multiply-charged ions of opposite polarity. We have conducted experiments and modeled the dynamics of the reactions of multiply-charged positive molecule-ions with multiply-charged negative molecule-ions. A key finding was that the rate determining step for the reaction appears to be the formation of an electrostatically bound ion pair, consistent with the Thomson three-body interaction. The formation of an ion pair, however, can take place at distances too far for chemistry to occur, depending upon the trajectory of the orbiting pair. Highly elliptical orbits, for example, can bring the two ions within sufficiently close proximity for proton (or electron) transfer to occur at an avoided crossing on the energy surface or sufficiently close for the ions to undergo an intimate collision. If charge transfer occurs at a crossing point, the attractive field of the ion pair is reduced such that some of the products can escape from one another and appear as partial charge transfer products. Regardless of the degree of eccentricity of the orbit, both tidal effects and collisions can collapse the trajectory of the bound ion-ion orbit to the point at which chemistry can occur.

Metal Ion Insertion/Removal and Peptide Cations. A major portion of the thesis work of Kelly A. Newton was devoted to the development of ion/ion reactions that enabled the replacement of protons in polypeptide ions with metal ions, including transition metals. The overall motivation for the work is to develop a capability for manipulating the make-up of the cationizing species associated with a polypeptide ion that is independent of the initial means for forming the ions. A general approach is to incorporate the metal ion in a negative singly charged metal-ligand complex that can be reacted with the polypeptide cation. A general net reaction can be written as:

$$[M+nH]^{n+} + [Me_mL_{m+1}]^- \nearrow [M+(n-1)H]^{(n-1)+} + HL + mMeL \qquad (1)$$

$$[M+nH]^{n+} + [Me_mL_{m+1}]^- \searrow [M+(n-x)H + (x-1)Me]^{(n-1)+} + xHL + (m-x+1))MeL \qquad (2)$$

where Me represents a metal and L represents a ligand and where x can range from 1 to (m+1). Reaction (1) represents a competitive process (i.e., proton transfer at a crossing point without subsequent formation of a long-lived complex) that does not result in the transfer of a metal ion whereas reaction (2) represents the transfer of one or more metal ions. Reaction (2) represents a pathway that includes formation of a long-lived complex, from which several product types can be produced. An overall paradigm for the process was proposed and evaluated using *ab initio* calculations to determine the relative energetics associated with the various reaction channels from the complex. This line of reasoning led to the hypothesis that the hexafluorophosphate anion, PF_6^-, might be used to remove metal ions from polypeptides. This was subsequently demonstrated for sodium containing peptide cations.

Charge Inversion. We have been examining charge inversion via multiple proton transfers in a single ion/ion interaction. We demonstrated that two such steps can provide a means for increasing the charge state of an ion in the gas-phase. In the past two years, we have focused on the dynamics and thermodynamics of the positive-to-negative ion charge inversion of polypeptides. This work constitutes a major portion of the thesis of Min He.

Plans for future research on this project.

Electron transfer ion/ion reactions. Reagent ions that transfer electrons to polypeptide ions have been identified. This leads to structurally informative fragmentation and, therefore, will likely be significant in proteomics. We have already studied characteristics of the anion that affect the electron transfer probability. We are now turning our attention to the characteristics of the cation that affect both the competition between electron transfer and proton transfer as well as the extent of electron transfer without dissociation and electron transfer followed by dissociation.

General model for fragmentation from ion/ion reactions. We are also modelling fragmentation that results from ion/ion reactions following either proton transfer, electron transfer, or complex formation. This work is relevant to all classes of ion/ion reaction.

Charge inversion. We plan to focus attention of the negative-to-positive charge inversion reaction for polypeptide ions. The practical outcome of this work will be the identification of reagents that maximize efficiency and also afford a degree of control over the magnitudes of the various possible charges of the positively charged product ions.

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Understanding the Electrochemistry of the Electrospray Ion Source

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Overall Research Goals:

The objective of this project is to understand the fundamental electrochemical operation of the electrospray (ES) ion source used in conjunction with mass spectrometry (MS) with the goal of gaining control over the electrochemical processes to enhance the analytical utility of ES-MS.

Significant Achievements in 2003-2005:

Understanding the electrochemistry of the ES ion source required research efforts aimed at understanding mass transport to the emitter electrode surface, factors influencing the current at the emitter electrode, and factors influencing the interfacial potential at the emitter electrode. The understanding gained from these studies provided the insight for the design of a novel three-electrode emitter cell that was incorporated into an ES ion source. The cell included a porous flow through working electrode to enhance mass transport to the electrode, a very small area auxiliary electrode to limit the possibility of analyte electrochemistry at this electrode, and a potentiostat to control the working electrode interfacial potential. This new emitter cell provided the ability to control which electrochemical reactions take place in the emitter electrode. Thus, the identity and abundance of redox active analytes observed in the gas-phase by ES-MS can now be precisely controlled. This control is demonstrated by the data in Figure 1. These data demonstrate the

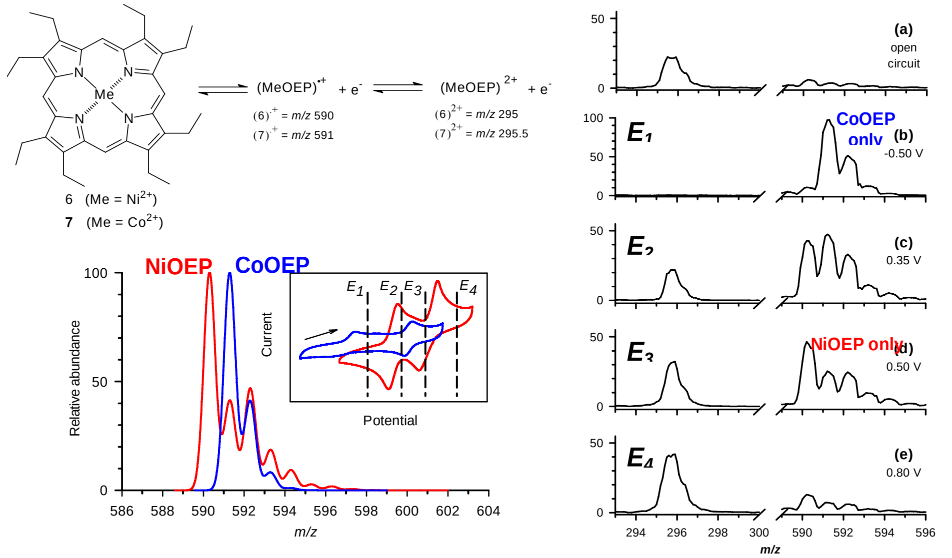

Figure 1. Electrochemical control of the abundance and identity of ions observed in the gas phase in ES-MS with a three-electrode controlled potential emitter cell..

ability to eliminate isobaric interferences in the analysis of a mixture of redox active analytes by electrochemically manipulating the ionic form of the various analytes in solution prior to their liberation into the gas-phase. This precise electrochemical ionization control is a new degree of freedom to be exploited for analytical benefit in the ES-MS experiment.

Specific Objectives for 2005-2006:

- Research on the electrochemistry of electrostatic sprayers will continue, but will shift in emphasis from the past studies focused on the fundamentals related to the direct heterogeneous electron transfer chemistry of the analytes under study in the ES-MS experiment to electrochemically initiated homogeneous chemical reactions.. This work will have two main goals: (1) To determine the influence of homogeneous reactions of electrochemically generated species on the resultant mass spectra under typical conditions used for ES-MS; (2) To determine the means to control and alter the homogeneous reaction chemistries for analytical benefit. The latter situation provides the opportunity to use homogeneous chemistries in the electrospray ion source to covalently tag analytes for enhanced detection and structure determination. These tagging studies will also include studies of the gas-phase fragmentation of the differently tagged analytes to develop tandem mass spectrometry approaches to the selective detection and structure determination of the tagged analytes.

- Fundamentals of the electrochemical formation and preservation into the gas-phase of multiply-charged ions formed by multiple electron gain and loss. Dissociation pathways and mechanisms for new types of ions will be studied (e.g., low mass n-mers of conductive polymers). These novel multiply-charged ions will also be exploited in gas-phase synthesis, ion/ion chemistry, and electron transfer dissociation studies.

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Ion Sampling and Transport in Plasma Source Mass Spectrometers

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Project Objective: The desired outcome of this research project is the development of a fundamental understanding of the flow of a weakly ionized gas through the differentially-pumped vacuum interfaces that are typically used in plasma source mass spectrometry. This fundamental understanding is critical for the characterization and optimization of the performance of inductively coupled plasma mass spectrometers, which are the premier tools for trace elemental analysis.

Significant Achievements to date:

1. Using planar laser-induced fluorescence imaging, we have created detailed maps of the densities of analyte species in the region upstream from the sampling cone of an ICP-MS, and across the diameter of the 1-mm sampling orifice. We have mapped densities of ground state atoms and ions and of excited state ions. A representative set of images is presented in Figure 1. By creating these maps for a range of plasma operating parameters and sample compositions, we have gained important new insights into the behavior of the ICP as an ion source.

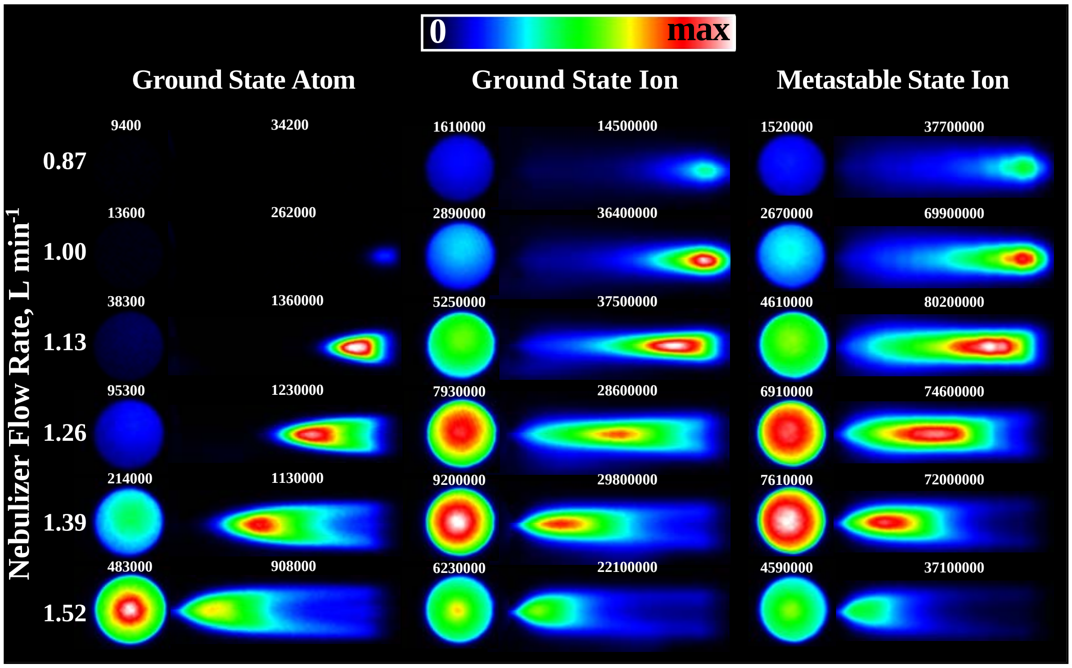

Figure 1. Maps of atom and ion densities in the region upstream from the sampling cone of an ICP-MS. The oblong images cover the 10 mm immediately upstream from the sampling cone. The circular images are of the 1-mm sampling orifice.

2. We have mapped flows of neutral argon in the supersonic expansion downstream from the sampling cone in an ICP-MS, including the barrel shock, the Mach disk, and the zone of silence. These data will serve as a baseline against which the flow patterns of charged species will be compared. They also provide an unambiguous measure of kinetic temperatures in the source upstream from the sampling cone.
3. We have conducted a series of experiments that demonstrate significant collision-induced changes in the composition of the plasma that occur in the first few mm of the supersonic expansion. These observations call into question the common assumption that the mix of ions reaching the mass analyzer in ICP-MS instruments is the same as the mix that exists in the plasma ion source.
4. We have documented a source of mass bias in the first vacuum stage of an ICP-MS that has been ignored in the ICP-MS literature.
5. We have developed and built a new differentially pumped interface that incorporates fluorescence probes in both the first and second vacuum stages. Simultaneous measurements in both regions will be essential as we study flow through the skimmer cone.
6. We have developed a Direct-Simulation Monte-Carlo code to simulate the flow in the first vacuum stage of an ICP-MS. Direct-Simulation Monte-Carlo is a good algorithm to use because it can handle the huge range of mean-free paths (10 microns to several millimeters) in this device. The code has been tested against the exact Chapman-Cowling theory of damped sound waves in a hard-sphere gas and good agreement has been obtained. It has also been tested against Bernoulli's law in the ICP geometry on the central axis in the region where the fluid equations should hold, and good agreement has again been found.

Goals for 2006-2007

1. Complete the comparison of neutral atom and ion flows in the first vacuum stage of the ICP-MS interface.
2. Begin measurements of flow through the skimmer cone in the ICP-MS interface and study the effects of space charge on ion beam formation downstream from the skimmer cone.
3. Incorporate mixed gas flows into the Monte Carlo simulation and use the simulation to develop a quantitative model of mass bias in the first vacuum stage.

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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: *ms-Pulsed Glow Discharge*. Recently, glow discharges (GD) operated in a power-pulsed mode have enjoyed increased attention because higher power levels can yield better analytical figures of merit. Also, they allow thermally labile sample analysis and speciation analysis via temporally resolved detection. However, pulsed GDs have not been as widely studied as their continuous-power counterparts; in fact, very little is known about their electron behavior. We have obtained for the first time spatially resolved gas-kinetic temperature (T_g), electron temperature (T_e) and electron number density (n_e) maps of an analytical ms-pulsed GD at different instants during the GD pulse. This has served to substantiate as well as question certain hypotheses on plasma fundamental mechanisms. For example, there is a decrease in n_e during the afterglow (5.1ms), compared to the plateau (4.9ms), which does not support the previously proposed mechanism (collisional radiative recombination) as the most significant for argon metastable formation. Higher thermalized electron energies were found in the prepeak (0.2ms), compared to the plateau, possibly as a result of slower primary electrons.

Effect of Mass Spectrometer Sampler on ICP. The ICP has become a popular ion source for mass spectrometry (MS). Yet, few studies have been performed to determine whether and how an ICP-MS sampling interface influences the plasma itself. It was unclear whether the plasma fundamental properties are affected upstream of the interface, a surprising fact considering the high gas flow taken in by the sampling-cone orifice, the relatively high thermal conductivity of the ICP, and the water-cooled metallic surface in contact with the plasma. Through the above-mentioned diagnostic techniques, we have found that T_e, n_e, T_g, analyte number densities and even matrix effects are affected by the presence of the MS sampler. Also, we found that the operating parameters (r.f. power, sampling depth, and central-gas flow rate) exert an influence on such effects. These findings show, for instance, that MS-based plasma diagnostic techniques are not directly comparable to methods that do not perturb the plasma.

Mechanisms of analyte excitation and their influence on matrix effects in ICP-AES. Matrix effects caused by a comprehensive list of elements (a total of fifty-one matrices) were evaluated using the recovery of ionic-to-atomic line intensity ratio and were correlated with various physical properties of the matrix elements. We discovered that matrix elements having low second (instead of the widely reported first) ionization potentials (IP) produce a stronger matrix effect in all cases. In addition, it was found that the presence or absence of low-lying energy levels in the doubly charged matrix ion is critical to the severity of the matrix effect. A clear transition in the severity of matrix effects was observed; matrices whose 2nd IPs fell below 15 eV (corresponding to the 1st IP of Ar – the main constituent of the ICP) exhibited the greatest interference. Penning ionization (i.e., the reaction $Ar^* + M \rightarrow M^{+*} + Ar + e^-$) was proposed as a dominant mechanism for analyte excitation and for causing matrix effects, in which the analyte and the matrix are competitors for Ar excited states. Also, second ionization of the matrix element is possible via Penning reaction for matrices with a low 2nd IP. Fast recombination between these doubly charged matrix ions and abundant electrons would provide a cycle that leads to effective quenching of Ar excited species;

this hypothesis is supported by the correlation found between the severity of the matrix effect and the presence of low-lying energy levels of the doubly-charged matrix ion. This scheme offers more possible reaction routes for Penning ionization, thereby increasing the overall quenching rate.

Charge-transfer excitation mechanisms in the ICP. A new method has been developed and verified for monitoring charge-transfer mechanisms in ICP-AES. This new technique, which exploits plasma-related matrix effects, is significantly faster and requires simpler instrumentation than previously available approaches. For instance, the charge-transfer behavior of only about fifteen elements was reported in the literature over the last two decades due to the complicated procedures and instrumentation required. The development of our new methodology has established the charge-transfer character of twelve additional elements in less than one year. The first experimental evidence for state-selective charge transfer in the ICP was reported and the similarity between core electronic configurations of two energy levels was shown to be critical in governing inter-multiplet mixing efficiency (and hence the efficiency of indirect charge transfer and the severity of matrix effects).

Plans for Future Research: *(1) Fundamental characterization of pulsed glow discharges.* Spatially resolved absolute emission maps of argon species will be obtained. Also, the temporal behavior of Ar_2^+ will be investigated to explore alternative mechanisms. *(2) Effect of trace-gas impurities on GD fundamental parameters.* Addition of small amounts of gases (H_2, N_2, etc.) has a significant effect on the GD characteristics and will be studied via laser scattering techniques. *(3) Mass spectrometer sampler effects on ICP*. The ICP fundamental parameters will be determined for different load-coil grounding configurations because they influence the occurrence of a secondary discharge between the plasma and the tip of the sampler. *(4) ICP analyte excitation and matrix effects.* Proposed mechanisms will be verified by two approaches: radial mapping of the excited-argon population and analyte excited states, and through the addition of mixed gases.

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Fundamental Studies of Gold Nanoparticles as MALDI Matrices

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The optical and electronic properties of nanoparticles, esp. gold nanoparticles (AuNPs), have been extensively investigated in recent years, and many applications are emerging in the fields of chemical physics and chemical biology. Importantly, these physical properties can be tuned as desired, as they are based on NP size, shape, composition, and surface derivitazation. Recently, we have demonstrated the utility of AuNPs as matrices for matrix-assisted laser desorption ionization (MALDI) mass spectrometry (MS).[1] Using 2, 5, and 10 nm AuNPs we have successfully ionized a number of peptides and small proteins and observed abundant ion signals in positive- and negative-mode UV MALDI. These alternative substrates offer a number of advantages over conventional MALDI matrices (*e.g.* small organic acids): (i) greater flexibility in sample deposition conditions (*e.g.* pH, solvents, etc.), (ii) relatively uncomplicated spectra in the matrix region (low mass range), (iii) Au-cluster species as internal standards for mass calibration, and (iv) AuNPs afford a very high shot-to-shot and spot-to-spot reproducibility (<10 % RSD). We present here further research to better understand fundamental nanoparticle chemistry and physics. Specifically, we have investigated how surface chemistry affects the MALDI ionization event. Surface association of species in solution (*e.g.* analytes, ions) and the solvent structure around these species have an effect on analyte interactions with the AuNPs, thus leading to changes in ionization efficiency. NPs prepared by the citrate reduction method have residual ions in solution (*i.e.* citrate) that adsorb to the NP surface and serve as electrostatic stabilizers. Citrate can be displaced by other anions (*e.g.* halides or oxyanions) as demonstrated here, and by others.[2] Better understanding of how surface chemistry affects MALDI will allow for the design of matrices towards specific applications, i.e. selective concentration of analytes prior to MS analysis or matrix incorporation into tissue samples, providing for *in vivo* imaging.

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Fluorescence Labeling of Surface Species (FLOSS) As a Probe of Chemical Composition of Complex Interfaces

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Overall Research Goals: The overall research goal is to study surface chemistry, in particular photon driven processes, at the level of single molecules. Two important objectives are chemical identification at the single molecule level and the ability to follow the dynamics of surface processes one molecule at a time.

Specific Research Goal:
To develop and use covalent attachment of fluorescent molecules to enable the identification and quantification of low concentrations of surface species. Surface functionalization is no longer restricted to the preparation of homogenous monolayers. Multicomponent systems are increasingly being used. However, determining the chemical composition of heterogeneous two-dimensional systems remains challenging. For example, how does one detect a low concentration of alcohol (-OH) functionality in a sea of carboxylic acid (-COOH) groups? We showed that by covalent fluorescent labeling of surface species (FLOSS), the inherent sensitivity of fluorescence spectroscopy can be exploited to identify and quantify very low concentrations of surface functional groups. The detection limit has been reduced from 10^{11} surface functional groups/cm^2 in the initial FLOSS paper to 10^9 groups/cm^2 (10 groups /μm^2). In principle single surface functional group identification is possible.

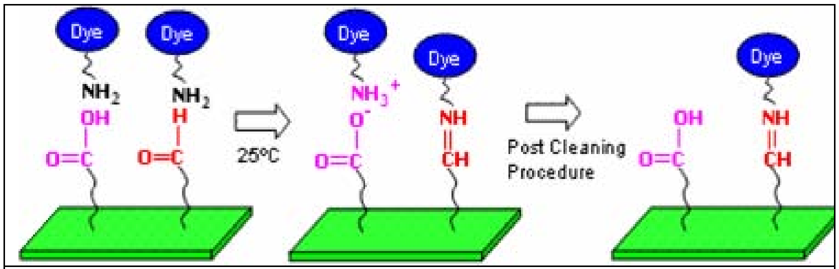

Figure 1 Chemical Specificity of FLOSS. The post reaction cleaning is effective in removing ionically bonded dyes from the surface. The presence of carboxyl groups on the surface does not affect detection of aldehyde groups using amino modified dyes.

FLOSS enables the identification of intermediates in the UV photoreactivity of self-assembled monolayers (SAMs), and the nature of oxygen containing functionality on carbon nanotubes (CNTs). The specificity of FLOSS for a particular functional group is key. Amino modified dyes can, in principle, bind to aldehyde and carboxyl groups, limiting specificity. However, the FLOSS protocol devised results in < 0.5 % carboxyl binding to amine groups. Therefore, the presence of carboxyl groups on the surface should have a limited effect on the detection of aldehyde groups by amine modified dye (Fig 1).

FLOSS showed the existence of COOH groups on activated carbon fibers (ACF) (Fig 2) and as-received CNTs (Fig 3) while concentrations CHO and OH groups on CNTs were under the FLOSS detection limit. Oxidative purification processes, used to remove metal catalyst particles and amorphous carbon, introduce more functional groups. Moreover, FLOSS showed that the functional groups are distributed heterogeneously on the nanotube surface (Fig 3). New functional groups favorably grew in proximity to each other, presumably at the defects sites introduced through the purification process, which was probed by the increase of dimer peak in fluorescence spectra.

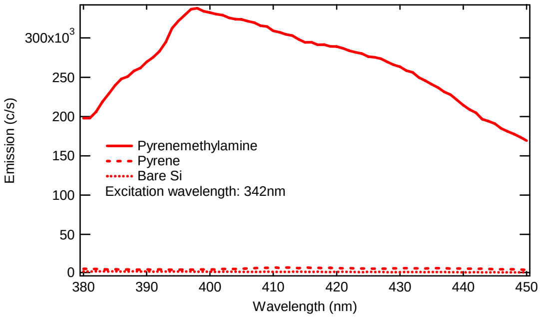

Figure 2. FLOSS for CHO groups on ACF surfaces. Emission spectra of pyrenemethylamine (solid), pyrene (dashed) reacted activated carbon fiber on silicon and bare silicon (dotted line).

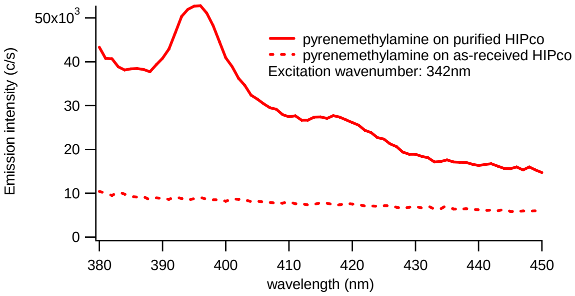

Figure 3 FLOSS spectra of pyrenemethylamine on purified (solid) & as-received (dashed) HiPco. Oxidative purification introduces aldehyde and ketone groups to the CNT surface.

Significant Achievements

We have reduced the detection limit of FLOSS so that we can identify surface bound chemical functional groups at densities as low as $10^9/cm^2$. This enables the intermediates of the UV photochemistry of alkylsiloxane self-assembled monolayers and the surface chemistry of carbon materials, such as activated carbon fibers (ACF) and carbon nanotubes (CNTs) to be identified. The presence of carboxyl groups does not affect the detection of aldehyde groups, confirming the specificity of FLOSS in the detection of aldehyde and amine groups.

"Plans for Future Research"

In the coming year we will focus on the extension of FLOSS towards single chromophore identification and quantification. We will pursue our goal of observation of observing the dynamics of photoactivated processes at the single molecule level.

"Related Publications Acknowledging DOE Support"

1. **The Specificity and Sensitivity of Fluorescence Labeling of Surface Species**
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2. **Detection of Low Concentration Oxygen Containing Functional Groups on Activated Carbon Fiber Surfaces through Fluorescent Labeling,** Xue Feng, Nikolay Dementev, Wenguo Feng, Radisav Vidic, and Eric Borguet, *Carbon 44, 1203-1209 (2006)*
3. **Mechanism of UV photoreactivity of alkylsiloxane self-assembled monolayers.**
   Tao Ye, Eric A. McArthur and Eric Borguet, *Journal of Physical Chemistry B 109(20), 9927-9938 (2005)*
4. **Fluorescence Detection of Surface Bound Intermediates Produced from UV Photoreactivity of Alkylsiloxane SAMs**
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Spectroscopic Methods to Characterize Adsorption or Binding to Immobilized Ligands

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The goals of this research are development of surface-sensitive spectroscopies for investigating chemical structure and reactions at liquid/solid interfaces. These spectroscopic tools are leading to understanding and control of interfacial chemistry that impacts both analytical methods (chromatography, solid-phase extraction, and sensors) and environmental transport and remediation (metal-ion complexation to bound ligands, adsorption interactions at surfaces). We are developing fiber-optic, surface-enhanced Raman, and fluorescence spectroscopy and microscopy capable of detecting sub-monolayer coverages of molecules at liquid/solid interfaces. We are currently using these tools to study binding of molecules and metal-ions to immobilized ligands and the effects of local surface structure and electric fields on these reactions.

A major goal of the current DOE project has been to develop *in situ* Raman spectroscopy for monitoring metal-ion binding to ligands immobilized on porous silica surfaces. An approach to generating multi-ligand metal-ion complexes with silica-immobilized 8-hydroxyquinoline (8HQ) has been developed, based on building a silica-framework around a *preformed metal-complex* using a silica sol-gel synthesis [1]. The stoichiometry of the resulting materials is probed with *in situ* Raman spectroscopy, and the metal-ion concentration responses of sol-gels prepared with varying amounts of metal ion during the syntheses were investigated. The results indicate stoichiometric control over the fraction of imprinted binding sites in these sol-gel structures [1]. A related project in collaboration with the Eyring research group involved multivariate least squares methods were applied to the Raman and ultrasound spectroscopic analysis of the complexation kinetics of zinc with thiocyanate [2].

A second area of spectroscopic research has been to adapt surface-enhanced Raman scattering (SERS) to characterize active-sites on metals, the self-assembly process for immobilizing ligands on the metal surface, the effects of electric fields at chemically modified-metal surfaces, and E-field control of metal-ion binding reactions. The underlying metal substrate provides the means of controlling and varying the interfacial potential at which this chemistry occurs. A first study addressed SERS-active sites on silver to determine the role of surface pretreatment on the generation and properties of these sites [3]. SERS-based spectroelectrochemistry was used to characterize the potential dependence and chemical heterogeneity of adsorption sites found on both highl polished and electrochemically-roughened polycrystalline silver electrodes. For the preparation of well-ordered, self-assembled monolayers on metal surfaces, it is critical to understand the chemistry of the self-assembly process. By collecting surface-enhanced Raman spectra versus applied potential to control the free energy for binding, multivariate statistical methods can resolve the component concentration profiles along with their corresponding Raman spectra [4]. A major breakthrough was recently achieved in the application of vibrational Stark-tuning measurements to probe interfacial electric fields was to map the field distribution near a SAM/solution interface by using a nitrile-terminated n-alkanethiol probe diluted into a series of shorter n-alkanethiols. Interfacial electric fields derived from the Stark-tuning rates allowed the structure of the diffuse double-layer region to be mapped with subnanometer resolution versus distance from the SAM/solution interface [5]. 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 that end, we synthesized the ligand p-([8-hydroxyquinoline]azo)benzenethiol (SHQ) which can be bound to 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 (Poisson-Boltzmann behavior), 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 SHQ [6]. The potential-dependent switching of the ligand 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: tautomerization of immobilized species offers a facile method for introducing molecular structural differences that can be exploited to produce electrically "switchable" surface properties. Finally, in an analytical application of chemically modified metal surfaces for SERS detection, metal colloids immobilized on a glass support substrate were modified with a self-assembled alkylsilane (C18) layer to promote adsorption of polycyclic aromatic hydrocarbons from aqueous solutions [7]. Detection of these compounds from low concentration solutions was accomplished by surface-enhanced Raman scattering. The adsorption and detection of PAH compounds adsorbed from low (ppb) concentration solutions onto C18-modified gold colloid substrates was reported.

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

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Overall Research Goal: 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, defect production and characterization are a focus of much of this work.

Significant Achievements in 2003-2005.

We have characterized the production and destruction of metallic colloids in calcium fluoride under 157-nm excimer laser radiation. Calcium fluoride is nominally transparent at 157-nm and is used for optical components at this wavelength. We have shown that prolonged exposure to 157-nm radiation at fluences near 1 J/cm^2 generates fluorine vacancies, which aggregate to form metal colloids. Mie theory suggests that these colloids display an absorption band near 157 nm, in addition to the well-studied band near 530 nm; we showed that colloid absorption at 532 nm is reduced by prolonged exposure to 157-nm radiation (bleaching) at low fluences. Transmission measurements at 157-nm also show an additional, transient absorption that disappears on time scales of minutes after high fluence irradiation ceases. Identifying the source of this transient absorption, and its possible role in the production of more stable defects, is a major goal for the next year of this grant.

We have observed defect-related positive ion emission from fused silica during 157-nm irradiation. Molecular dynamics simulations indicate that photo-ionization of surface oxygen vacancies would account for emission of positive ions adsorbed at these sites.

We have characterized many of the atomic and molecular emissions produced during 157-nm irradiation of polytetrafluoroethylene (PTFE). Although the band gap of PTFE is unusually large for a polymer, it absorbs strongly at 157-nm. Etch pits produced at 157-nm show much less evidence for thermal damage than at longer wavelengths, consistent with photochemical, as opposed to photothermal decomposition. This is supported by the presence of fast, neutral products, presumably produced photochemically.

We have found that small partial pressures of water vapor (10^{-3} Pa) can strongly enhance the dissociation of NaCl during exposure to energetic radiation (248-nm photons, 2-keV electrons). In addition, we have characterized the induction process in different alkali halides (NaCl, KCl, KBr) during 248-nm irradiation. Differences may be related to initial defect densities and mobilities. The evolution of vacancy defects (F-centers, M-centers) during and after femtosecond exposure at 400, 800, and 267 nm also show interesting differences associated with charge transfer between these defects on time scales ranging from nanoseconds to hours.

Specific Objectives for 2005-2006.

We are incorporating a VUV spectrophotometer into one of our vacuum systems for absorption measurements near 157 nm. The growth and decay of spectral features in this region will provide critical information on the nature of the defects responsible for the transient absorption in calcium fluoride described above. We will also check Mie theory predictions of VUV colloid absorption—important due to the uncertainty of dielectric constants at VUV wavelengths. The role of material quality and water exposure on 157-nm absorption will also be probed.

Further analysis of product velocities during 157-nm irradiation of PTFE will be performed to address the question of surface temperature. Simple models indicate high temperatures. Although material removal is primarily photochemical at 157 nm and not thermal (as at 248 nm), it is not clear that high surface temperatures can be avoided—although the affected volume is small.

In collaboration Kenichi Kimura and Stefano Orlando, we will investigate the role of pre-existing defects (or their absence) in defect production at fluences below the threshold for optical breakdown in NaCl, KCl, and KBr during nanosecond (248-nm) and femtosecond (400, 800, 267 nm) irradiation. Interactions with pure and doped MgO will be studied in collaboration with Wayne Hess, PNL, and Lynn Boatner, ONRL.

Finally, we plan to use atomic force microscopy (AFM) to characterize the onset of material removal from a number of wide bandgap single crystal materials, including calcium fluoride.

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Ion Formation and Fragmentation in UV and IR Soft Laser Desorption Ionization

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Overall research goals: Soft laser desorption/ionization (SLDI) in combination with mass spectrometry (MS) is a key method in the analysis of large biomolecules. New approaches are explored for SLDI from robust nanostructures that enable controlled fragmentation. Alternatives for atmospheric pressure SLDI and mass spectrometric imaging of surfaces are developed.

Significant achievements in 2004-2006:

SLDI from nanostructured surfaces: nanowires, nanoparticle films and silicon microcolumn arrays

New desorption surfaces including nanoporous silicon, silicon nanowires, gold nanoparticle films and silicon microcolumn arrays were synthesized and studied. Ion yield, internal energy transfer and fragmentation studies indicate that silicon microcolumn arrays offer unique advantages.

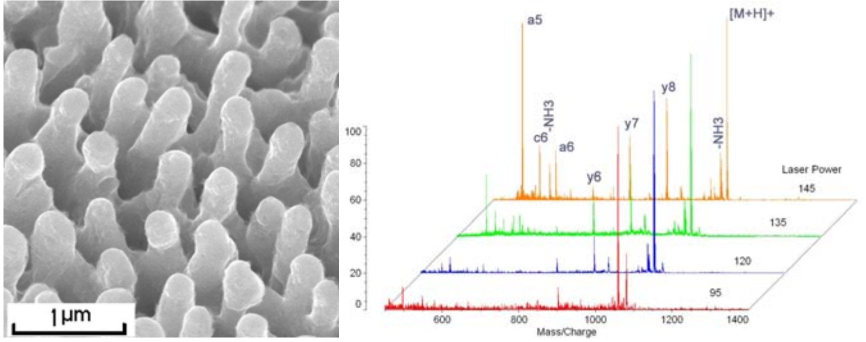

Figure 1. Left panel shows silicon microcolumn arrays produced with 600 laser shots in water. Mass spectra of bradykinin (ArgProProGlyPheSerProPheArg), in right panel, obtained from this surface at various laser powers demonstrate molecular ions at low and structure-specific fragmentation at elevated laser intensities.

Repeated exposure of silicon wafers to frequency tripled mode-locked Nd-YAG laser radiation produced two dimensional arrays of microcolumns. The radius of curvature for the column tips varied with the processing environment, e.g., it was ~120 nm in water (left panel in Figure 1). At low laser fluence in the SLDI experiment, this structure readily produced molecular ions from peptides and synthetic polymers. The threshold fluence for ion production was comparable to matrix-assisted laser desorption ionization (MALDI). At higher laser power, structure specific fragments were formed due to in-source decay (right panel in Figure 1). For example, extensive peptide sequence information was recovered from the spectra with consistent abundance for all fragments. The versatility and robustness of these microcolumn arrays was attributed to the submicron morphology, the modified thermal and optical properties of silicon and to thermal and chemical confinement effects.

Atmospheric Pressure Mid-Infrared Laser Desorption for Surface Analysis and Imaging

Laser processing and analysis of biological samples often require the use of mid-infrared lasers. Due to the strong OH absorption band of water contained in these systems, ablation and desorption from biological tissues is efficient at ~3 µm wavelength. Atmospheric pressure (AP) MALDI is being explored as an efficient way to produce ions and neutrals for mass analysis. In this project we compare UV and IR excitation for AP-MALDI from surfaces and explore their utility for mass spectrometric imaging. In the left panel of Figure 2, IR-AP-MALDI analysis of a peptide mixture is demonstrated using 2,5-dihydroxybenzoic acid (DHB) matrix.

The plume dynamics in these AP experiments is dramatically different from the vacuum case. The most important consequences of the AP environment are the significant slowdown and eventual stopping of the laser plume and the enhanced formation of clusters and nanometer size particulates through condensation. Fluid dynamics modeling of these processes helps our experimental efforts.

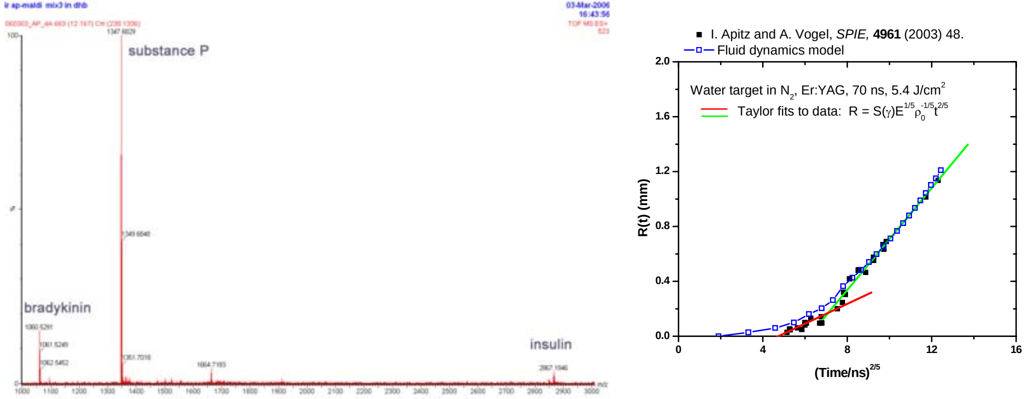

Figure 2. Left panel shows IR-AP-MALDI mass spectrum of a peptide mixture (bradykinin, substance P and bovine insulin) from DHB matrix. (Right panel) Comparison of shock front displacements from our fluid dynamics model (blue symbols) with experimental data (black squares) in mid-IR laser ablation of water.

The results for the position of the shock front predicted by the model are compared to experimental data in the right panel of Figure 2. Two distinct phases of the plume expansion were distinguished; a slower surface evaporation phase (red line) followed by phase explosion (green line). The model (blue symbols and line) accurately reflects the transition and the latter process but overestimates the surface evaporation phase. A detailed analysis of the results from this new model is underway.

Specific objectives for 2006-2007:

- Explore the effect of the structural characteristics of silicon microcolumn arrays on laser desorption ion yields and internal energy transfer;
- AP-MALDI imaging experiments with UV and mid-IR laser excitation.

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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 direct solid sample chemical analysis. Ablation processes include laser-material-interactions, mass ejection, laser-plasma interactions, plume/plasma dynamics, and particle formation.

Significant achievements in 2004-2005: The research emphasis has been on shockwave behavior and particle formation. For chemical analysis, the ablated mass must be either excited vapor for LIBS (laser induced breakdown spectroscopy) or particles for ICP-MS (inductively coupled plasma mass spectrometry). Dynamics of the shockwaves and the plume/plasma govern the character of the ablated mass. From the beginning of the laser pulse to ~1 μs after the laser pulse, the propagation of the vapor plume and shockwave were studied by using shadowgraph and spectral emission imaging. We found that the strong expansion of the vapor plume starts at ~2ns after the beginning of the laser pulse. A laser supported detonation wave (LSD) is observed at the top of the shockwave (fig. 1) between ~4 to ~9ns after the beginning of the laser pulse, which blocks the coupling of the laser energy to the sample. In addition to the shockwave in the background gas region, an internal shockwave in the vapor plume is also observed from the emission images. Liquid sample ejection is observed to coincide with the interaction of the internal shockwave with the sample surface, assuming the thermal diffusivity supports a molten region when the internal shockwave arrives at the surface. A theoretical analysis was developed to describe the shockwave during this time interval, and simulated trajectories of the vapor plume and shockwaves show good agreement with the experimental results under different laser condition (fig. 2). By using this analysis, we are able to determine the laser energy conversion ratio and the sample mass vaporized during the laser ablation, both are unable to be measured and effectively determined during all previous studies.

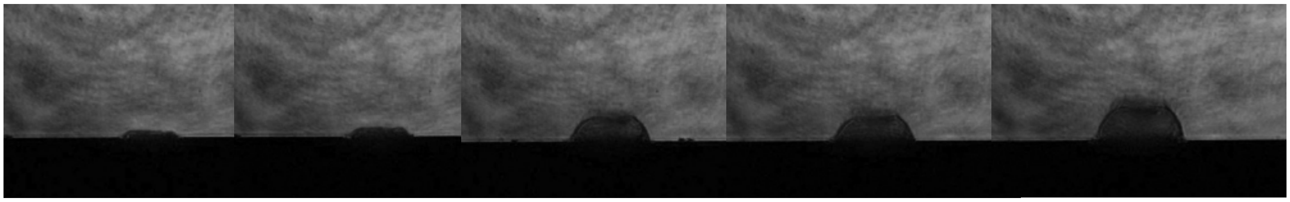
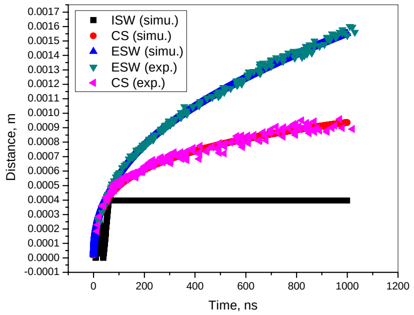


Figure 1. Shadowgraph images of laser ablation in argon with E=30mJ (from 2-6ns). Spatial scale is approximately 500 μm across bottom of each image.

From a few μs to tens of μs after the laser pulse, we determined that the temperature and the dynamic changes of the vapor plume were due to radiative heat loss. Also, from optical measurements, we found that the temperature variation of the vapor plume followed a bi-exponential function of time rather than an exponential function as used in most previous literature studies. An analytical model was established for radiative cooling during this time interval; the simulation shows good agreement with experimental measurements (fig. 3).



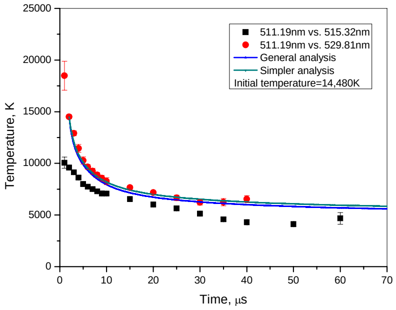


Figure 2. Trajectories in argon for laser energy E=10mJ. $E / E_{laser} = 35\%$; $M = 5.5 \times 0^{-12}\, kg$

Figure 3. Comparison of the simulation with the measurements for temperature of the vapor plume.

A significant effort involved the measurement and understanding of particles. The cooling rate of the laser plume plays a strong role in the size and size distribution of the ablated particles. In addition, particles are formed by melt ejection and spallation. SEM images, DMA (differential mobility analyzer) and chemistry are used to study nanoparticle formation mechanisms. Figure 4 shows particles formed using nanosecond and femtosecond pulsed laser ablation of aluminum and copper.

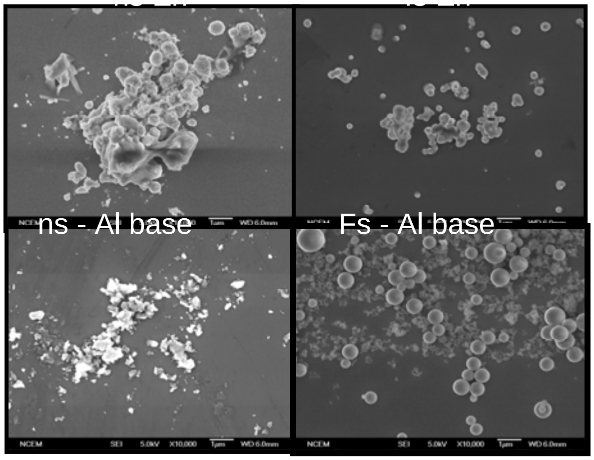


Figure 4. SEM of particles produced by nano- and femtosecond laser ablation

Specific objectives for 2006:

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

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Progress in Chemical Analysis Through Sample Engineering: New Challenges, Opportunities, and Paradigms of 21st Century LIBS

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Laser Induced Breakdown Spectroscopy (LIBS) has rapidly evolved in the last five years from a relatively young 20 year-old intriguing technique with considerable potential, towards a major analytical technology that will soon take its rightful place along with other technologies such as mass spectrometry, FTIR, Raman, and gas chromatography. Very simply, LIBS is exceptional in its ability to determine the stoichiometry of any given sample. Moreover, it is a technique that generates the most fundamental information about such samples, namely their elemental compositions, better than any other technique. At the turn of the century a new LIBS paradigm evolved- high resolution, broadband, single-shot detection. This happened because of (1) the development of new instruments (e.g. LIBS 2000+ and various echelles), (2) the rapid growth in the application of chemometrics to the large amount of spectral data that these instruments generate, as well as (3) the urgent need to develop new fieldable hazardous materials detectors for the post- 9/11 world capable of analysis of residues with a single shot. Real-time response, no sample preparation required, high sensitivity, close-contact or standoff analysis, and now the ability to detect all chemical elements in a single laser shot are attributes of a detector technology with unprecedented performance characteristics.

A key additional development in the last few years has been an explosion of new creative approaches that effectively are transforming traditional single-shot LIBS into a much more sophisticated technological arsenal for manipulating and engineering the sample for optimal analysis. New results in (1) multiple-pulse LIBS, (2) multiple-wavelength LIBS, (3) LIBS enhancement techniques, (4) fusion of orthogonal techniques with LIBS as the anchor, and (5) femtosecond LIBS, have opened up completely new directions of research and LIBS performance improvement.

Light interaction with materials has been the cornerstone of spectrochemical analysis for multiple centuries. Finally now, *laser* light interaction with materials is evolving into a major new frontier in chemical analysis. With this new vision of LIBS performance capabilities comes the increasing need for generating fundamental understanding of not just the basic single-shot phenomenon, but especially the multiple variants and physico-chemical nuances that are in play in sample engineering. Very simply, the evolution of the promise of LIBS will depend directly on the funding that is applied to fundamental studies of this rich phenomenon. As a measure of how far we need to go and how much work is involved, consider that currently there is no single model that can successfully simulate and predict the spectrochemical interaction of just a single laser pulse with a simple sample material. Sample engineering in LIBS will require an unprecedented approach from multiple basic science and engineering disciplines to aid in capitalizing on its full promise. Ultimately, LIBS will not only claim its position in the typical analytical laboratory benchtop along with the other key instruments, but it also will make an unprecedented impact in field analyses of virtually all chemical and biological materials, both hazardous and benign. LIBS will impact a very broad range of human activities, both military and civilian.

Chemistry and Microphysics of Small Particles

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Overall research goals: The objective of this project is to develop and apply unique tools to investigate the properties and behavior of particles on the nanoscale.

Significant achievements in 2004-2006: The work in this project proceeded along two parallel pathways: 1) design and construction of an advanced 2nd generation single particle mass spectrometer; 2) study the behavior and properties of small particles.

SPLAT II: The design and construction of the 2nd generation instrument is now complete. SPLAT II is smaller, robust, and exhibits higher sensitivity. It is a flexible platform that easily transforms to accommodate variable applications.

A Highly Resolved Study of Morphologically Engineered PSL Particles with Na-containing Nanolayers and Nanonodules: Our understanding of the fundamental processes that control pulsed UV laser ablation of nanoparticles is extremely limited. In this project we generated three morphologically distinct internally mixed particles composed of 240 nm PSL cores that are coated with Na-containing compounds. The mass spectra of these particles as a function of size, determined with 1 nm precision made it possible to quantify for the first time the charge transfer processes between an alkali metal and carbon-containing cations that take place in the ablation zone. Figure 1 shows that while it is possible to detect the presence of a monolayer of Na, depending on the particle morphology, the PSL core signal decays to one half its intensity as the coating thickness approaches ~1 nm. Taking advantage of the particle morphology we have demonstrated, for the first time, that during ablation these particles are fully evaporated.

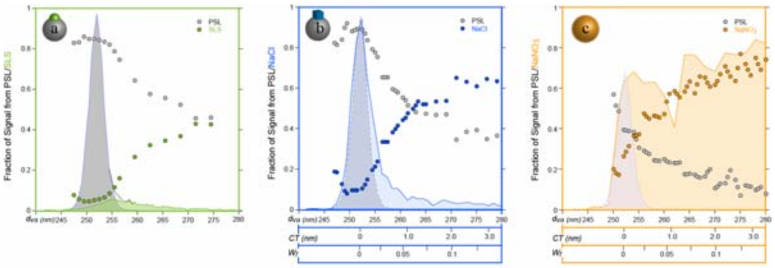

Figure 1 A comparative view of the behavior of the three types of coated PSL particles as the first few nanometers of coating are added.

High Precision Measurements of the Density of Metastable Phases: One of many special properties of nanoparticles is their ultra-purity and absence of heterogeneous nucleation sites. Solution nanodroplets can shed off nearly all their solvent to form glassy, highly metastable, "dry" particles whose properties relate to those of matter far from equilibrium. We have used the high precision of SPLAT to measure the densities of a number of these metastable particles and found them to be between 1 and 9% lower than the density of the crystalline phases.

On the Behavior of Aspherical Particles in the DMA and in the Vacuum: Particle shape is an important attribute that influences its physical and optical properties. However, because it is one of the most difficult to quantify the tendency is to treat nanoparticles as if they were spherical. We have performed an experimental exploration of the effect of particle shape on the behavior of particles in the DMA and in the vacuum by quantifying the relationship between mobility and vacuum aerodynamic diameters. We studied three particle types: 1) Agglomerates of PSL spheres, 2) Common irregularly shaped particles of known density; and 3) Internally mixed particles, containing organics and ammonium sulfate, of unknown density and shape. We carried out the first direct determination of dynamic shape factors (DSFs) for a number of particle systems and showed that asphericity can lead to particle alignment in the DMA and that the DSF can be a function of flow regime.

Physically Separating Particles on the Basis of Their Shape: A detailed study of the behavior of aspherical particles in the DMA revealed that at high electric fields in the DMA asymmetric particles align parallel to the field and at low electric field they are in a nearly random orientation. We have used these observations to develop a novel approach that is based on a tandem of DMAs in which each of the DMAs is operated at very different sheath flow rates to quantify particle alignment. We show that the magnitude of the effect can be related to particle shape. Moreover, as shown in Figure 2, we demonstrated that this system can be used to physically separate particles on the basis of their shape alone.

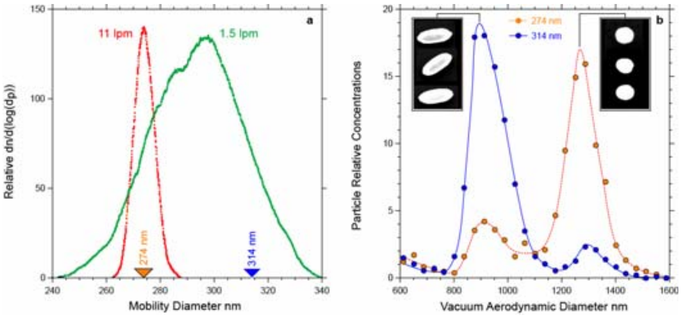

Figure 2 a) Two mobility size distributions of hematite particles, selected by the first DMA at 274 nm **b**) Measured vacuum aerodynamic size distributions of particles selected by the 2nd DMA at 274 and 314 nm. The inset shows micrographs of the two particle types.

SpectraMiner: A Data Analysis and Visualization Software: To take full advantage of the vast amounts of detailed, high-dimensionality data that SPLAT II produces, we have developed a data mining and visualization software that we call SpectraMiner. SpectraMiner makes it possible to explore the data on a multitude of levels with unprecedented speed and ease. This software provides an interactive interface between the scientist and the data. Recently we conducted a study that puts SpectraMiner to the test. Mass spectral signatures of 36,000 of 12 types of laboratory generated particles were acquired, classified and explored using SpectraMiner.

Specific Objectives for 2006-2007:

- In collaboration with Prof. Barney Ellison (U. of Colorado); study the reactions of size-selected organic aerosol particles with OH radicals, using SPLAT and the aerosol flow reactor at EMSL.
- Characterize the chemical and microphysical transformations of nanoaggregates generated by combustion and spray pyrolysis by measuring shape, density, fractal dimension and composition.
- In collaboration with Prof. Klaus Mueller (SUNY Stony Brook) develop a user-guided data clustering approach, called ClusterSculptor, to be used at the front-end of SpectraMiner. This will provide a convenient window to inject scientific domain knowledge, expertise, and intuition to control and steer the clustering process. This is inline with the new science of visual analytics, where scientists are put into the loop of computational analysis processes.

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A Fundamental Study of Transport within a Single Nanoscopic Channel

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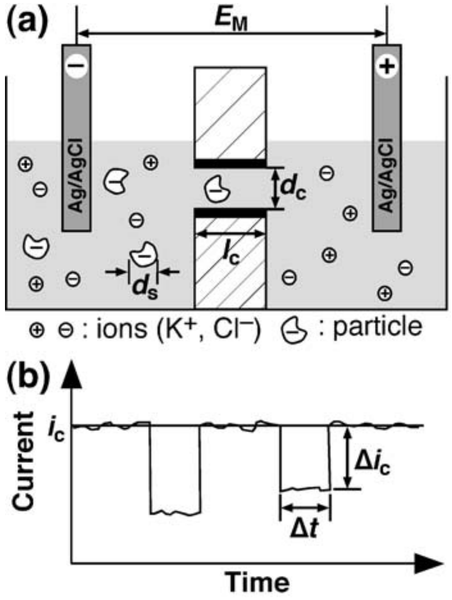
Overall research goals: The two objectives of this project are to measure the hydrodynamic hindrance factors in carbon nanotube channels and to study the effects of probe-pore interactions on transport rate.

Significant achievements in 2004-2006: Quantifying mass transport through nanoporous media is important, because it is the foundation for many technologically significant processes including separations, analysis, and catalysis. Mass transport through nanopores involves restricted motion (hindrance) of molecular and larger probes when their sizes are comparable to the pore size; thus hindered transport is of particular interest when the pore size is on the nano scale. For example, understanding hindered transport is critical for developing an understand of the selectivity of catalytic reactions in zeolites and size-exclusion-based separation techniques. In addition, chemical interactions between probes and pores are crucial for zeolite-based catalytic reaction and nanopore-based chemical sensing.

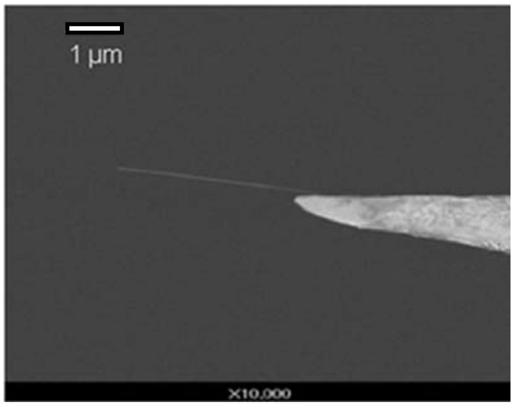


We are studying transport through carbon nanotubes using an electrochemical device we call a carbon nanotube Coulter counter (CNCC). The basic experimental arrangement is shown in the figure to the left. When a potential is applied between the two electrodes, an ion current (i_c)flows through the nanotube-defined channel. When another object, like a polymeric nanoparticle, a virus, or DNA, enters the channel it effectively reduces its volume and therefore reduces the ion current by an amount (Δi) for a time (Δt). From these two parameters it is possible to calculate the size and charge on the object transiting the channel. No labeling or calibration is required.

Since the last contractors' workshop we compared the precision and accuracy of measurements of the diameter and electrophoretic mobility (μ) of polymeric nanoparticles using four different analytical tools: carbon nanotube-based Coulter counting, dynamic light scattering (DLS), transmission electron microscopy (TEM), and phase analysis light scattering (PALS). CNCCs use a 132 nm-diameter channel to simultaneously determine the diameter (28 - 90 nm) and μ for individual nanoparticles. CNCCs can be used to measure the size of individual nanoparticles dispersed in aqueous solutions, which contrasts with the TEM-measured size of individual dehydrated particles and the ensemble size averages of dispersed particles provided by DLS. CNCCs provide more precise values of μ than PALS.

Specific objectives for 2006-2007

The most significant barrier we face in this work has to do with the fabrication of the nanopore membranes. There are three basic problems. First, the throughput is very slow, because each set of membranes is fabricated by hand using tools better suited for microfabrication than nanofabrication. Second, the current process limits us to interior channel diameters of about 100 nm, but we are most interested in smaller channels. Third, it is difficult for others to duplicate the membrane fabrication procedure without spending time in our lab. Accordingly, we are developing a new approach for membrane fabrication. This method employs sophisticated nanofabrication tools that enable the handling of individual nanotubes and simultaneous visualization by electron microscopy. The figure to the left shows a field-emission SEM image of the tip of a Zyvex nanomanipulator that has grabbed a single nanotube about 20 nm in diameter. This nanotube will be placed onto a FIB-machined substrate and then anchored by FIB-assisted CVD of platinum. Subsequently the mounted nanotube will be encased in epoxy and microtomed to yield single-pore membranes.



Manipulation of a single multiwall carbon nanotube with a tungsten probe of the Zyvex nanomanipulator. The experiment is performed and monitored in the vacuum chamber of a dual beam SEM/FIB.

Once this new fabrication method has been optimized, we will begin examining transport of virus through the nanotubes. The interesting part of this study is that the size of the viruses will approach the interior dimensions of the nanotube, which will permit us to quantitatively study hindered transport.

Publications citing only DOE support

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- T. Ito; L. Sun; R. R. Henriquez; R. M. Crooks "A Carbon Nanotube-Based Coulter Nanoparticle Counter" *Acc. Chem. Res.* **2004**, *37*, 937-945. (This publication was reported as 'submitted' in our last progress report.)
- T. Ito; L. Sun; M. A. Bevan; R. M. Crooks "Comparison of Nanoparticle Size and Electrophoretic Mobility Measurements using a Carbon Nanotube-Based Coulter Counter, Dynamic Light Scattering, Transmission Electron Microscopy, and Phase Analysis Light Scattering" *Langmuir* **2004**, *20*, 6940-6945. (This publication was reported as submitted in our last progress report.)
- R. R. Henriquez; T. Ito; L. Sun; R. M. Crooks "The Resurgence of Coulter Counting for Analyzing Nanoscale Objects" *The Analyst* **2004**, *129*, 478-482. (This publication was reported as 'in press' in our last progress report.)

Chemical Analysis at Nanodomains: Structure-Function Relationships

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Collaborators: E. Yeung and R. S. Houk, Ames Laboratory-USDOE and Dept. of Chemistry
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Research goals. Structure and environment in nanodomains dictate efficiencies in catalysis, energy conversion, electronic device performance, immune system response, and chromatography. As part of an integrated program at the Ames Laboratory, this project is focused on development of fundamental insights into structure-function relationships at length scales central to the performance of electrochemical and chromatographic interfaces.

Significant Achievements in 2004-2006.
a. By monitoring retention with respect to applied potential (E_{app}), electrochemically modulated liquid chromatography (EMLC) can be configured as a tool for examination of electrosorption processes. The approach adapts the Gibbs adsorption equation to determinations of interfacial excesses of solutes in different supporting electrolytes, changes in interfacial tension, the charge on the electrode, and the potential of zero charge (PZC). With this capability, we have now investigated the role of the supporting electrolyte in terms of its competition with solute adsorption. Results have shown that the elution strength of typical supporting electrolyte anions increase as $F^- < OH^- < BF_4^- < ClO_4^- < PF_6^-$. Furthermore, both the concentration and composition of the supporting electrolyte affected retention in a manner that varied with the charge of the analyte and E_{app}. This behavior is explained using Gouy-Chapman diffuse double layer theory, coupled with comparisons of this theory to closely related models for ion-pair chromatography. These data reveal that an ion-exchange mechanism controls the retention of negatively charged solutes at values of E_{app} removed from the PZC. However, when close to the PZC, the electrostatic model is less effective in predicting the strength of adsorption, which is diagnostic of contributions from hydrophobic interactions.

b. With the Yeung group, experiments to delineate interactions that dictate retention at chromatographic bonded-phases continue. This work uses YOYO-I labeled λ-DNA as a nanometric probe of interactions central to adsorption at compositionally patterned adlayers formed by the self-assembly of amine-, alcohol-, and acid-terminated thiols of varied chain lengths on optically transparent gold substrates. By recording the real-time dynamic motion of individual λ-DNA at these liquid-solid interfaces, parameters governing analyte retention can be systematically unraveled by probing the role of solution pH, λ-DNA concentration, and adlayer domain size. While the negatively charged backbone is not adsorbed, the 12-base unpaired ends of λ-DNA, which expose purine and pyrimidine groups, appear to play a key role in dictating adsorption. In addition to quantifying the relative adsorption strength as a function of the terminal group identity ($NH_2 > COOH > OH$), the importance of structural defects was also revealed. This result, found both at the disordered boundaries between domains and at adlayers with structural order affected by the length of the alkyl chain, points to the subtle but preferential adsorption of the "sticky ends" of λ-DNA. These studies also demonstrated an intriguing dependence of preferential adsorption with respect to domain size in that there was no detectable adsorption below a domain size of a few square microns. Experiments to assess the basis of this intriguing observation are now being designed.

Specific Objectives in 2006-2007.
a. The next step in probing adsorption thermodynamics at electrified interfaces will examine processes for simple cations (e.g., K^+, Na^+, Li^+, Ca^{2+}) and anions (e.g., F^-, NO_3^-, Cl^-, SO_4^{2-}, ClO_4^-,

PF_6^-). By quantitatively extracting dependence of key interfacial descriptors on E_{ap}, new and important details of this important class of electrified interfaces. This work will be carried out with the Houk group to utilize inductively coupled plasma or electrospray mass spectrometry as a means for the low level detection of these model ionic species.

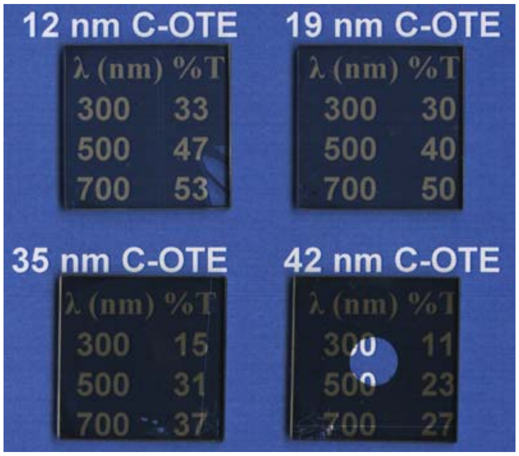

Fig. 1. Pyrolyzed photoresist transparency.

b. Perspectives gained by macroscopic measurements of retention reflect the integrated response of a large ensemble of analytes over a large, potentially diverse population of adsorption sites. To probe adsorption at a single molecule level, we created carbon-based optically transparent electrodes (C-OTEs) via the pyrolysis of thin films of photoresist (Fig. 1). Pyrolysis of these samples at 1000°C in a reducing atmosphere yields optically transparent carbon films that have thicknesses ranging between 10 and 80 nm. Results show that the transparency of this material improves as film thickness decreases, but at the expense of an increase in film resistance. At a wavelength of 500 nm, for example, 13- and 79-nm thick films have transparencies of 47% and 10% and sheet resistances of 1100 and 210 Ω/□, respectively. Importantly, preliminary results using these C-OTEs in what we refer to as single molecule spectroelectrochemistry can be applied to follow the potential dependence of the adsorption of individual YOYO-I labeled λ–DNA. In continuing this project with the Yeung group, experiments to exploit this new capability are planned and will attempt to monitor electrosorption not only with respect to solution pH, but also as a function of modest changes in temperature in order to potentially determine the thermodynamics of retention at the single molecule level.

Publications Acknowledging DOE Support in 2005.

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Bidimensional Liquid Chromatography

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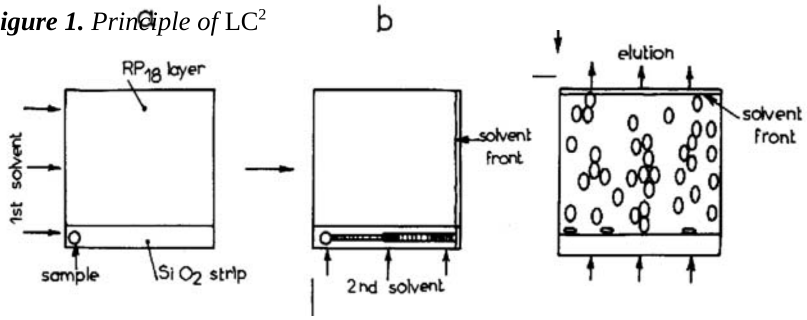
Overall Research Goals. The separation of complex mixtures (e.g., protein digests of microorganisms) is impossible with the most efficient HPLC columns available. The combination of two chromatographic separations that use two different separation mechanisms could provide much better results than merely increasing the length of current columns. Several approaches are possible since a chromatographic separation can be made in space (e.g., thin layer chromatography) or in time (e.g., column chromatography). Our goal is to investigate and compare different schemes combining these approaches. Figure 1 illustrates the combination of two successive separation in space. However, instead of doing the first separation along a strip of the plate, it could be done on a column and the eluate applied as a line on the plate. The advantage of this approach would be to allow the complete evaporation of the first solvent and a concentration of the separated components.

Figure 1. *Principle of* LC^2



Current Results. We have investigated several possible retention mechanisms for the separation of protein digests. The best independent mechanisms are those that give separations based on a reversed phase, an ionic mechanism, or the molecular size. So, we have considered several columns available in each type of separation.

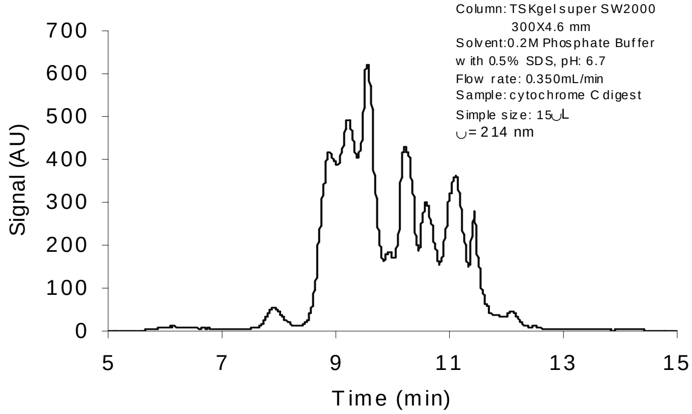


Figure 2. SEC separation of a cytochrome C digest.

The separation carried out in the first dimension can last far longer than the one done in the second dimension. Figures 2 and 3 illustrate the results obtained with a sample of cytochrome C digest using either a size exclusion column (SEC, Fig. 2) or a RPLC column (Fig. 3). The first one of these two separations could easily be improved by using a four times longer column, doubling the resolution. The second one is excellent, almost all the components being completely resolved. It corresponds to a peak capacity in excess of 200 and

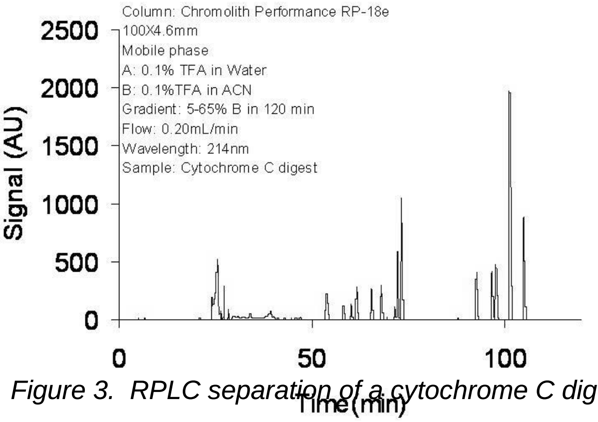


Figure 3. RPLC separation of a cytochrome C digest.

should be satisfactory for all our further studies using a column.

The separation carried out in the second dimension must be fast. Figure 4 (below) shows two examples of separations under consideration. Important reductions of the analysis time were obtained using the two most useful approaches available. The first (left) was obtained in gradient elution, the second (right) at 110°C.

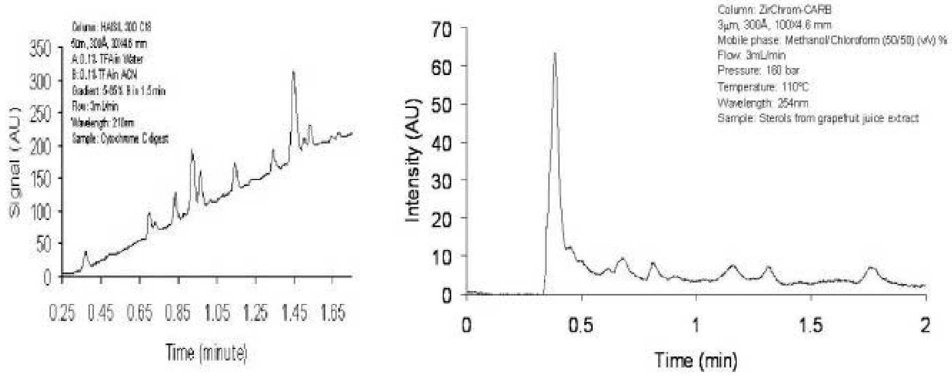


Figure 4. Chromatograms on RPLC columns of a protein digest and of sterols at high temperature

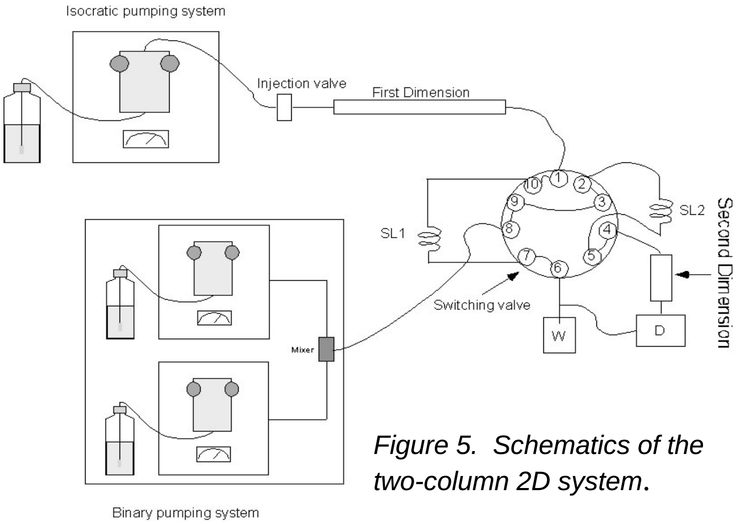


Figure 5. Schematics of the two-column 2D system.

Figure 5 includes a pump to operate the first dimension column and a binary system with two identical units, including one pump and one second dimension column each. This allows more time to carry out the second separation and alleviates the time constraint on this step. Figure 5 shows the schematics of the pumping system. It includes a pump to operate the first dimension column and a binary system with two identical units, including one pump and one second dimension column each. This allows more time to carry out the second separation and alleviates the time constraint on this step.

Specific Objectives for 2006-7. Our objectives for the third year of the grant project are: (1) Investigate further retention mechanisms available for the separation of peptide digests; (2) Determine the degree of correlation between them; (3) Select pairs of independent mechanisms; (4) Prepare compatible columns for implementing LC×LC; (5) Apply different 2D methods to the separation of mixtures of digests of different proteins; (6) Compare the results obtained with these methods.

Experimental Studies of Photoacoustic and Photothermal Effects

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Overall research goals: The objectives of the research have been to investigate both experimentally and theoretically thermal diffusion in a sinusoidal temperature field, to formulate a theory of transient grating signals from particulate suspensions, and to carry out experiments with picosecond and nanosecond lasers to verify the predictions.

Significant achievements in 2002-2005:

We have predicted and verified the nonlinear behavior of the separation that takes place when a binary liquid mixture is subjected to a temperature field, known as the Ludwig-Soret effect. Our results are calculated for a sinusoidal temperature field, which is used in what is perhaps the most reliable method for measuring this effect. We have shown that the partial differential equation for the Ludwig-Soret effect can be reduced to a Hamiltonian system of equations which provides a means for numerically determining the motion of the two components of the mixture. A solution in closed form was found for the linearized Ludwig-Soret equation for a binary mixture using the method of characteristics, which is valid for short times after the temperature field has been applied. A numerical integration of the Hamiltonian system (with mass diffusion ignored) shows that a pair of shock waves are generated that counter propagate in space and eventually come to a halt. Additionally, we have obtained a closed form solution to this problem in terms of elliptic functions that describes the entire behavior of the motion. Time resolved experiments that record the production of diffracted light beams or directly record the profile with a CCD camera have been carried out with a continuous 532 nm laser beam irradiating a solution of nanoparticles in a solvent.

A method for determining the time dependence of the diffracted light beams in transient grating experiments with particulate suspensions has been obtained. The method relies on separating the thermal and acoustic modes of wave motion in the grating and adding the contributions from the ultrasound and heat emitted from individual particles to each of the two modes. The method relies on an integration of three dimensional sources to give the signal expected from what is approximated as a one dimensional grating. Three examples of the use of the method are used: the uniformly irradiated droplet, the point heat source, and the point heat source with the effects of the nonlinearity of the thermal expansion coefficient of water included.

Additional experiments and theoretical work have been carried out on the use of the transient grating method to determine the efficiency of singlet oxygen production by photodynamic therapy agents, determination of thermophysical properties of ionic liquids, laser initiated reactions of particulates in suspensions, and the photoacoustic effect at reflecting surfaces.

Specific Objectives 2005-2006:

- Research is planned to investigate the theory of thermal diffusion for a linear temperature gradient, perhaps the most fundamental problem in the field. Preliminary experiments with nanoparticles in an epoxy that can be cured with uv radiation are underway. The experimental method relies on curing several identical suspensions with uv radiation at predetermined times after application of the thermal gradient in order to freeze the motion the particles. The solidified suspension is then removed from the thermal gradient and the density fraction determined with a microscope.

- Research on methods to determine transient grating signals from suspensions of particulates is in progress. The successful completion of a new theory for determining transient gratings directly from the heating function will make possible further experimental studies with laser induced gratings. Exploratory research on photochemical generation of gas bubbles is in progress as well.

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Nanoparticle imaging at surfaces

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Prof. Tingying Zeng, Chemistry, Western Kentucky University

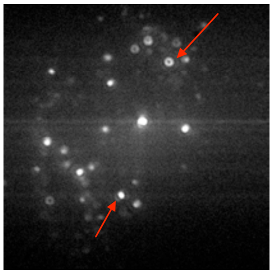
Overall research goals:

The objective of this program is to advance high sensitivity and high specificity laser-based chemical measurements to further our understanding of chemical systems at the molecular level. Our approach is surface nonlinear optical spectroscopy as a means to probe molecules at chemically important surfaces and interfaces. We are integrating second harmonic generation (SHG) and sum frequency generation (SFG) with spatial resolution for creation of images and with picosecond and femtosecond time resolved measurements to yield dynamic information. That combination of imaging capability and ultrafast dynamics is the unique feature of our effort.

Significant accomplishments in 2004-2006:

We have observed highly anisotropic optical emission from individual 2-3 nm indium phosphide quantum dots on a glass substrate. Optical anisotropy has been reported for quantum dots grown epitaxially on crystalline substrates where the orientation and shape of the particles is influenced by the substrate. However, for cubic semiconductor crystals grown from solution, the existence of a preferred direction for optical absorption or emission is not expected. These InP quantum dots will benefit chemical imaging at the molecular level due to their potentially anisotropic interaction with particular surface analyte molecules and their stability under intense illumination.

A total internal reflection illumination geometry yields an image of the optical emission pattern. There is zero intensity radiated parallel to the direction of the dipole, giving a donut-shaped pattern if the optical dipole is vertically oriented. If the dipole is horizontal, the emission pattern is elliptical. In the images that we obtained, most of the particles appeared to be oriented either perpendicular or parallel to the glass substrate, with few having intermediate orientations. A typical image is shown at the left, with vertical and horizontal particle axes shown by the red arrows. The reasons for this behavior are not clear, but may be due to an interaction with the glass surface. Another possibility is that the particles are not single quantum dots but aggregates of more than one. Photon correlation measurements are underway to prove that the particles observed are indeed single



Fluorescence image of InP nanoparticles with different orientations.

nanoparticles. Particles with either orientation were observed to blink off and on, a phenomenon that occurs for individual quantum dots.

We have imaged two-photon light from particles of NPP molecules [i.e., (s)-(-)-1-(4-nitrophenyl)-2-pyrrolidine-methanol], a molecule with a large second order susceptability. We have discovered the conditions required to produce crystalline NPP particles ranging from micrometers in diameter to single molecules on substrates. Fluorescence from these collections of particles showed blinking and varying photobleaching lifetimes. We have imaged light at 400 nm from non-linear optical processes (800 nm excitation) for these particles and are currently determining the contribution of SHG to the total signal.

Specific objectives for 2006-2007:
The objective of our work is to create capabilities for observing reactions spectroscopically on individual nanoparticles. Optical spectroscopy, particularly in the infrared region, has traditionally been the means to achieve molecular understanding. Spectral signatures corresponding to particular bonding geometries and molecular vibrations define chemical structures. The nonlinear optical techniques under investigation here – SHG and SFG -- add surface selectivity to this spectroscopy. These techniques require ultrafast light pulses, and are well-suited to dynamical studies of excitation decay and kinetic processes. Near field concepts are emerging that permit signal collection from a small sample area; then, when the sample is rastered in two dimensions, a chemical image results. Richard Saykally and his group have made great strides in the use of nonlinear optical methods for such surface imaging. Our scanning AFM head will be modified to convert from a cantilever tip to a tapered fiber optic probe to be used in a near-field geometry to collect SFG signals, thereby providing spatial resolution expected to reach 50-100 nm. Two initial experimental tasks – generation of mid-infrared laser light and production of tapered optical fibers – are underway. We are exploring various technologies including fiber drawing, etching, and nanofabrication methods to reduce the tip diameters. Enhanced catalytic activity of nanoscale noble metals is an area of great current interest. Our samples will be silica/titania catalyst supports that have been decorated with a sparse collection of nanoscale noble metal particles.

Reported results supported by this project:
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Modeling and Application of the Laser Induced Plasma

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Overall research goals: Our research program includes the study of fundamental aspects of the laser plasma induced on a solid material in vacuum or gas atmosphere. We are developing a theoretical model which can open up the possibility for absolute analysis, i.e. an analysis which requires no standards and tedious calibration. Plasma diagnostics is a part of this work as it provides the model with the necessary experimental input and leads to a better understanding of plasma processes.

Significant achievements in 2003-2005: We have developed a model of laser-induced plasma (LIP) that allows a back-calculation of the composition of the plasma. The model has an immediate experimental input in the form of LIP spectra and a few other experimentally determined parameters. We have demonstrated that the model works satisfactory for plasmas expanding into vacuum. Calculations and measurements were performed on a binary SiC system, on a series of multi-component aluminum samples doped with Si, Mg, Cu, Zn, Fe, and on pure iron, silicon and carbon. Monte Carlo optimization was used for finding initial plasma temperature and number densities. Good agreement (Fig.1) was obtained between the computed and the experimental spectra. We could therefore roughly predict the plasma composition and plasma temperature using easily measurable initial plasma size and plasma spectrum. This can be considered as absolute analysis of the gaseous components of the plasma. If stoichiometric ablation is assumed, the method can also estimate the elemental composition of the condensed phase material.

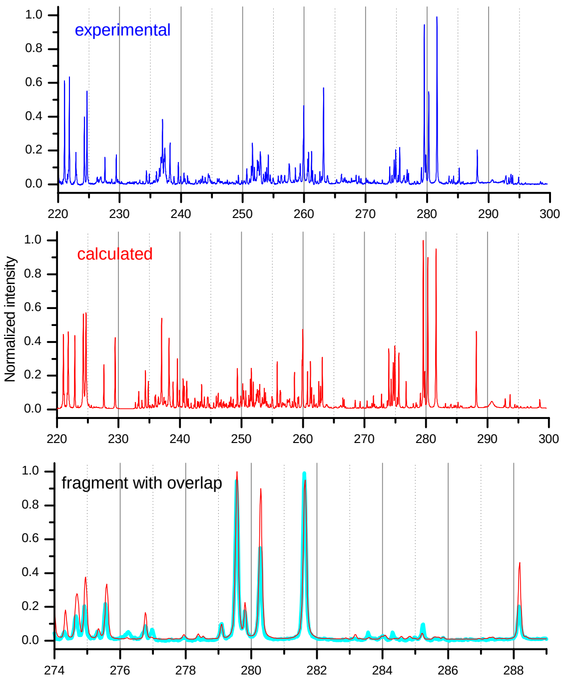

Figure 1. a) Experimental spectrum from Al alloy; b) Synthetic spectrum for the initial temperature of 22000 K; c) Narrow band overlap of the experimental and synthetic spectra.

A similar model has also been developed for LIP expanding into an ambient gas as this is the most practical analytical situation. This modified model described the expansion of a LIP accompanied by a shock wave into an argon atmosphere. Our results clearly demonstrated that on the basis of the model, the inverse problem, e.g., the determination of intrinsic plasma characteristics from the experimentally determined parameters, can be solved.

We have also developed and verified experimentally a theoretical model for an asymmetric expansion of laser induced plasmas into vacuum. It was proved that the self-similar plasma expansion with a velocity proportional to the distance from the center does not hold true for thermally anisotropic plasmas with radiative losses. The model predicted the flip over effect (Fig.2) observed experimentally (Fig.3). The spectra were calculated for silicon plasma expanding asymmetrically into vacuum. It was shown (Fig.4) that spectral line intensities are strongly dependent upon the direction of spectrum observation. This result is important for both the spectrochemical plasma analysis and plasma diagnostics based on plasma symmetry.

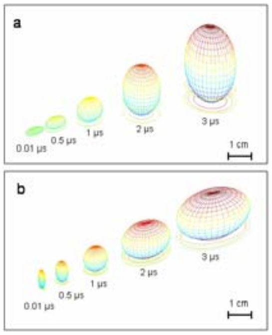

Figure 2. Calculated plasma shapes.

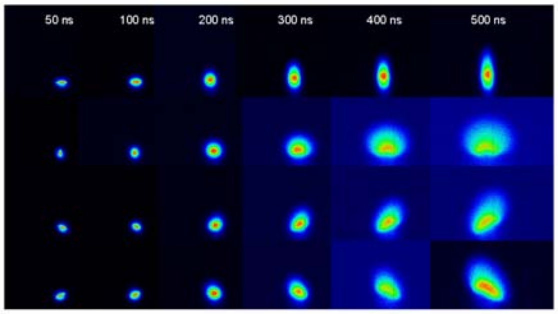

Figure 3. Experimentally observed evolution of plasma shape.

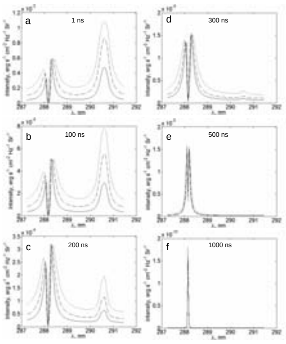

Figure 4. Spectra calculated along plasma ellipsoidal axes

Specific objectives for 2005-2006: 1. Further expand the theoretical model of LIP for atmospheric conditions. 2. Carry out the experimental verification of the atmospheric model; explore the possibility of determining the plasma composition from spectral data. 3. Continue plasma diagnostics (spatial and temporal distribution of plasma temperature, species number densities, etc.) using imaging and interferometric techniques.

Selected Publications Acknowledging DOE Support – 2003-2006

1. I.B. Gornushkin, N. Omenetto, B.W. Smith, J.D. Winefordner, *Determination of the maximum temperature at the center of an optically thick laser induced plasma using self-reversed spectral lines*, Appl. Spectrosc. 58 (2004) 1023-1031.
2. I. B. Gornushkin, C. L. Stevenson; G. Galbács; B. W. Smith; J. D. Winefordner, *Measurement and Modeling of Ozone and Nitrogen Oxides Produced by Laser Breakdown in Oxygen-Nitrogen Atmospheres*, Appl. Spectrosc. 57 (2003) 1142-1450.
3. I.B. Gornushkin, A.Ya. Kazakov, N. Omenetto, B.W. Smith, J.D. Winefordner, *Radiation dynamics of post-breakdown laser induced plasma*, Spectrochim. Acta Part B, 59 (2004) 401-418.
4. I.B. Gornushkin, A.Ya. Kazakov, N. Omenetto, B.W. Smith, J.D. Winefordner, *Experimental verification of laser induced plasma expanding into vacuum*, Spectrochim. Acta Part B 60 (2005) 215-230.
5. A.Ya. Kazakov, I.B. Gornushkin, N. Omenetto, B.W. Smith, J.D. Winefordner, *Radiation dynamics of post-breakdown laser induced plasma expanding into ambient gas*, Appl. Optics, in press (2006).
6. I.B. Gornushkin, S.V. Shabanov, N. Omenetto, J.D. Winefordner, *Non-isothermic asymmetric expansion of laser-induced plasma into vacuum*, J. Appl. Phys., (2006) submitted.

Facilitation of Chemical Sciences at BESSRC CAT

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Overall research goals: The purpose of this project is to develop X-ray small angle scattering and X-ray spectroscopy techniques for *in situ* and time-resolved studies of chemical problems. An important aspect of this program is the development and implementation of fast detectors.

Significant achievements in 2004-2006: Grazing incidence small angle X-ray scattering **(**GISAXS) and anomalous GISAXS have been used to characterize the structure and the reactivity of gold and platinum laser vaporization deposited, size selected clusters on surfaces designed to model catalyst supports. The GISAXS experiments were performed with a heated sample holder mounted on a goniometer at the APS beamline 12-ID at or near the critical angle with detection on a large area CCD. The data is analyzed by taking cuts in the q_{xy} direction for horizontal information and in the q_z direction for vertical information (see Figure 1).

Sintering of supported nanocatalysts often leads to the loss of the catalytic activity and selectivity. The thermal stability of supported platinum nanoparticles produced by cluster deposition on the naturally oxidized surface of a silicon wafer ($SiO_2/Si(111)$) has been studied using GISAXS up to above 400 °C. The data analysis reveals an unexpectedly high stability of the supported particles, which preserve their original size up to about 320 °C, at which an abrupt onset of the agglomeration takes place. The size evolution of platinum nanoparticles formed on a $SiO_2/Si(111)$ substrate has been studied as a function of the level of surface coverage with deposited clusters. The anisotropic shapes of sub-nanometer-size nanoparticles are changed to isotropic on the amorphous substrate as their sizes increased. Using AGISAXS, the scattering from nanoparticles on the surface of a substrate is well separated from that of surface roughness and fluorescence. It was shown that with AGISAXS it is possible to subtract the background and provide unbiased information about particle size of less than 1 nm. Furthermore, AGISAXS allows the possibility of performing element-specific studies of multi-component systems.

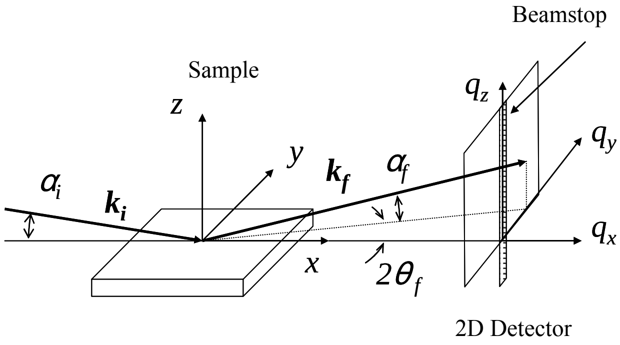

Figure 1. Schematic of GISAXS experiment.

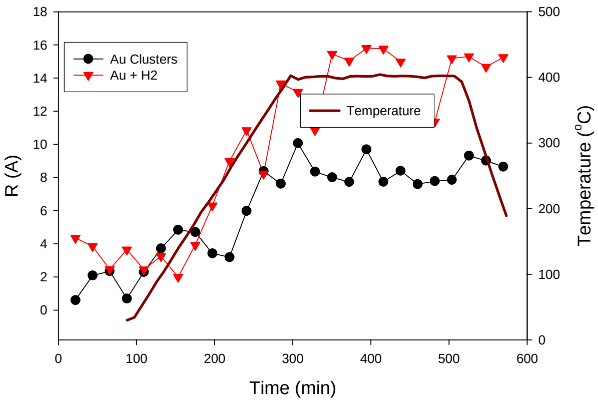

Figure 2. Change in r for $Au_{6\text{-}10}$ clusters on $Al_2O_3/Si(111)$ as a function of temperature.

The effect of hydrogen on the stability of the gold clusters has been examined. The results shown in Figure 2 demonstrate that the particles agglomerate under hydrogen to a greater extent in the horizontal direction. In a comparison of surfaces, the clusters were more thermally stable on Al_2O_3 compared to SiO_2 or TiO_2. It is important to note that these data were obtained on 1 – 3% of a mono-layer coverage, demonstrating the sensitivity of this experiment.

A 3.7 μs resolution small angle X-ray scattering (SAXS) detector has been designed, and construction is complete. This past December, X-rays from an intense "pink" beam were available for the first time in the experimental hutch 12-ID-C where the TRSAXS experiments are performed. This beam is several orders of magnitude more intense than the monochromatic beam previously used for SAXS studies. This increased flux allows us to perform both time-resolved experiments and static experiments. Results demonstrated that we can now measure time-resolved scattering profiles with a temporal resolution of 3.68 μs and a precision that is comparable to the precision of measurements that take much longer to acquire. It also demonstrates that for steady state systems, taking thousands of measurements in fractions of a second allows averaging that extends the precision of the measurements.

Specific objectives for 2006-2007:

- X-ray methods, including time-resolved methods, will be incorporated into an *operando* mode of studying chemical processing. Operando means that in situ characterization methods and product detection methods (such as MS) are used simultaneously to monitor the chemical processing. This approach will be illustrated by an application to catalysis, in particular the catalyzed oxidation of alkenes to alkene oxides.

- Time-resolved GISAXS and DXAFS detectors based on the same principles as the TRSAXS detector will be developed with the detectors groups at ANL.

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1. R. E. Winans; S. Vajda; B. Lee; S. J. Riley; S. Seifert; G. Y. Tikhonov; N. A. Tomczyk, *Thermal Stability of Supported Platinum Clusters Studied by in Situ GISAXS*. Journal of Physical Chemistry B**, 108**, (47), 18105-18107(2004)
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4. R. Tanaka; E. Sato; J. E. Hunt; R. E. Winans; S. Sato; T. Takanohashi, *Characterization of Asphaltene Aggregates Using X-ray Diffraction and Small-Angle X-ray Scattering*. Energy & Fuels**, 18**, (4), 1118-1125(2004)
5. S. Vajda; R. E. Winans; J. W. Elam; B. Lee; M. J. Pellin; S. Seifert; G. Y. Tikhonov; N. A. Tomczyk, *Supported Gold Clusters and Cluster-Based Nanomaterials: Characterization, Stability and Growth Studies by In Situ GISAXS under Vacuum Conditions and in the Presence of Hydrogen*. Topics in Catalysis**,** in press (2006)
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Electrochemically-Modulated Separation of Uranium and Plutonium

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Overall research goals:

The objective of this project is to understand the processes involved in electrochemically-modulated separations (EMS) of actinide elements.[1-3] Conventional and modified electrodes are used to improve mass spectrometric measurements via on-line coupling of EMS in a flow-injection approach. Mass spectrometry is used to elucidate mechanisms responsible for actinide accumulation and release under electrochemical cell potential control.

Significant achievements in 2003-2005:

In this project, a three-electrode flow-by electrochemical cell is interfaced via flow injection to an inductively coupled plasma mass spectrometer. Mechanistic studies of EMS of Pu and U continued. Using various anodization procedures, it was determined that actinide accumulation and signal enhancement are strongly dependent upon electrolytes used during anodization (i.e., the surface preparation step). Adsorption of anions into the GC matrix during the anodization procedure is the proposed mechanism for EMS separation of redox-specific species. Uranium and plutonium separations were found to be strongly dependent on the relative anion affinity between mobile (0.46 M HNO_3, 0.46 M HCl, and 0.46 M H_2SO_4) and stationary phases. Anodization in 0.46 M H_2SO_4 provides significantly greater accumulation for both U and Pu as compared with anodization in 0.46 M HNO_3 (standard practice) and other anions. Anodization in 0.46 M HCl, 0.46 M acetic acid, and 0.5 M NaOH resulted in little or no accumulation of U and Pu.

Interaction follows traditional Pu solution-phase pairings with strongest to weakest pairings being $SO_4^{2-} > NO_3^- > Cl^-$. For example, a GC electrode anodized in HNO_3 showed good accumulation for analytes (both U and Pu) in HCl and HNO_3 matrix but little accumulation for analytes in H_2SO_4 matrix. These results suggest that the mechanism of accumulation for both U and Pu are due to competitive and preferential complex formation with anions incorporated on the surface of the anodized GC electrode relative to those in solution. Investigations of oxidation potentials agree with literature studies. These suggest that the accumulation of Pu is dependant on a conversion of Pu (III) and Pu(IV) and Pu(V) to Pu(VI). Complexation is most favored for Pu(IV)>>Pu(III)~Pu(VI)>Pu(V). Observed accumulation efficiencies are consistent with anticipated abundances at the accumulation potential (+1.0V) and solution pH. The mechanism for release is consistent with known electrochemical reduction potentials for conversion of all Pu species to Pu(III).

Specific objectives for 2005-2006:
Many aspects of the Pu and U EMS-ICP-MS separation and analysis approach require further investigation. Future studies will focus on improving our understanding of the mechanisms for electrochemically-controlled accumulation and release of Pu and U. The nature of anion binding during GC preparation and its retention or removal during the release step is to be investigated. For example, are anions retained in the anodization film of the ~~electr~~ode? Are SO_4^{2-} and NO_3^- anions exchanged in the EMS process? If not, how are anions is SO_4^{2-} retained during negative potential scans? If anions migrate freely into and out of the film, why are differences observed in EMS performance dependant on the anion used during anodization? How do complex-forming anions in solution affect retention and release of Pu and U?

The role of colloid size in Pu accumulation is also of interest. The ability to accumulate Pu colloids and the related size dependencies of EMS accumulation will be investigated in collaboration with Dr. Richard Haire (ORNL, BES/Heavy Element Chemistry). A range of colloid sizes (0.2-10 nm) will be synthesized. Procedures and techniques will be established using cerium colloids as a surrogate.

Analytical benefits of the online EMS-ICP-MS approach will be demonstrated and on-line electrochemical separations of other actinides (e.g., Am, Np, Cm) will also be investigated.

<u>References of work that were supported by this project</u>

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Enhancement of the Analytical and Fundamental Utility of Radio-Frequency Ion Trap Mass Spectrometers by Development of a Comprehensive Model

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Overall research goals: The objective of this work is to enhance the analytical and fundamental utility of radio-frequency ion trap mass spectrometers by developing a comprehensive, quantitative model for ion motion and the underlying physico-chemical processes involved in their operation.

Significant achievements in 2003-2005:

- A kinetic theory based on the Boltzmann equation was developed for the trapping of atomic ions in a radio-frequency quadrupole ion trap. Microscopic definitions were obtained for the damping and stochastic forces that originate from ion-neutral collisions. These definitions contrast with corresponding phenomenological terms added ad hoc in previous treatments to create damped Mathieu and Langevin equations. The kinetic theory is not dependent on any special assumptions about the electric field strengths, the ion-neutral interaction potentials, or the ion-neutral mass ratio. It also provides an *ab initio* way to describe the ion kinetic energies, temperatures, and other properties by a series of successive approximations.

- General two-temperature and multi-temperature moment equations were developed from the Boltzmann equation for atomic ion motion in apparatus where the external electric and/or magnetic fields may vary with time and position. The expressions obtained, which do not appear to have been given previously, tend to complement those presented in previous ion trap studies. That is because of the difference in viewpoint between the moment equation approach, which focuses on average behavior of an ion ensemble, and others that concentrate on the individual trajectories of single (or multiple) ions.

- The differential equations governing the average ion velocity and energy given by the momentum-transfer approximation of the two-temperature moment theory were applied to both ideal and non-ideal quadrupole ion traps. Solutions of the set of coupled differential equations provided the ion number density, average velocities, average energy and average temperature as functions of time and position in the apparatus. The results are expected to be accurate, both by analogy with other situations where the momentum-transfer theory has proved accurate and because of the good results obtained when our results were compared with simulations based on the widely used ion trap simulation program ITSIM.

Specific objectives for 2005-2006:

- The two-temperature and multi-temperature moment theories will be applied to both ideal and non-ideal linear quadrupole ion traps. As in the previous work with three-dimensional quadrupole traps, the time- and position-dependent ion effective temperature will be determined as a function of time.

- Replacing the Boltzmann equation with the Wang Chang-Uhlenbeck-de Boer equation that accounts for inelastic collisions, our two-temperature moment theory for apparatus in which the external electric and/or magnetic fields may vary with time and position will be extended to include molecules.

References of work that were supported by this project

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2. L.A. Viehland and D.E. Goeringer, "Moment Theory of Ion Motion in Traps and Similar Devices. I. General Theories," *J. Phys. B: At. Mol. Opt. Phys.* **38**, 3987-4009 (2005).

3. D.E. Goeringer and L.A. Viehland, "Moment Theory of Ion Motion in Traps and Similar Devices. III. Two-Temperature Treatment of Quadrupole Ion Traps," *J. Phys. B: At. Mol. Opt. Phys*. **38**, 4027-4044 (2005).

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Chemical Microscopy of Conjugated Organic Macromolecules

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Overall Research Goals: Our primary research objective is to combine single-molecule imaging and spectroscopic tools with scanning probe microscopies to understand details of structure and internal order to in macromolecular systems and their relation photonic, or optoelectronic properties.

Significant Achievements:

- Understanding the role of internal molecular order and the relation to optical properties in luminescent conjugated polymers and composite macromolecular structures is important in device applications using these materials. In collaboration with Prof. Paul Lahti, we have been successful in synthesizing a family of fluorescent poly- and oligo-fluorenes and fluorenones with well defined architecture to address issues of molecular folding (in specific ways) and the impact on single-molecule fluorescence properties. In device applications involving polyfluorenes, a significant (and often undesirable) red component of the luminescence is often observed and some disagreement exists within the OLED community as to whether this effect is due to molecular defects or excimeric interactions in aggregates of many molecules. Our recent studies (publications are currently under preparation) provide conclusive proof that the effect in bulk films is excimeric in nature.

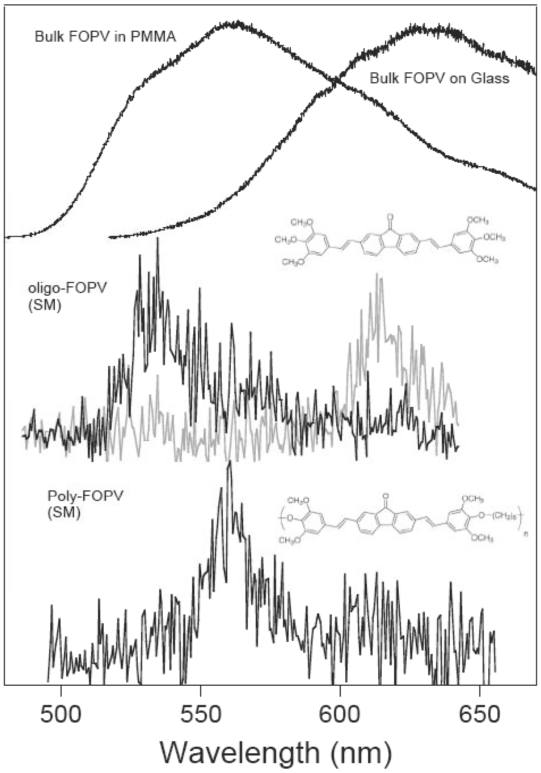

Figure 1. Bulk spectra of oligomeric fluorenone molecules dispersed in a PMMA matrix and neat film on glass. Isolated single molecules of oligo-FOPV do not show the deep red shift (640 nm) associated with neat films.

- Novel composite nanomaterials made from inorganic (quantum dot) and conjugated organic species could provide an important new route to highly efficient optoelectronic and energy-harvesting devices. In collaboration with Prof. Todd Emrick (UMass Polymer Science and Engineering Dept.), we have investigated the single molecule spectroscopy of CdSe quantum dots whose surfaces have been coordinated with conjugated organic ligands. We have found that the photophysics of individual composite nanostructures are profoundly altered with respect to bulk blends of the same components. Combining single-molecule spectroscopy with scanning probe microscopy on these species, we have been able to correlate spectral and temporal properties of the fluorescence with structural properties. Our results show that there is a significant heterogeneity in the surface coverage of organic ligands that strongly influences measurable optical properties such as spectral stability or fluorescence intermittency in the composite system.

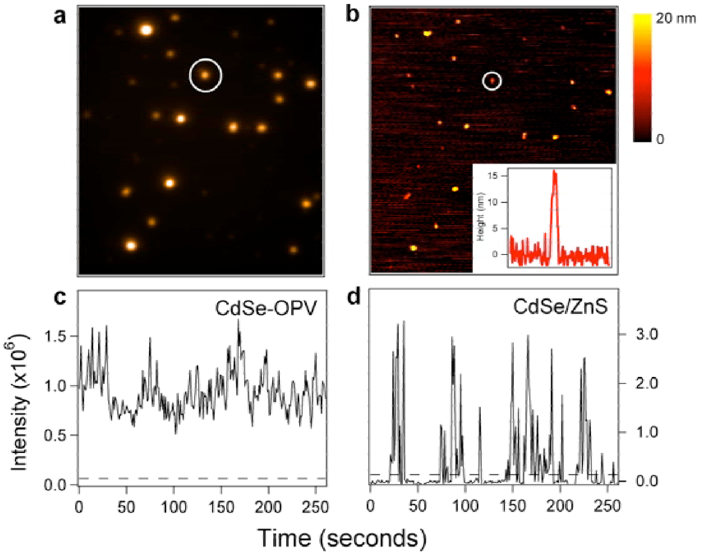

Figure 2. Spatially registered fluorescence and surface height images of CdSe-OPV nanostructures (**a** and **b**) along with fluorescence intensity vs. time trace for a 14 nm particle (**c**), and ZnS:CdSe reference (**d**).

Specific Objectives for 2005-2006:

- We are currently investigating intensity correlations, and fluorescence polarization anisotropy and the correlation between fluorescence lifetime and emission spectra in the fluorescence of poly-fluorene and fluorenone systems to understand how molecular architecture affects the degree of molecular order in these systems.

- Our specific objectives in the QD-organic composite systems for the coming year will be to investigate spectrally-resolved fluorescence dynamics and intensity correlations from single CdSe-OPV nanostructures. This will provide us with new information on the contribution of organic luminescence to the total fluorescence, as well as information on efficiency of energy transfer within a single nanostructure.

References to work supported by this project:

"Modification of blinking statistics in quantum dot-conjugated organic composite nanostructures," Nathan I. Hammer, Kevin T. Early, Kevin Sill, Michael Y. Odoi, Todd Emrick, and Michael D. Barnes, submitted to *Nature Materials* (status: under review).

"Optimizing OLED Efficacy of 2,7-Diconjugated 9,9-Dialkylfluorenes by Variation of Periphery Substitution and Conjugation Length" Hemali P. Rathnayake, Ali Cirpan, Zeynep Delen, Paul M. Lahti, Frank E. Karasz, submitted to *Advanced Functional Materials* (status: under review).

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