2004 DOE/BES Analysis Program Contractors' Meeting

Annapolis, Maryland
February 12 – 14, 2004

Sponsored by
The U.S. Department of Energy
Office of Basic Energy Sciences

Workshop Chair: John Miller

2004 DOE/BES Analysis Program
Contractors' Meeting

Program and Abstracts

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

FOREWORD

This abstract booklet provides a record of the 2004 U.S. Department of Energy, Office of Basic Energy Sciences, Analysis Program Contractors' Meeting. This group of scientists last met as part of the larger Separations and Analysis Program Contractors' Meeting held in San Diego April 5-7, 2001. The agenda and abstracts of that meeting may be found on the web at http://www.sc.doe.gov/bes/chm/Publications/publications.html.

There is wide agreement that a gathering of researchers with common interests and sponsorship provides a fruitful environment for exchange of research results, research techniques, and research opportunities. The primary means of communicating research achievements and perspectives at this meeting is oral presentations, formal discussion periods and informal breaks and meals. The agenda has been organized so that papers in related disciplines – such as mass spectrometry or optical spectroscopy – are loosely clustered together.

I am pleased to have the privilege of organizing this meeting and of serving as the program manager of this world-class research program. In carrying out these tasks, I 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. It is also hoped that this meeting will enhance your research efforts and will nurture future collaborations and initiatives.

Thanks are due to all of the researchers whose dedication and innovation have advanced our research and made this meeting possible and, I hope, productive. I am sure that all of you will build on your successes and that we will assemble in a very few years for our next meeting.

I offer special thanks to Jody Shumpert of the Oak Ridge Institute for Science and Education and to Karen Talamini of the Chemical Sciences, Geosciences and Biosciences Division in DOE for assisting in the technical and logistical aspects of this meeting.

John C. Miller

2004 DOE/BES Analysis Program Contractors’ Meeting

AGENDA

2004 DOE/BES Analysis
Program Contractors' Meeting

AGENDA

(Note: Speakers are bolded - Other contributors are named in abstracts)

Wednesday, February 11, 2004

7:00-9:00 pm Registration, Cash Bar and Light Hors d'oeuvres – **Lobby Level, Room 260**

Thursday, February 12, 2004

7:30-8:00 Registration and Continental Breakfast - **Arundel C**

8:00 Welcome – **John C. Miller**
U.S. Department of Energy, Office of Science
Chemical Sciences, Geosciences and Biosciences Division

8:15- 9:15 Plenary Lecture - **Dr. Sune Svanberg**, Lund Inst. of Tech., Sweden
Chemical analysis by optical and laser spectroscopy *P1*

9:15-9:45 **Break**

Session 1

9:45-10:05 **Richard E. Russo**
Laser Material Interactions (Ablation) for Chemical Analysis *S1-1*

10:05-10:25 **J. Thomas Dickinson**
UV Laser-Surface Interaction Relevant to Analytic Spectroscopy of Wide Band Gap Materials *S1-2*

10:25-10:45 **Nicolo Omenetto** (with J.D. Winefordner and Ben Smith)
Modeling, Diagnostic and Application of the Laser Induced Plasma *S1-3*

10:45-11:05 **Akos Vertes**
Excitation, Relaxation and Internal Energy Content in Matrix-Assisted Laser Desorption Ionization *S1-4*

11:05-11:25 **Willard W. Harrison**
Laser Desorption/Discharge Ionization Sources for Mass Spectrometry......................... *S1-5*

11:25-11:45 **Alla Zelenyuk**
Chemistry and Microphysics of Small Particles *S1-6*

12:00-1:15 **Lunch**

Session 2

1:15-1:35	**Julia Laskin** (with Jean H. Futrell**)** *Surface-Induced Dissociation of Complex Polyatomic Ions*	*S2-1*
1:35-1:55	**David H. Russell** *Fragmentation Chemistry of Peptide Ions as a Function of N-terminal Residue and Charge Carrier: [M+H, Li, Na, K, or Cu(I)]+*	*S2-2*
1:55-2:15	**T. Gregory Schaaff** *Mass Spectrometry of Nanocrystal and Cluster Compounds*	*S2-3*
2:15-2:35	**Paul B. Farnsworth** *Ion Sampling and Transport in Plasma Source Mass Spectrometers*	*S2-4*
2:35-2:55	**Robert Noll** (for Gary M. Hieftje) *Fundamental Studies of the Inductively Coupled Plasma and Glow Discharge*	*S2-5*
2:55-3:15	**Akbar Montaser** *Fundamental Nebulization Processes and Analyte Transport in High-Temperature Plasmas*	*S2-6*
3:15-3:30	**Break**	

Session 3

3:30-3:50	**Richard M. Crooks** *Measurements of Mass Transport Rate Through Well-Defined Nanoscopic Tubes*	*S3-1*
3:50-4:10	**Marc D. Porter** *Chemical Analysis at Nanodomains: Composition, Structure, and Function Relationships*	*S3-2*
4:10-4:30	**Eric Borguet** *Fluorescence Labeling of Surface Species (FLOSS) a Key to Understanding the UV Photoreactivity of Alkylsiloxane SAMs*	*S3-3*
4:30-4:45	Move to Alternate Room – **Calvert Ballroom**	
4:50-6:00	Discussion	
6:00	Adjourn and Dinner (on your own)	

Friday, February 13, 2004

7:30-8:00 Registration and Continental Breakfast – **Arundel C**

8:00 Welcome - **John C. Miller**
U.S. Department of Energy, Office of Science
Chemical Sciences, Geosciences and Biosciences Division

8:15- 9:15 Plenary Lecture - **Dr. Michael T. Bowers**, University of California, Santa Barbara
Ion Mobility: The Method and Its Applications to Problems in Materials and Biochemistry *P2*

9:15-9:45 **Break**

Session 4

9:45-10:05 **Scott A. McLuckey**
The Dynamics and Thermodynamics of Gaseous Macro-ions *S4-1*

10:05-10:25 **Douglas E. Goeringer**
Physicochemical Processes in RF Quadrupole Ion Traps *S4-2*

10:25-10:45 **R. S. Houk**
Inorganic Mass Spectrometry with ICP and Electrospray Ionization Sources *S4-3*

10:45-11:05 **Douglas C. Duckworth**
Mass Spectrometry of Room Temperature Ionic Liquids *S4-4*

Gary J. Van Berkel
Electrostatic and Electrochemical Processes in Electrospray *S4-5*

11:05-11:25 **James E. Delmore**
Surface Ionization Mass Spectrometry *S4-6*

11:25-11:45 **Gerardo Gamez** (for R. Graham Cooks)
Ion Motion and Ion Excitation in the Quadrupole Ion Trap Mass *S4-7*
Spectrometer: Simulation and Experiment Cooks

12:00-1:30 **Lunch**

Session 5

1:30-1:50 **Michael D. Barnes**
Oriented Polymer Nanostructures: New insights into intramolecular *S5-1*
structure and photophysics of conducing polymers

1:50-2:10 **Bruce A. Bushaw**
Triple Resonance Ionization: From Ultra-trace Isotope Analysis to *S5-2*
High Precision Spectroscopy

2:10-2:30 **Jeanne E. Pemberton**
Vibrational Spectroscopy of Chromatographic Stationary Phases *S5-3*

2:30-2:50 **Edward M. Eyring**
Characterization of Intermediates by Attenuated Total Reflectance Infrared Spectroscopy *S5-4*

2:50-3:10 **Janos H. Fendler**
Quantification of Interparticles Forces and Aggregation of Nanoparticles *S5-5*

3:10-3:30 **Robert J. Hurtubise**
Solid-Matrix Luminescence Analysis and Coupling Solid-Matrix Luminescence with Separation Methodology *S5-6*

3:30-4:00 **Break**

Session 6

4:00-4:20 **Gary E. Maciel**
Multinuclear Magnetic Resonance Study of Silica and Modified Silica *S6-1*

4:20-4:40 **Gerald Diebold**
Thermal Diffusion Shock Waves *S6-2*

4:40-5:00 **Bruce S. Hudson**
Inelastic Neutron Scattering and Periodic DFT Studies of Hydrogen Bonded Structures *S6-3*

5:00-6:00 Discussion

7:00 Cash Bar and Dinner (provided by DOE) – **Calvert AB**

Saturday, February 14, 2004

8:30-9:00	Continental Breakfast – **Arundel C**	

Session 7

9:00-9:20	**Paul W. Bohn** *Molecular Aspects of Transport in Thin Films of Controlled Architecture*	*S7-1*
9:20-9:40	**Sheng Dai** *Novel separation processes via hierarchically structured materials and ionic liquids*	*S7-2*
9:40-10:00	**George Guiochon** *Study of the Homogeneity of Adsorbent Surfaces*	*S7-3*
10:00-10:20	**Frank Bright** *Studies of Solvation Processes in Supercritical Fluids*	*S7-4*
10:20-10:50	**Break**	
10:50-12:30	Discussion and Wrap Up	
12:30	Adjourn	

2004 DOE/BES Analysis Program
Contractors' Meeting

Abstract
Plenary Lecture 1

2004 DOE/BES Analysis Program Contractor´s Meeing
Annapolis, Md., February 12-14 2004

Chemical analysis by optical and laser spectroscopy

Sune Svanberg

Department of Physics, Lund Institute of Technology,
P.O. Box 118, S-221 00 Lund, Sweden
sune.svanberg@fysik.lth.se

Optical spectroscopy, and in particular laser spectroscopy, provide many interesting possibilities for chemical analysis [1]. Attractive features of laser spectroscopy include a high spectral resolution and associated selectivity, strong signals and associated high sensitivity (sometimes down to the single-molecule limit), as well as real-time data acquisition. In addition, non-intrusive measurements can frequently be performed. The latter concept also includes remote sensing monitoring of the atmosphere, hydrosphere and terrestrial vegetation. The extremely wide field indicated by the title of this talk will be illustrated by some examples selected from research activities performed in the author´s research group.

Atmospheric monitoring includes long path absorption and laser radar (lidar) measurements. Tuneable lasers, such as semiconductor lasers, dye lasers and optical parametric oscillators (OPO) allow measurement on molecular electronic transitions in the UV region or on rotational-vibrational transitions in the IR region. We have performed extensive range-resolved monitoring of industrial pollutants as well as gases of geophysical (volcanic, geothermal, mining) origin [2,3]. Recently, complex mixtures of hydrocarbons were remotely analyzed employing lidar and multivariate techniques [4] An IR, passive gas-correlation technique has recently been demonstated to be very efficient in hydrocarbon gas imaging [5].

Laser-induced fluorescence (LIF) is a powerful technique for monitoring even complex liquid or solid samples. We have performed extensive work in such diverse fields such as cancer tumour detection [6], marine probing, vegetation status assessment and remote imaging of historical monuments [4,7-9].

Absorption spectroscopy in scattering media as a rapidly developing field with wide applications ranging from living tissue spectroscopy [10] to pharmaceutical preparations [11]. Recently, the method has been extended to the analysis of free gas dispersed in scattering media [12-14]. Here, the narrow absorption lines are easily recognized in the presence of the very broad spectral structures characteristic of the solid or liquid matrix material. The new technique allows concentration, pressure and diffusion measurements.

References

1. S. Svanberg, *Atomic and Molecular Spectroscopy - Basic Principles and Practical Applications,* 4th edition (Springer-Verlag, Heidelberg 2004).
2. S. Svanberg, Geophysical gas monitoring using optical techniques: volcanoes, geothermal fields and mines, Optics and Lasers in Engineering **37**, 245 (2002)
3. M. Sjöholm, P. Weibring, H. Edner and S. Svanberg, Atomic mercury flux monitoring using an optical parametric oscillator based lidar system, Submitted to Optics Express (2004)
4. P. Weibring, H. Edner and S. Svanberg, Versatile mobile lidar system for environmental monitoring, Appl. Optics **42**, 3583 (2003)
5. J. Sandsten, P. Weibring, H. Edner and S. Svanberg, Real-time gas-correlation imaging employing thermal background radiation, Optics Express **6**, 92 (2000)
6. S. Svanberg, Tissue diagnostics using lasers, in *Lasers in Medicine,* ed. R. Waynant (CRC Press, Boca Raton 2002), p. 135-16937.
7. S. Svanberg, Fluorescence lidar, in T. Fujii (Ed.) *Recent Advances in Laser Remote Sensing* (Marcel Dekker, 2004), to appear.
8. P. Weibring, Th. Johansson, H. Edner, and S. Svanberg, B. Sundnér, V. Raimondi, G. Cecchi, and L. Pantani, Fluorescence lidar imaging of historical monuments, Applied Optics **40**, 6111 (2001)
9. D. Lognoli, G. Cecchi, L. Pantani, V. Raimondi, R. Chiari, Th. Johansson, P. Weibring, H. Edner and S. Svanberg, Fluorescence Lidar imaging of the Parma cathedral and batistery, Appl. Physics B. **76**, 457 (2003)
10. S. Svanberg, Some applications of ultrashort laser pulses in biology and medicine, Meas. Sci. Technology **12**, 1777 (2001)
11. J. Johansson, S. Folestad, M. Josefson, A. Sparén, C. Abrahamsson, S. Andersson-Engels and S. Svanberg, Time-resolved NIR/VIS spectroscopy for analysis of solids: pharmaceutical tablets, Appl. Spectrosc. **56**, 725 (2002)
12. M. Sjöholm, G. Somesfalean, J. Alnis, S. Andersson-Engels, and S. Svanberg, Analysis of gas dispersed in scattering solids and liquids, Opt. Lett. **26**, 16 (2001)
13. G. Somesfalean, M. Sjöholm, J. Alnis, C. af Klinteberg, S. Andersson-Engels and S. Svanberg, Concentration measurement of sas imbedded in scattering media employing time and spatially resolved techniques, Appl. Optics **41**, 3538 (2002)
14. J. Alnis, B. Anderson, M. Sjöholm, G. Somesfalean and S. Svanberg, Analysis of gas in wood materials, Appl. Phys. B**77**, 691 (2003)

Abstract

Sune Svanberg, Department of Physics, Lund Institute of Technology, P.O. Box 118, S-221 00 Lund, Sweden, *Chemical analysis by optical and laser spectroscopy*

Several examples of chemical analysis in the environmental and medical fields are given, illustrating the power of modern optical and laser spectroscopy techniques

2004 DOE/BES Analysis Program
Contractors' Meeting

Abstracts
Session 1

Laser Material Interactions (Ablation) for Chemical Analysis

Richard E. Russo, PI
Xianglei Mao, Staff Physicist
Chunyi Liu and Xianzhong Zeng, Graduate Student Research Associates
Jhanis Gonzalez, Visiting Scientist
Lawrence Berkeley National Laboratory
Mail Stop 70-108B
Berkeley, CA 94720
rerusso@lbl.gov

Overall Research Program and Goals:

Laser ablation for direct solid sample chemical analysis has tremendous potential for DOE applications, for example to directly characterize waste-site and nonproliferation samples. Laser ablation sampling is a process in which a high-power pulsed laser beam explodes a small portion of the solid sample into an aerosol with subsequent analysis of the aerosol performed by optical or mass spectrometry. Laser ablation sampling is almost entirely based on empirically establish parameters; models or mechanisms have not been established, one cannot predict the quantity and composition of the ablated aerosol for a given set of laser and sample properties. The desire to understand mechanisms is based on the need to ablate samples without matrix dependence and without fractionation (ablated mass vapor is not chemically equal to the original sample).

The goals of this BES-supported research are to elucidate fundamental mechanisms describing laser-material-interactions (ablation) for chemical (elemental) analysis at atmospheric pressure. This research program studies generation, transport, and detection of the ablated aerosol. Fundamental issues addressed include electron emission, mass ejection, plume/plasma dynamics, and chemistry (chemical composition of the ablated aerosol compared to the original sample material). Mass spectroscopy, emission spectroscopy and imaging are utilized to study ablation processes; the data from these studies are related to fundamental models. Goals are to understand fundamental issues related to laser-energy coupling efficiency, preferential removal of elements during ablation, effect of plasma shielding, and the influence the induced surface plasma on ablation. Time-resolving the ablation process and measuring the chemistry of the aerosol in each of these non-linear regimes forms the basis of this research program.

Specific Objectives for 2002 – 2003

The research was organized into the following three components of the ablation process: electron emission on the picosecond time scale after the laser pulse, the ejection of vapor (atomic, ionic) nanoseconds after the pulse, and particle ejection. These research components were studied based on two primary experimental procedures: imaging (spectroscopic and shadowgraph) and elemental detection.

Imaging

A significant portion of this research was based on time-resolved images of the ablation plasma and its expansion dynamics. Two types of time-resolved imaging were employed; spectroscopic (figure 1a) and shadowgraph (figure 1b) imaging.

Fig 1a: Femtosecond Pump-Probe Imaging

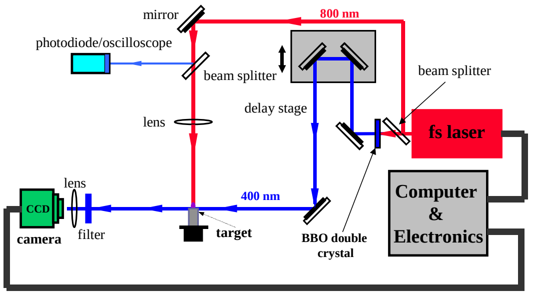
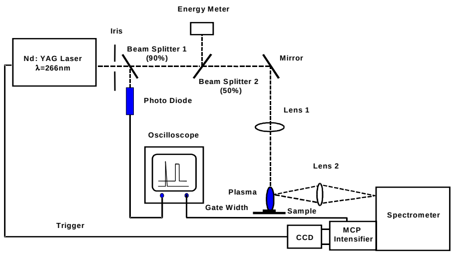


Fig 1b: Spectroscopic Diagnostics of Laser-Induced Plasma



Overall, the imaging system has been used to show that, electrons are emitted from the surface on the picosecond time scale, followed by atomic/ionic mass ejection (plasma plume) on the nanosecond time scale, followed by surface explosion with ejection of large (>1 micron) particles microseconds after the laser pulse is finished. The picosecond electron plasma was modeled based on five ionization mechanisms and shown to have a significant influence on the absorption of the laser beam. Large (>1micron) particle ejection was measured only after a threshold fluence. The process for larger particle ejection was modeled using a phase explosion mechanism. The spectroscopic system was used to measure the temperature and electron number density of the plume between 100 and 300 nanoseconds after the laser pulse. Plasma/plume temperature and electron number density were measured from the broadening of atomic and ionic emission lines within the luminous plasma. The spectroscopic measurements showed a significant change in plasma temperature and electron density at the same threshold at which the large particles were ejected.

Particles

Laser ablation sampling produces particles with a size distribution ranging from nanometers to micrometers. Particle ejection currently is one of the most important parameters of interest to the analytical community. The particle size distribution is a function of the laser and sample-material properties. The particle-size distribution influences the ability to transport ablated mass, and the behavior of that mass in an analytical source (inductively coupled plasma). An ion-mobility measurement system was used to measure particle size distribution as a function of laser, material, and ambient properties. Particle chemistry versus size was measured using an SEM with EDAX capabilities. The particle chemistry was found to be a function of the particle size; the Zn/Cu ratio measured for the various particle sizes ablated from a brass sample showed that particles smaller than about 100 nm were rich in zinc concentration, whereas larger particles were copper rich. The particle-size chemistry dependence may be the root cause of fractionation (a case in which the elemental composition of the ablated mass does not equal that of the original sample).

Plans for Future Research

The research program will continue to study fundamental laser-material-interaction (ablation) processes and utilize this expertise to benefit laser sampling for chemical analysis. The organization of the program will be maintained with emphasis on imaging vapor-plasma emission and particle generation. The goal of this work is to relate the vapor-phase emission mechanisms to the measured chemistry of the plasma. We plan to continue to use interferometric and Schlieren imaging to study plume/plasma formation. Further experiments will be conducted to image electron excitation in (and outside) transparent materials, to understand defect formation, space charge, and shielding processes. Femtosecond time-resolved absorption imaging and interferometry experiments would have the capability of monitoring highly non-equilibrium laser ablation process. The research will emphasize the comparison of nanosecond versus femtosecond pulses for the ablation experiments. Information collected from the ICP-MS will be compared with the femtosecond imaging results, paying particular attention to the possible correlation between the compositions of ablated mass with plasma development between 100 femtoseconds to about 10 picoseconds. This is a critical period of time at which non-thermal effects, which are not well understood, may dominate over thermal effects that manifest themselves typically at nanosecond time scale. In other words, although the laser pulse may not induce thermal effects in the sample, the subsequent high temperature micro-plasma near the sample surface can radiatively heat the sample. These experiments will provide information on the influence of the plasma on chemical analysis, as well as fundamental information on the evolution of the plasma.

Publications Acknowledging DOE Support 2002-2003

1. Nanosecond and Femtosecond Laser Ablation of Brass: Particle Size Distribution and ICPMS Measurements, C. Liu, X.L. Mao, S. Mao, X. Zeng, R. Greif and R.E. Russo, *accepted in Analytical Chemistry September, November 2003.*
2. Laser Plasma Interactions in Fused Silica Cavities, X. Zeng, X.L. Mao, S.S. Mao, J.H. Yoo, R. Greif, and R.E. Russo, *accepted in J. Appl. Phys. July 2003.*
3. Comparison of Ultraviolet Femtosecond and Nanosecond Laser Ablation ICP-MS Analysis in Glass, Monazite and Zircon, F. Poitrasson, X.L. Mao, S. S. Mao, R. Freydier, R. E. Russo, *Analytical Chemistry **75(22):** 6184-6190 (2003).*
4. Laser Ablation Sampling, R.E. Russo and D.P. Baldwin, book chapter Sample Preparation in Analytical Chemistry, 2003
5. Laser-Induced Plasmas in Micro-machined Glass Cavities, X.Z. Zeng, S.S. Mao, C. Liu, R. Greif, X.L. Mao, R.E. Russo, *Applied Physics Letters. **83(2):** 240-242, (2003).*
6. Plasma Diagnostics During Laser Ablation in a Cavity, X.Z. Zeng, S.S. Mao, C. Liu, R. Greif, X.L. Mao, R.E. Russo, *Spectrochimica Acta Part B-Atomic Spectroscopy. **58(5):** 867-877 (2003).*
7. Imaging Femtosecond Laser Induced Electronic Excitation in Silica, X.L. Mao, S.S. Mao and R.E. Russo, *Applied Physics Letters **82(5),** 697-699 (2003).*
8. Femtosecond Laser Ablation ICP-MS, R.E. Russo, X.L. Mao, S.S. Mao, and J.J. Gonzalez, *J. Analytical Atomic Spectrometry **17(9)**, 1072-1075 (2002).*
9. Comparison of 193nm, 213nm, and 266nm Laser Ablation ICP-MS, J.J. Gonzalez, S.S. Mao, X.L. Mao, J. Roy, and R.E. Russo, *J. Analytical Atomic Spectrometry **17(9),** 1108-1113 (2002).*
10. Delayed Phase Explosion during High-Powered Nanosecond Laser Ablation of Silicon, Q. Lu, S.S. Mao, X.L. Mao, and R.E. Russo, *Applied Physics Letters **80(17)**, 3072-3074 (2002).*
11. The Physics of Laser Ablation in Micro Chemical Analysis, R.E. Russo, X.L. Mao, and S.S. Mao, *invited A-page article in Analytical Chemistry **74**, 70A-77A (2002).*
12. Laser Ablation in Analytical Chemistry – A Review, R.E. Russo, X.L. Mao, H.C. Liu, J. Gonzalez, and S.S. Mao, *invited review article in Talanta **57(3)**, 425-451 (2002).*

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

J. Thomas Dickinson, PI
Steve Langford, Sergey Avanesyan, Postdoctoral Research Associates
Loren Cramer, Khin Nwe, Joel Lonzaga, Yong Fan, Graduate Research Assistants
Pasha Petite, Brian Schubert, Ty Cumby, Undergraduate Research Students
Department of Physics, Washington State University, Pullman, WA 99164-2814
E-mail: jtd@wsu.edu Group website: http://www.wsu.edu/~jtd

Overall Research Goals. Our work supports important aspects of mass spectroscopic methods for chemical analysis of inorganic materials such as waste, vitrified materials, soils and minerals. Our primary concern is to understand the mechanisms of excitations that lead to single particle emission and ionization from insulating surfaces under laser radiation. Thus fundamental issues of laser desorption and laser ablation are addressed. Recent new areas are studies of 157 nm laser radiation and ultrafast laser interactions with inorganic materials. Crystal defects often dominate and control these processes at lower laser intensities; their role is a dominant focus of our research.

Specific Objectives for 2003-2004. (1) Examine the effect of changing the UV photon energy from 5 eV to 7.9 eV on the mechanisms for charged and neutral particle emission from wide bandgap single crystal insulators; (2) Explore the possibility and consequences of two-photon absorption in materials such as CaF_2 (bandgap ~12.2 eV) exposed to 157 nm radiation, including F-Center formation, aggregation, and metallic Ca nanoparticle formation; (3) Examine the interaction of lasers with single crystals containing metallic nanoparticles; (4) Study the effect of low pressure water vapor on laser and electron beam interactions with single crystal NaCl and $NaNO_3$; (5) Examine color center formation in wide bandgap materials exposed to femtosecond laser radiation; and (6) Examine laser induced fracture as a way to create small particles for LIBS and ICP-MS.

Significant Achievements

Single Crystal $NaNO_3$. $NaNO_3$ is a major component of high-level waste at the Hanford site. We have extended our studies of ion and neutral emissions from single crystal $NaNO_3$ to excimer laser irradiation at 157 nm (F_2 laser; 7.9 eV photons) and 193 nm (ArF laser, 6.4 eV photons), and have compared this response to emission at 248 nm (KrF 5.0 eV photons). This spans the dominant nitrate $\pi^* \rightarrow \pi$ absorption at 6 eV, where 157 nm and 248 nm show relatively weak absorption. We use quadrupole mass-selected time-of-flight spectroscopy to simultaneously determine both species and kinetic energies. At all wavelengths, ion emission is dominated by Na^+ and NO^+ with kinetic energies in the 2-4 eV range. The fluence dependence is similar at all wavelengths. The major finding is that these emissions do not correlate with the nitrate absorption. Rather, surface defects are the dominant source of emissions. A defect-moderated electrostatic repulsion model including laser-induced electron transfer describes our results quite well.

Ion and neutral emission from single crystal CaF_2 *vs. Laser Wavelength.* At all three wavelengths (157, 193, and 248 nm), ion emission from the CaF_2(111) cleavage surface is dominated by Ca^+. The fluence dependence is similar at all three wavelengths. Again, surface defects were shown to be dominant source of emissions, which are well described by defect-moderated electrostatic repulsion model. At 157 and 193 nm, the kinetic energy distributions typically show two peaks separated by about 2 eV (typically 8 eV and 6 eV), suggesting that ions are emitted from two distinct surface environments. Importantly, the emissions are significantly more intense from polished material than from cleaved material. Polishing produces defects via plastic deformation which interact with laser radiation. These interactions are possibly under-appreciated by the optics community. With increasing laser fluence, ion emissions with lower kinetic energies appear (typically 2 eV and 0.6 eV). Under 248-nm radiation, only the low energy ions are observed, suggesting that 248-nm (5 eV) photons lack the energy to photoionize the defects responsible for high energy ion emission. A point-defect model is being developed to account for these kinetic energies.

We have also shown that prolonged exposure to 157-nm radiation increases the ion intensity from CaF_2, i.e., the ion emissions “induct.” Such induction or incubation is not seen at 193 nm or at 248 nm. This is potentially an important issue for optical applications CaF_2. at 157 nm. Conversely, when very high defect densities are introduced by electron irradiation, exposure to 157-nm radiation can actually reduce ion intensities. The competition between defect production and destruction is being further investigated. Further studies are underway on the neutral emission (principally calcium Ca^o) with emphasis on production mechanisms. We hope to determine an activation energy for Ca° emission, if any, by measuring emission intensities versus effective temperatures determined from neutral time-of-flight data. Efforts to detect possible negative ions (F^- and/or F_2^-) are also planned.

Optical bleaching of absorption due to metal colloids in single crystal CaF_2 at 532 nm and 157 nm. The darkening of optical materials by prolonged exposure to UV light limits the lifetime of UV optics in some applications; similar processes affect other wide bandgap materials in high dose radiation environments. We have used UV-VIS spectroscopy to characterize defects in single crystal CaF_2 generated by exposure to 2 keV electrons. CaF_2 is an important optical material for VUV applications. In this context, electron exposure is a conveniently rapid means of producing high defect densities that visibly darken the material. Exposure to energetic electrons greatly increases the ion emissions during subsequent laser irradiation. Spectroscopic evidence indicates that electron irradiation produces metallic colloids which grow with increasing electron dose. Subsequently exposing the darkened CaF_2 to 157 nm (F_2 excimer) or 532 nm (doubled Nd:YAG) radiation alters the absorption spectra in a fashion consistent with a gradual decrease in the average size of the colloid particles and eventually restores most of the lost transparency. Given the high transparency of CaF_2 at 532-nm, we attribute this bleaching effect to the localized heating of individual colloids. Detection of blackbody radiation accompanying bleaching supports this mechanism.

Effect of water vapor on laser interactions with single crystal inorganics: We have shown that water vapor at partial pressures of 10^{-5} Pa dramatically enhances the electron- and photon-induced emissions from single crystal NaCl and $NaNO_3$, especially at temperatures well above room temperature. Measurements as a function of sample temperature show convincingly that a rate-limiting emission process is thermally activated. Nevertheless, water vapor has no discernable effect on the activation energy. Unique morphological structures with nanometer-scale dimensions are produced by these treatments. Optical properties of structured surfaces often show strong "stealth-like" behavior in the visible portion of the spectrum. We attribute the effect of water vapor to a weakening of critical chemical bonds, which are then more readily attacked by both laser photons and energetic electrons. One of the most exciting results is that at low exposures we can characterize the very beginnings of surface modification on NaCl(100) surfaces, including atomic step erosion and the formation of one atomic layer deep etch pits! The rate of pit formation and growth are dramatically enhanced by the presence of water vapor. Thus, we are positioned to open up an entire new area of radiation/surface interaction studies based on defects generating defects to eat up the surface.

Photochemical and photothermal processes in the ablation of photoactive polymers. Laser interactions with polymers can be enhanced by incorporating photoreactive moieties into the polymer itself. One possible application is the use of such polymers for MALDI matrices. In collaboration with Thomas Lippert and Marcus Kuhnke, Paul Scherrer Institute, Switzerland, we have studied in our laboratory the ablation behavior of two triazene polymers (TP's), an azide polymer (GAP) and two polyimides (a spin-on-polymide and Kapton^{TM}) under 157 nm irradiation. At 157 nm, Kapton^{TM} displays the lowest threshold fluence for the detection of decomposition products by mass spectroscopy (20–25 mJ/cm^2), followed by the triazene polymers (~28 mJ/cm^2) and the spin-on polyimide (~42 mJ/cm^2). Interestingly, the polymer with the most reactive group (GAP, < 1.3 eV) shows the highest threshold, typically 80–90 mJ/cm^2, possibly due to the absence of suitable absorption sites for 157-nm photons. The most intense emissions from the TP polymers at 157 nm are at 30 amu (N_2), consistent with work on similar materials at shorter wavelengths (248 nm, 308 nm). However, at 157 nm, all the studied polymers decompose into small fragments with masses generally less than 30 amu, presumably due to the ability of 157 nm (7.9 eV) photons to both break C-C backbone bonds and to photoionize many of the resulting fragments.

Color center formation in soda lime glass and alkali halides with femtosecond laser pulses. The high instantaneous powers associated with femtosecond lasers can color many nominally transparent materials. Absorption produced in single crystal KCl by 400 nm femtosecond pulses is illustrated in Fig. 1. Although the excitations responsible for coloration occur on subpicosecond time scales, subsequent interactions between the resulting electronic and lattice defects complicate the evolution of color center formation and decay. We have studied the evolution of color centers produced by femtosecond laser radiation in soda lime glass and single crystal NaCl on time scales from microseconds to hundreds of seconds. Using an appropriate probe laser focused through the femtosecond laser spot, we can follow the changes in coloration due to individual or multiple femtosecond pulses, and follow the evolution of that coloration for long times after femtosecond laser radiation is terminated. For soda lime glass, the decay of color centers is well described in terms of bimolecular annihilation reactions between electron and hole centers. Similar processes appear to operate in single crystal sodium chloride. Absorption due to point defects in the alkali halides has been extensively studied, facilitating the interpretation of changes during and after irradiation. Controlled defect formation is useful for simulating the consequences of exposure to high dose radiation, e.g., in nuclear wastes and host materials for waste storage, and exploring their chemical as well as optical properties.

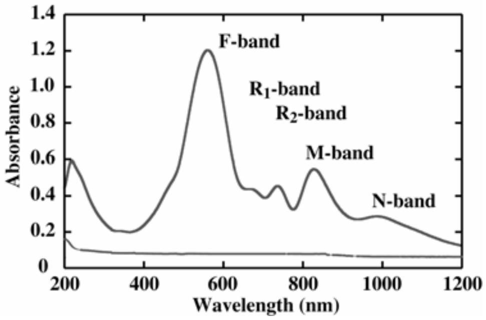


Fig. 1. Absorption spectra of single crystal KCl before and after darkening with 400 nm femtosecond laser radiation. The defects responsible for the absorption features below 400 nm are noted immediately above each peak. The R, M, and N bands are produced by F-center aggregates.

Production of particles by laser-induced fracture of single crystals for chemical analysis. Laser-induced breakdown spectroscopy (LIBS) and LAICP-MS have been often been plagued by major limitations: uncertainty in the effective temperature of the breakdown plume (in LIBS), and the depletion of volatile components during irradiation and the formation of non-stoichiometric droplets (in ICP-MS). We have been addressing the latter problem by using a Nd:YAG laser operated at 1.06 µm to produce fracture particles from $NaNO_3$ and other minerals suitable for subsequent evaporation and analysis by LIBS using a second laser. Fracture particles are generated at laser fluences somewhat below the threshold for optical surface damage, which does not melt the sample. In contrast with the melted particles produced at the higher fluences typical of most LIBS operations, the composition of these fracture particles should be free of thermal depletion effects. Most particles from cleaved minerals are produced by fracture along previously existing cleavage steps. We are comparing these fracture particles with particles produce at fluences above the threshold for optical breakdown, where extensive melting is observed.

Plans for Future Research on this Project: Two thirds of the above work is still underway with very clear objectives aimed at filling in missing mechanistic steps. For example, only recently were we able to detect 157-nm induced neutral emission from CaF_2, and we intend to fully understand how these particles are generated. Preliminary AFM studies on CaF_2 show that low radiation exposures generate structures similar to those observed by AFM on NaCl, suggesting that steps play a major role. These concepts need considerable study. Our ultrafast laser is being coupled to one of our UHV vacuum systems for ultrafast studies of particle emission from materials currently being studied with nanosecond pulses to compare yields, kinetic energies, and emission mechanisms. We are also examining the chemical reactivity of surfaces exposed to various lasers (primarily 157 nm and the fs laser). After irradiation, the samples are immersed in potentially reactive fluids on the stage of an AFM. AFM images showing surface evolution indicate reactivity. The fracture particle work will be moved to an ICP-MS unit in our building (Geology Department) where we will compare analysis results at laser fluences yielding fracture only vs. fluences the produce plumes (which is always accompanied by droplet formation).

Recent Publications Supported by this Grant (2003-4):

1. T. Lippert and J. T. Dickinson, “Chemical and spectroscopic aspects of polymer ablation: Special features and novel directions,” invited review, Chemical Reviews, 103(2) 453-486 (2003).
2. Myoung-Won Kim, L. C. Jensen, S. C. Langford, and J. T. Dickinson, “Emission of neutral Mg from MgO during abrasion with diamond,” J. Appl. Phys. 93(4) 1819-1825, (2003).
3. J. B. Lonzaga, S. M. Avanesyan, S. C. Langford, and J. T. Dickinson, “Color center formation in soda lime glass with femtosecond laser pulses,” J. Appl. Phys. 94(7),4332-4341 (2003)
4. J.T. Dickinson, S. Orlando, S.M. Avanesyan, and S.C. Langford, "Color center formation in soda lime glass and NaCl single crystals with femtosecond laser pulses" to appear in Appl. Phys. A. (2004).

Modeling, Diagnostic and Application of the Laser Induced Plasma

J.D. Winefordner, PI, B.W. Smith, co-PI, Scientist,
N. Omenetto, Scientist, I.B. Gornushkin, Adjunct Assistant Scientist
Department of Chemistry, University of Florida, Gainesville, FL 32611
(353) 392-0556, jdwin@chem.ufl.edu

Overall research goals. Our research program includes the study of fundamental aspects of the laser plasma induced in a gas (atmosphere) or on a solid substrate. The goal is to improve the general understanding of physical-chemical processes taking place in the laser plasma and its close vicinity. We intend to further develop a comprehensive theoretical model for an optically thick inhomogeneous laser induced plasma (LIP). The practical implication of the research will be improving the performance of spectrochemical analysis, especially, in terms of its accuracy. The analysis accuracy in LIBS is often degraded by strong matrix effects. Understanding the nature of these matrix effects will allow corrections for both spectral and chemical matrix interferences. We also persue the goal of miniaturization of LIBS for potential field applications. The latter include the development of a portable instrument for reliable in-situ, real time characterization of potential bio- and chemical hazards.

Specific objectives for 2002-2003. 1. Derive a suitable formalism for the computer simulation of LIP radiation dynamics with preset initial conditions such as the distribution of plasma species and the distribution of plasma temperature. 2. Investigate the possibility of using a similar theoretical model (the classic Bartels approach) for experimental diagnostics of LIP. 3. Demonstrate the feasibility of using the first commercial microchip laser as a part of a miniature LIBS setup which includes a small non-gated detector.

Significant achievements.

Plasma modeling. A radiation dynamic model of a post-breakdown plasma expanding into vacuum was developed. The model was based on a system of gas dynamic equations coupled with the equation of radiative transfer. Calculations were performed for a dual SiC system, although calculations for any arbitrary number of system's components were also permitted.

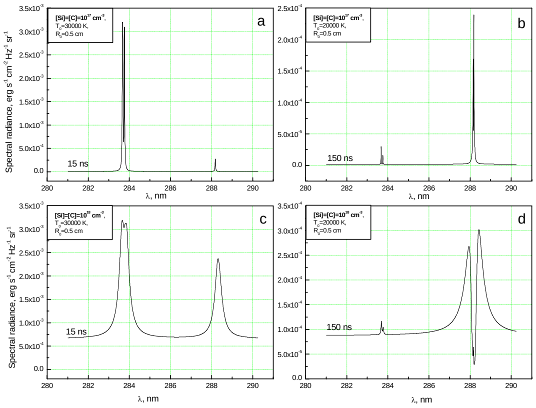


Figure 1. Synthetic spectra calculated at discrete times of 15 ns and 150 ns, using different initial temperatures and initial concentrations.

The model predicts the evolution of plasma temperature, the spatial and temporal distributions of atoms, ions, and electron number densities and the evolution of the plasma spectrum in a desirable spectral window (e.g. 280-290 nm for the SiC system chosen in this work, Fig.1). The model solves a two-fold task. First, it yields an analytical expression for the plasma radiation dynamics (and the synthetic spectra) under arbitrarily chosen initial conditions. Second, the developed computational routine allows finding the initial conditions by a direct comparison of calculated synthetic spectra with experimentally measured spectra. The model provides a rather simple theoretical mean to link the observed spectral features, such as the intensity and the shape of the lines to the plasma composition. In this respect, it can be considered as a step toward the possibility of performing absolute analysis.

Plasma diagnostics. A method of temperature measurement based on the model of an optically thick inhomogeneous plasma was applied to a laser plasma induced on a barium-containing target. The method involves the intensity ratio measurement of two self-reversed Ba II lines. The temperature thus determined corresponded to the maximum temperature in the plasma center. The plasma temperature was measured for delay times between 0.5 μs and 10 μs in two spectrometer operating modes: the scanning mode and the dual-wavelength mode, the latter resulting in better precision. A detailed analysis of experimental errors was performed. The error strongly depended on the wavelength separation of the lines used. The most accurate results were obtained for the largest line separation. Using one line in the UV and the other in the VIS (Fig.2a), the relative error was 2-6 % for temperatures between 8000 K and 20000 K (Fig.2b). The distribution of the plasma temperature along the plasma height was measured in the same delay time range. The temperature was found to be uniform along the plasma vertical axis, thus confirming the plasma cylindrical symmetry.

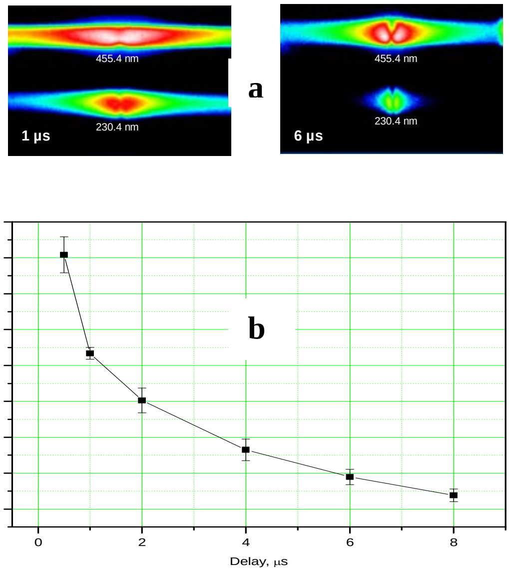


Figure 2. a) Plasma images obtained in the dual-wavelength mode; b) Evolution of maximum plasma temperature in the plasma center obtained in the dual-wavelength spectrometer mode.

Microchip laser in LIBS. A commercial 7 μJ/pulse, 550 ps microchip laser was used to induce plasma on metal foils and a Si wafer. The measured plasma lifetime was comparable with the duration of the laser pulse (a few ns). The plasma continuum radiation was low, while some of the strong resonance lines (e.g., Zn 213.86 nm) showed self-reversal. Tight laser focusing with a microscope objective was essential in order to achieve the breakdown irradiance. The mass removed (0.5 - 20 ng/pulse) was sufficient to yield spectra which were detected with portable grating

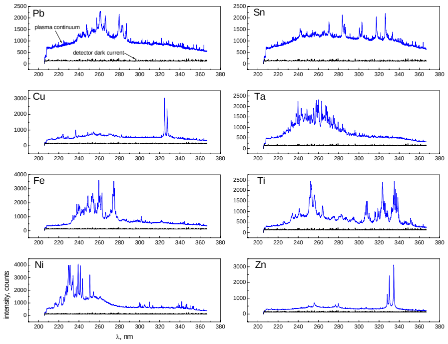


Figure 3. Spectra obtained with the USB2000 Ocean Optics spectrometer with a 500 ms integration time.

spectrometers equipped with non-gated, non-intensified detector arrays (Fig.3). The combination of the broadband spectrometer and the microchip laser can be very promising for material identification, especially in field applications. Quantitative analysis, however, does not seem sensitive with current instrumentation, detection limits being only in the low percentage range.

Plans for future research on this project. Our objectives for the following year are as follows. 1. Expand our theoretical model of LIP by considering more complex multi-element compounds and atmospheric conditions. 2. Carry out the experimental verification of the model; explore the possibility of the prediction of the plasma properties from spectral data. 3. Continue plasma diagnostics using models of inhomogeneous optically dense plasma including our model; comparison of the plasma properties obtained with those found in the literature. 4. Continue investigation of micro-plasmas induced on different targets by miniature microchip lasers in terms of both fundamental plasma studies (temperature, species number densities, etc.) and practical spectrochemical analysis.

Publications Acknowledging DOE Support – 2002-2003.

1. S.I. Gornushkin, I.B. Gornushkin, J.M. Anzano, B.W. Smith, J.D. Winefordner, "Effective normalization technique for correction of matrix effects in laser_induced breakdown spectroscopy detection of magnesium in powdered samples", Appl. Spectrosc. 56 (2002) 433-436.
2. I. B. Gornushkin; P. E. Eagan; A. B. Novikov; B. W. Smith; J. D. Winefordner, Automatic Correction of Continuum Background in Laser-Induced Breakdown and Raman Spectrometry, Appl. Spectrosc. 52 (2003) 197-207.
3. 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.
4. 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, in press.
5. I.B. Gornushkin, N. Omenetto, B.W. Smith, J.D. Winefordner, Determination of temperature of an optically thick laser induced plasma using self-reversed spectral lines, *Appl. Spectrosc.*, submitted (2003).
6. I.B. Gornushkin, N. Omenetto, B.W. Smith, J.D. Winefordner, High resolution two-grating spectrometer for dual wavelength spectral imaging, Appl. Spectrosc., submitted (2003).
7. I.B. Gornushkin, B.W. Smith, N. Omenetto, and J.D. Winefordner, Investigation of feasibility of using microchip lasers in LIBS, Appl. Spectrosc., submitted (2203).

Excitation, Relaxation and Internal Energy Content in Matrix-Assisted Laser Desorption Ionization

Akos Vertes, PI
Vasiliy Znamenskiy, Eugene Moskovets Postdoctoral Research Associates
Yong Chen, Guanghong Luo, Ioan Marginean and Lida Parvin Graduate Research Assistants
L.A. Heffernan, Eunyoung Park, Louise Ye Undergraduate Research
Department of Chemistry
The George Washington University
Washington, DC 20052
vertes@gwu.edu
http://www.gwu.edu/~vertes

Overall research goals. Matrix-assisted laser desorption ionization (MALDI) mass spectrometry is one of the cornerstones of modern protein analysis. In order to broaden the utility of this method, key processes in the ion formation and the properties of the generated ions are studied.

Specific objectives for 2002-2003. The quantitative photophysical description of MALDI is explored by using a wide range of optical pumping rates established by 22 ps and 4 ns laser pulse lengths. Furthermore, the sample morphology dependence of ionization is tested on pellets compacted at different pressures, yielding surfaces of varying roughness. An objective measure of the correlation between the internal energy content of ions generated by MALDI and the matrix properties is also established using thermometer molecules (TMs).

Significant achievements.

Laser pulse length and sample morphology dependence of ionization processes in MALDI. Recent advances in the quantitative modeling of MALDI indicate a mechanism based on two-step excitation, exciton pooling, charge transfer, ion recombination and gas-dynamic expansion. These processes in combination with radiative and non-radiative relaxation seem to be at the core of ion formation in MALDI. Studies of MALDI with lasers of different pulse lengths promise to give insight into the role of different mechanistic steps and further elucidate the model. Molecular dynamics simulations of MALDI desorption indicate that phase transition and ionization events occur on the picosecond time scale. Thus, it is expected that using vastly different pumping rates (ns vs. ps laser pulse) and comparing MALDI ion yields as function of laser fluence helps to clarify the model.

An important factor that is currently not part of the description is sample morphology. It is well known however, that the sample preparation method has a profound effect on MALDI ion yields. In order to understand the contribution of sample morphology, its systematic variation is necessary in concert with ion yield measurements.

For both ns and ps lasers, the ion signal from 2,5-dihydroxybenzoic acid (DHB) pellets was more stable and more persistent than from neat dried droplet (DD) samples. The ionization threshold fluence showed an increase with increasing compacting pressure (see Figure 1). For the ps laser, the ionization threshold values were approximately a factor of two higher than for the ns pulses. Analysis of the pellet SEM images showed that the fractal dimension decreased with increasing compacting pressure, –which is an indication of fractal coarsening (Figure 2). The corresponding ion yield measurements revealed that higher compacting pressure required higher laser fluences for comparable ion production. This points to the intriguing new phenomenon of diminishing of the ion yields with fractal coarsening of the surface.

The DHB matrix ions were dramatically more likely to fragment when irradiated with the longer laser pulse, indicating significant differences in plume dynamics. Furthermore, for both lasers fragmentation escalated with the increase in laser fluence, although this effect was significantly more pronounced for ns pulses (Figure 3). The DD samples of sinapinic acid (SA) and α-cyano-4-hydroxycinnamic acid (CHCA) also showed higher fragmentation with the longer laser pulse. These differences in MIYs can only be explained with the current mechanism if fragmentation reactions are included. Short pulses (fast pumping) can directly excite the matrix molecules to their ionization potential through ladder climbing and exciton pooling, whereas long pulses result in more fragmentation as the dissociation rate becomes comparable to the pumping rate.

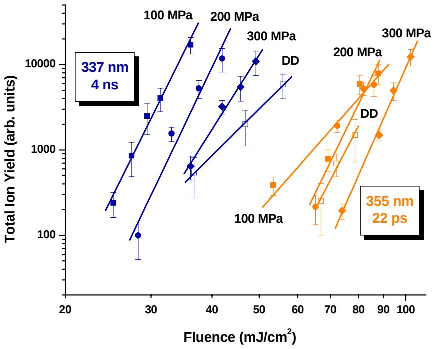


Fig. 1. Fluence-dependence of total ion yields (fragment and molecular ions) of DHB pellets made with 100 MPa (ν), 200 MPa (λ) and 300 MPa (υ) pressures, and of DD samples (❑).

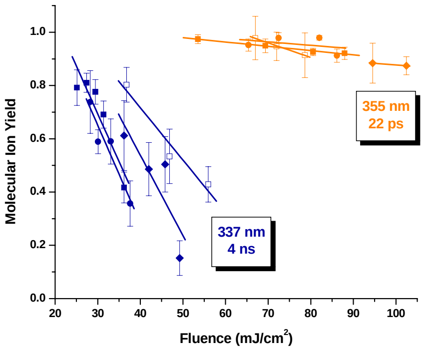
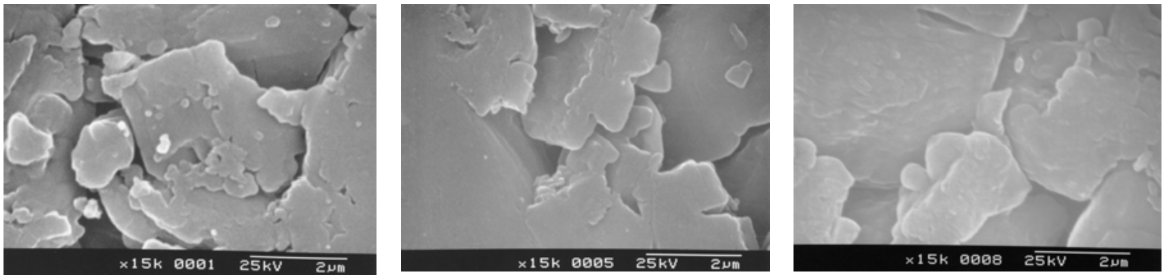


Fig. 3. DHB MIYs of pellets made with 100 MPa (ν), 200 MPa (λ) and 300 MPa (υ) pressures, and of DD samples (❑).



100 MPa
D = 1.348±0.004

200 MPa
D = 1.275±0.003

300 MPa
D = 1.185±0.003

Fig. 2. SEM images of pressed pellets taken at 15000× magnification and their fractal dimensions

For small analytes (≤ 2,000 Da), molecular ion signal was easily acquired with both lasers, whereas for larger molecules (≥ 5,000 Da), the analyte signal was difficult to acquire with the ps laser while it is easy to obtain with the ns laser. These observations are compatible with the assumption that the longer laser pulse can sequentially desorb and ionize analyte molecules due to the extended interaction of the laser pulse and the MALDI plume, whereas the shorter pulse can only desorb the analyte molecules but cannot promote their ionization due to its limited temporal overlap with the plume.

Internal energy measurement in MALDI. To provide an objective measure of the correlation between the internal energy content of ions generated by MALDI and the matrix properties, a series of well-characterized benzyl-substituted benzylpyridinium salts were used as thermometer molecules (TMs). The R substituents were 4-chloro- (4C), 4-floro- (4F), 4-methoxy- (4MO), 3-methoxy- (3MO), 4-methyl- (4M), 3-methyl- (3M), and 2-methyl- (2M), respectively. These molecules have simple ion fragmentation schemes (only one type of fragment) and the degree of fragmentation is proportional to their internal energy.

To determine the internal energy variations of analyte ions, the survival yields of TM molecular ions were measured in three different matrixes, α-cyano-4-hydroxycinnamic acid (CHCA), 3,5-dimethoxy-4-hydroxycinnamic acid (sinapinic acid, SA) and 2,5-dihydroxybenzoic acid (DHB). Statistical analysis of extensive survival yield data indicated that there were discernable differences among the studied matrixes. Molecular ions of the analytes showed decreasing survival yields and consequently increasing internal energies in the three matrixes in the following order: CHCA, SA and DHB with ‘cold’, ‘intermediate’ and ‘hot’ characteristics, respectively (Figure 4).

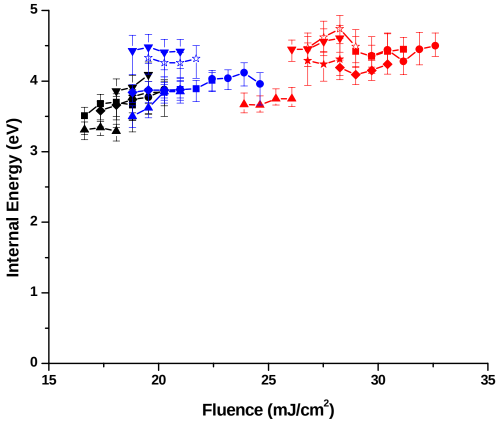


Fig. 4. Internal energies of substituted benzylpyridinium ions (2M (ν), 3M (λ), 4M (υ), 3MO (τ), 4MO (σ), 4C (H) and 4F (I)) in matrixes: CHCA (black), SA (blue) and DHB (red) as a function of laser pulse energy.

Qualitatively, this could be interpreted as a significant departure from earlier observations for peptides suggesting an opposite trend. The classification as ‘hot’ and ‘cold’ matrixes should be further qualified primarily by accounting for the influence of laser pulse energy and the nature of the analyte. Higher laser pulse energy led to an elevated level of energy transferred to the analyte, which in turn resulted in a diminished survival yield of the analyte molecular ion. It is quite possible that the assignment of 'hot' and 'cold' reverses as the laser energy changes. Furthermore, the nature of the analytes in previous experiments (peptides) and in the ones presented here (benzyl-substituted benzylpyridinium salts) is significantly different. The dramatic difference in internal energy data raises the possibility that the energy transfer from matrix to analyte also depends on the nature of the analyte and the interaction between matrix and analyte. These findings further clarify the nature of the energy transfer process, help predict the outcome of post-source decay experiments and clarify the concept of 'hot' and 'cold' matrixes in MALDI mass spectrometry.

Plans for future research on this project.

The pumping rate studies continue on other matrix molecules (e.g., CHCA and SA) that show significantly different photochemistry from DHB. In order to uncover the role of fractal coarsening in MALDI, we plan to compare the fractal dimension of matrix surfaces before and after laser exposure. Based on these results, a photophysical model will incorporate the effect of matrix fragmentation and sample morphology. Further insight into the internal energy deposition into the analytes is expected from utilizing TMs with and without preformed ions. Additional information on the energy transfer can be gained from comparing matrix and analyte internal energy content at ns and ps laser excitation.

Publications Acknowledging DOE support – 2002-3

1/ A. Bogaerts, Z. Chen, R. Gijbels and A. Vertes, “Laser ablation for analytical sampling: what can we learn from modeling?” *Spectrochim. Acta B*, **2003**, *58*, 1867-1893.
2/ Y. Chen and A. Vertes, “Pumping Rate and Surface Morphology Dependence of Ionization Processes in Matrix-Assisted Laser Desorption Ionization” *J. Phys. Chem. A*, **2003**, *107*, 9754-9761.
3/ V. Znamenskiy, I. Marginean, and A. Vertes, “Solvated Ion Evaporation from Charged Water Nanodroplets**,**” *J. Phys. Chem. A*, **2003**, *107*, 7406-7412.
4/ Guanghong Luo, Ioan Marginean and Akos Vertes, “Internal Energy of Ions Generated by Matrix-Assisted Laser Desorption Ionization,” *Anal. Chem*., **2002**, accepted.
5/ J. H. Callahan, M. C. Galicia and A. Vertes, "Atmospheric Pressure Matrix-assisted Laser Desorption Ionization as a Plume Diagnostic Tool in Laser Evaporation Methods," *Appl. Surf. Sci.*, **2002**, *197-198C*, 117-124.
6/ M.C. Galicia, A. Vertes and J.H. Callahan, "Atmospheric Pressure Matrix-Assisted Laser Desorption/Ionization in Transmission Geometry," *Anal. Chem.*, **2002**, *74*, 1891-1895.
7/ E. Moskovets and A. Vertes, "Fast Dynamics of Ionization in Ultraviolet Matrix-Assisted Laser Desorption Ionization of Biomolecules," *J. Phys. Chem. B*, **2002**, *106*, 3301-3306.

Laser Desorption/Discharge Ionization Sources for Mass Spectrometry

Willard W. Harrison; PI
Elizabeth Pierz Hastings, Kevin Turney; Graduate Research Assistants
Department of Chemistry
University of Florida
P.O. Box 117200
Gainesville, FL 32607
harrison@chem.ufl.edu
http://www.chem.ufl.edu/Groups/Harrison

Overall research goals. The surge in biological mass spectrometry can be traced to the invention of two novel and often complementary ionization methods, electrospray ionization (ESI) and matrix-assisted laser desorption/ionization (MALDI). An unfortunate consequence of this rapid and widespread acceptance has been the neglect of fundamental research aimed to understand the ionization processes involved in MALDI, and to a somewhat lesser extent in ESI.

Our research contributes in this area by expanding upon atmospheric pressure ionization techniques and their unique applications. Ultraviolet compatible liquid matrices, which have not been studied at AP, allow possible formulations based on desorption and ionization versus vacuum stability and source contamination. Liquid sampling reduces sample preparation, compared to solid matrices; however, during biological analysis separations are often the rate determining step. We are exploring further reductions in preparation time for biomolecules with the use of nanoparticles. Functionalized nanoparticles may provide specific extraction, retention, and concentration of low abundance biopolymers in complex systems.

MALDI studies have suggested that for every 10^4 molecules desorbed perhaps only 1 ion is produced. Supplemental ionization techniques can offer a clear view of the majority species (i.e., neutral molecules) produced during MALDI. Using new tools to probe the MALDI plume, we expect to gain insight into several pressing questions regarding MALDI, such as: what is the role of the matrix in ionization, to what extent is matrix absorptivity necessary, how does the incident radiation interact with the matrix surface, etc.

Specific objectives for 2002-2003. Our research has been directed toward advances in the area of atmospheric pressure ion source design, development, and implementation. We have made progress in several important areas: (1) the development of a liquid matrix for UV APMALDI and its use with functionalized nanoparticles; (2) the fundamental study of reagent gases for use with chemical ionization; (3) and the characterization of a corona discharge for chemical ionization of laser desorbed neutrals.

Significant Achievements

Liquid Matrices for Atmospheric Pressure MALDI. Atmospheric pressure MALDI has the advantage of operating at ambient conditions, allowing other approaches to matrix preparation. Because of the limitations imposed on a vacuum-stable matrix, a liquid matrix system was instead explored. The liquid matrix includes a UV absorbing chemical doped into a non-absorbing liquid. Doping a known organic chromophore, α-cyano-4-hydroxycinnamic acid (CHCA), into liquid media yielded a homogenous sample system with simplified sample preparation, increased sample lifetime, and an added utility for APMALDI ionization sources.

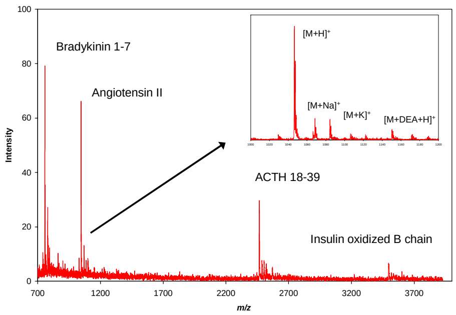


Figure 1 shows a peptide mixture analyzed using the liquid matrix. The insert shows salt adducts present with the angiotensin II peptide.

To demonstrate the liquid matrix's utility for peptide analysis, a mixture of standard peptides was examined as a test sample. Figure 1 depicts a one minute summed mass spectrum for a mixture of bradykinin fragment 1-7, angiotensin II, ACTH fragment 18-39, and insulin oxidized B chain (2 picomoles each). The spectrum shows the liquid matrix's ability to analyze mixtures.

For the liquid matrix we examined, chromophore concentration adjustments provided insight into the necessary absorbance for UV APMALDI and demonstrated the importance of laser penetration in liquid MALDI. The shot-to-shot reproducibility, as examined with individual ion packets, suggests that the liquid matrix can alleviate some inconsistencies seen with solid MALDI. The liquid system also provides a convenient avenue for fundamental studies of desorption. The measurements for laser penetration depth, solution viscosity, and solvent additives could add to the information on MALDI mechanisms. The liquid matrix offers advantages that complement current MALDI methods.

Functionalized Nanoparticles for Biopolymer Extraction and Concentration. The use of nanoparticles with liquid UV APMALDI provides an opportunity for specific analyte capture and controlled release from complex systems. The sizes and types of nanoparticles available allow a variety of functionalization chemistries, which could permit affinity chromatography and sample concentration in a single step.

Using a functionalization group for the nanoparticles allows affinity related experiments. Figure 2 shows the selective retention of peptides using the octadecyltrimethoxysilane, C18, functionalized silica nanoparticles (60 nm). Based on the binding interactions of hydrocarbon chains, the chromatographic properties of the nanoparticles were examined. While this process remains a low resolution separation mechanism, the elution order of the peptides is maintained. More specific analyte-nanoparticle interactions (higher level functionalization) will permit wider applications. Important is that the nanoparticles do not interfere with the APMALDI process when using a liquid matrix. This approach introduces nanoparticles as an extraction and concentration mechanism for low abundance analytes in complex systems.

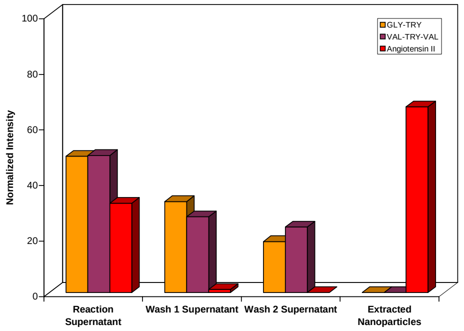


Figure 2 shows the selective retention of peptides using functionalized nanoparticles. A mixture of three varied length peptides was reacted with the nanoparticles.

The size of the nanoparticles allows them to be in large numbers while maintaining a small sample volume. This equates to the nanoparticles ability to concentrate biopolymers. A comparison of a 1 µM angiotensin II solution before and after nanoparticle concentration shows ~15 fold signal enhancement of the analyte. More work in determining the correct particle-to-analyte ratios will also increase extraction efficiency to enhance concentration. With the increased synthesis of novel functionalized nanoparticles, this application has the possibility of advancing rapidly.

Fundamental Study of Ionized Reagent Gases. Our lab has broadly used the Grimm-type microsecond pulsed glow discharge (PGD), which exhibits flexibility of operation in discharge gas composition and pressure. We have examined various gas media, beginning with pure argon and then introduced common atmospheric gases such as nitrogen and oxygen. With the addition of these gases, the discharge composition changes and therefore, the mechanisms involved in ionization are also altered. Using temporal resolution mass spectrometry, we have compared net ion signals and sputter yield variations.

Experimentation with methane additions, a common molecular gas used for chemical ionization, demonstrates an increased spectral complexity. A better understanding of the ionization processes is of interest here, with the potential of selectively ionizing organic vapors that are introduced into the discharge.

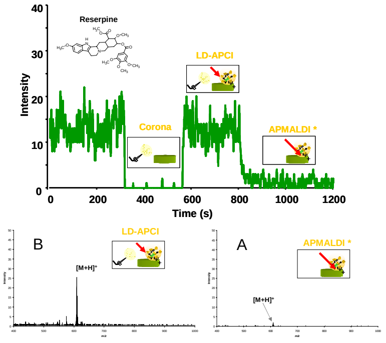


Figure 3 shows the analyte, reserpine, ion intensity during three analysis modes for the ion source. The modes examined were the corona alone, lower fluence APMALDI, and LD-APCI. Figure 3A shows a mass spectrum for lower fluence APMALDI and 3B is of LD-APCI.

UV Laser Desorption APCI Source (LD-APCI). The LD-APCI source consists of two major components: laser desorption at atmospheric pressure and a corona discharge for ionization. While the addition of a secondary ionization technique to laser desorption is not a novel principle, we believe there are additional advantages compared to both traditional APCI and APMALDI.

To explore reagent ion interaction with the desorbed neutrals, we viewed mass spectra with the corona powered on and off with APMALDI being conducted. Figure 3 shows the total ion chromatogram as the source is operated in different modes: LD-APCI, corona only, and APMALDI. When the APMALDI signal was reduced, due to an attenuated laser, the analyte ion signal could be enhanced by switching on the corona.

The most promising aspect of the initial UV LD-APCI results is the corona's ability to enhance weak APMALDI signals. MALDI necessitates an energy absorbing media for desorption and ionization, yet if poorly absorbing matrices are used, yielding weak APMALDI signals, the LD-APCI source may allow an enhanced limit of detection.

Research Activities Planned

(1) Ionization Source Optimization and Temporal Mass Spectrometry.

Unlike most MALDI ion sources, our laser pulse is not synchronized to the TOF repeller pulse. At a laser repetition rate of ~20 Hz a semi-continuous ion stream is produced. Instead, a timed repeller delay with the laser pulse could increase ion signals and decrease chemical noise. Additionally, the synchronization may also present temporal benefits within the ion packet. Preliminary results have shown individual ion packets present regions of maximum analyte signal and minimum chemical background.

(2) APMALDI Matrices and Nanoparticle Applications.

While the liquid matrix provides immediate benefits for APMALDI analysis with its ease of use, additional possibilities include an on-line liquid UV APMALDI ion source for chromatography and reaction monitoring.

Nanoparticle use with liquid APMALDI also presents interesting applications for bioanalytical analysis. Based on the ratio of analyte molecules to nanoparticles incubated, more specific functional groups, and biopolymer removal from complex mixtures, further evidence is anticipated for advantageous nanoparticle usage in biological mass spectrometry.

(3) Corona Discharge Secondary Ionization with APMALDI.

There are many aspects of the UV LD-APCI source that still must be considered. For the immediate future, our plans are to continue to evaluate source parameters and further appraise liquid matrices for their use with a secondary AP ionization process. The source parameters for LD-APCI to be studied include laser fluence, corona position, corona voltage, and target potential fields.

As we further develop the LD-APCI source, information from reagent gas studies will be incorporated into our ionization scheme. The understanding of reagent ion populations and interactions will allow a more developed reasoning to ion-molecule interactions in the APCI environment.

Publications Acknowledging DOE Support – 2002-3

1. J. J. Coon, K. J. McHale, W. W. Harrison ”Atmospheric Pressure Laser Desorption/Chemical Ionization Mass Spectrometry: A New Ionization Method Based on Existing Themes”, *Rapid Communications in Mass Spectrometry*, 16, 681 (2002)

2. A. K. Ottens, T. P. Griffin, T. P. Helms, W. W. Harrison, “Real-Time Quantitative Analysis of H2, He, O2 and Ar by Quadrupole Ion Trap Mass Spectrometry,” *J. Am Soc. Mass Spectrom.*, 13, 1120 (2002)

3. J. J. Coon, W. W. Harrison “Laser Desorption-Atmospheric Pressure Chemical Ionization Mass Spectrometry for the Analysis of Peptides from Aqueous Solutions,” *Analytical Chemistry*, 74, 5600 (2002)

4. J. J. Coon, H. Steele, W. W. Harrison, P. Laipis, “ Laser Desorption-Atmospheric Pressure Chemical Ionization (LD-APCI); A Novel Ion Source for the Direct Coupling of Polyacrylamide Gel Electrophoresis (PAGE) to Mass Spectrometry,” *J. Mass Spectrom.*, 37, 11, 1163-1167 (2002)

5. C. L. Yang, E. S. Oxley, W. W. Harrison “The Mass Spectrometry of Glow Discharges,” in Glow *Discharge Plasmas in Analytical Spectroscopy*, John Wiley and Sons, 71-95 (2003)

6. J. Pisonero, K. Turney, N. Bordel, A. Sanz-Medel, W. W. Harrison, “A Double Microsecond-Pulsed Glow Discharge Ion Source,” *J. Anal. At. Spectrom.*, 18, 624-628 (2003)

7. E. Oxley, K. Turney, J. Gasser, W. W. Harrison, “Direct Pin Sample Analysis Using a Grimm-Type Glow Discharge Source and Time-of-Flight Mass Spectrometer,” *J. Anal. At. Spectrom.*, 18, 1376-1382 (2003)

8. E. Oxley, C. Yang, J. Liu, W. W. Harrison “Ion Transport Diagnostics in a Microsecond Pulsed Grimm-Type Glow Discharge Time-of-Flight Mass Spectrometer,” *Analytical Chemistry*, in press (2003)

9. J. J. Coon, H. Steele, W. W. Harrison, P. Laipis, “Direct Atmospheric Pressure Coupling of Polyacrylamide Gel Electrophoresis to Mass Spectrometry for Rapid Protein Sequence Analysis,” *Journal of Proteome Research*, in press (2003)

10. K. Turney, W. W. Harrison, “Liquid Supports for Ultraviolet Atmospheric Pressure Matrix-Assisted Laser Desorption/Ionization,” *Rapid Communications in Mass Spec trometry*, submitted (2003)

Abstract S1-6

Chemistry and Microphysics of Small Particles

Alla Zelenyuk, Dan Imre, PIs
Chemical Sciences Division
Pacific Northwest National Laboratory
P. O. Box 999
Richland, WA 99352
alla.zelenyuk@pnl.gov

Cai Yong, Postdoctoral Research Associate, PNNL; Peter Imrich, Bin Xu, Graduate Students, SUNY SB; Robert McGraw, BNL, Wei Zhu, Klaus Muller, SUNY SB, Collaborators

Overall research goals. Nanoparticles play an important role in many areas. The unique properties of matter on the nanometer size range are a new frontier in science and technology with the potential to revolutionize our lives. On a very different note, nanoparticles released into the atmosphere mainly as byproducts of energy consumption affect our health, impair visibility, and impact climate change. These vastly different fields share the need for powerful ultra-sensitive analytical tools for the study of physical and chemical properties of these nanoparticles.

This program addresses these needs by exploring the application of fundamental scientific principles to novel methods for real-time *in-situ* particle characterization. The challenge in particle characterization lies in the fact that under most conditions particles are present in a wide range of internally mixed compositions and sizes. To understand the system one must first determine the properties of the individual particles. This calls for a fundamentally different analytical approach and a very different approach to data analysis as well.

Specific objectives for 2003-2004. FY 2003 and the beginning of FY 2004 were dedicated to parallel efforts: 1. Improvements of SPLAT-MS and design of a second-generation instrument. 2. Field and laboratory testing. 3. Development of data mining software.

Significant Achievements.

SPLAT-MS Basics. Within the past 2 years we have designed and constructed our first generation Single Particle Laser Ablation Time-of-flight Mass Spectrometer (SPLAT-MS) that is capable of efficiently detecting and characterizing particles in the 50nm to 3.5µm size range. To characterize this particle mode, we use an aerodynamic lens inlet to transport over 90% of particles and concentrate them into a particle beam less than 0.5 mm in diameter. The particle beam is crossed twice by green continuous wave (CW) lasers and the observed scattered light is used to detect the particle. The time delay between the two detection events

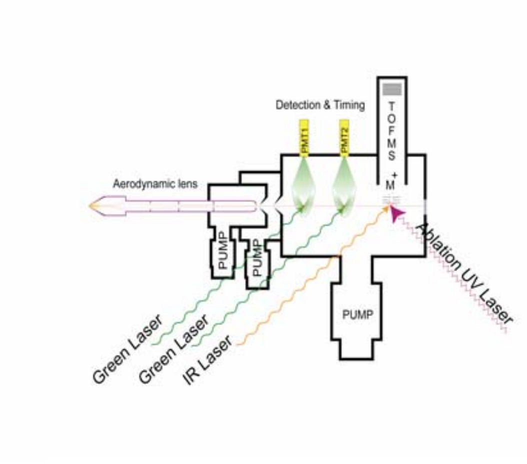


Figure 1 Schematic of SPLAT-MS

yields particle velocity, which is a function of the particle aerodynamic diameter. A trigger synchronized with particle arrival to the mass spectrometer fires the ablating excimer laser to produce ions for composition analysis by time-of-flight mass spectroscopy. We have now operated SPLAT-MS in this configuration both in the laboratory and in field application at sites as different as Houston, TX, and Cheju Island in Korea. We have shown that we can detect and characterize particles down to 50 nm with high efficiency at a rate of 20particles/second. This experience with SPLAT-MS in the laboratory and under real field conditions both attest to instrument capabilities and point out some of its shortcomings.

IR Evaporation/UV Ionization. It has become clear that ablation cannot be used for a detailed characterization of the organic fraction of the particle composition. We have now shown that greatly improved spectra can be obtained by separating the process of ion formation into evaporation by a CO_2 laser followed by delayed ionization of the plume with an excimer laser. This mode of SPLAT-MS operation was successfully implemented during a recent field deployment at the Oak Ridge National Transportation Research Center.

Beyond Size and Composition. Within the past year we have demonstrated that combining SPLAT-MS with a Differential Mobility Analyzer (DMA) to enable simultaneous measurement of particle size, composition, density, volatility, and water uptake. For example, we used this approach to measure the density of freshly formed soot particles and found an inverse relationship between soot size and density. These data yield a fractal dimension of 2 for diesel soot. In another system we were able to measure the density of ammonium nitrate and ammonium bisulfate nanoparticles in their metastable anhydrous state. We have previously shown that in these systems it is possible to form anhydrous salt droplets in a liquid state that are stable over many days. This is the first measurement of the density of these metastable phases.

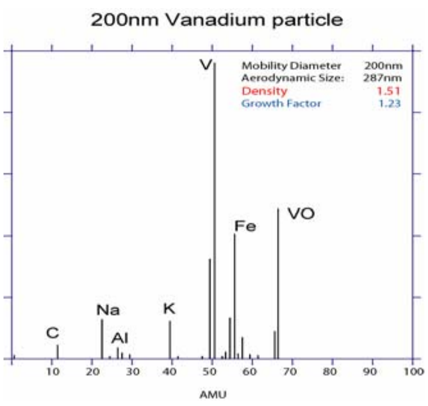


Figure 2 The mass spectrum, density and water uptake of a 200nm ambient vanadium containing particle.

Design of a Second Generation Instrument. We have completed the design phase of a second-generation instrument whose construction has been begun. The new instrument is compact and user-friendly and designed to fit in a small aircraft to enable in-situ atmospheric research. We have introduced a novel approach to aerodynamic sizing that should make it possible to measure the size of over 1000 particles per second and at the same time eliminate the need to dilute the sample.

We shall explore a novel method based on spatially resolved light scattering to determine particle density and optical properties together with size and composition. This approach eliminates the need to use a DMA upfront providing a factor of 1000 improvement. We expect this instrument to be complete by the end of the summer of 2004.

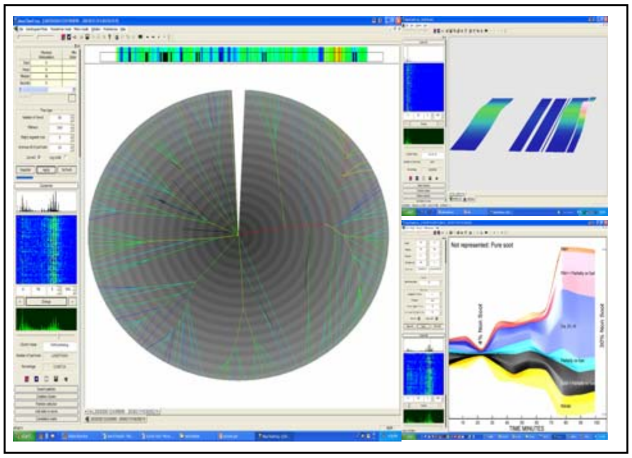


Figure 3 Screen capture, illustrating one of many interfaces of SpectraMiner.

Data Analysis and Visualization. To take full advantage of the vast amounts of detailed data produced by our single particle mass spectrometer we have developed a data mining and visualization software that we call SpectraMiner. It relies on statistical analysis to cluster the data and produce an interactive hierarchical tree. The data can be explored at a multitude of levels, from the individual particle and to classes representing millions of particles just by clicking a mouse on the tree. This project is carried out in collaboration with SUNY SB.

Plans for Future Research.

Comprehensive real-time particle characterization. The spatial pattern of light scattered by particles is a function of their size, shape, and index of refraction. By exploring these relationships we hope to identify an approach that makes it possible to extract these particle characteristics in real-time. We will use light scattering at two different wavelengths detected with a spatial resolution of 16 elements. Preliminary modeling suggests that a point in this 32 dimensional space uniquely defines the complex index of refraction and an effective particle size. These will be combined with measurements of aerodynamic size, density and composition to provide comprehensive, real-time particle characterization.

Chemistry of nanoparticles. Using the aerosol flow reactor at EMSL we plan to explore the chemistry of size selected nanoparticles. Reactions of organics in the liquid and solid phase with ozone or with free radicals like OH will be studied. The single particle mass spectrometer will make it possible for us to monitor changes in particle size with the accuracy of a monolayer, density, composition, and optical properties.

Publications Acknowledging DOE Support – 2002-3

1. P. Imrich, K. Mueller, D. Imre, A. Zelenyuk, W. Zhu, Visual Data Mining with the Interactive Dendrogram and 3D ThemeRiver, Submitted to *Information Visualization* Journal.

2. G. Buzorius, A. Zelenyuk, F. Brechtel and D. Imre, Simultaneous Determination of Individual Ambient Particle Size, Hygroscopicity and Composition, *Geophysical Research Letters*, vol. 29, No. 20, 1974, 2002.doi:10.1029/2001GL014221 (2002).

2004 DOE/BES Analysis Program
Contractors' Meeting

Abstracts
Session 2

Surface-Induced Dissociation of Complex Polyatomic Ions

Jean H. Futrell, PI
Chemical Sciences Division
Pacific Northwest National Laboratory
P. O. Box 999
Richland, WA 99352
Jean.futrell@pnl.gov

Collaborators Julia Laskin, Co-PI, PNNL; Graham Cooks, Purdue University; Vicki Wysocki, University of Arizona, Bill Hase, Texas Technical University; Richard Smith, PNNL; Anil Shukla, PNNL

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. Because of their large number of internal degrees of freedom the kinetics of dissociation of large molecular ions are both qualitatively and quantitatively different from the analogous behaviour of small molecule counterparts. This makes the study of complex systems interesting from both a fundamental and applied (analytical mass spectrometry) perspective. Our research emphasizes the fragmentation of protonated model peptides as a technically important class of complex molecules whose characterization by tandem mass spectrometry is central to the emerging field of proteomics.

Ion activation by collisions with surfaces or with neutral molecules in the gas phase is extensively used to obtain fragmentation spectra of peptides and proteins. However, collisional activation of large molecules is rather poorly characterized from a fundamentals perspective. Our research utilizes surface-induced dissociation (SID) as a means for depositing relatively large and controllable amounts of internal energy very rapidly (e.g., in a few hundred femtoseconds). 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 2003-2004. (1) Determine the effect of the type and position of a basic amino acid in the peptide chain on its fragmentation energetics and dissociation mechanisms using RRKM modeling of experimental fragmentation efficiency curves. (2) Extend our study of kinetic energy dependence of the kinetics of the time dependant fragmentation of model peptides to characterize the transition from predominantly RRKM fragmentation to non-ergodic dissociation. (3) Carry out theoretical calculations and modeling dynamics studies of the same set of peptides. (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 of Peptide Fragmentation. We have studied the energetics and dynamics of selective cleavages at acidic residues for a series of peptides that have been previously studied using tandem-in-space instruments. This was done by modeling the survival curves for the precursor ion using an RRKM based approach developed in our laboratory. Our results revealed some interesting trends that have not been observed in other studies. For example, we found that addition of a basic residue arginine to the C-terminus of a peptide has a very small effect on the dissociation threshold. However, the dynamics of dissociation is dramatically affected by the presence of arginine. Furthermore, the fragmentation energetics is affected by the position of the arginine residue in peptide sequence. A rather surprising result is the precision with which we can determine thermodynamic and kinetic parameters for these large molecules. This high sensitivity results from two factors the large kinetic shift that offsets experimental survival curves by typically an order of magnitude more than the thermochemical threshold difference and the efficiency, typically 20% or less, in conversion of kinetic energy into internal energy in SID. This is shown in Fig. 1 in which the survival curves are shifted by 4 eV compared to the thermochemical difference dissociation energy of 80meV. It follows that in this example a small difference in thermochemical thresholds is amplified by a factor of 50. A corollary is that energy differences of less than 50 meV are readily detected in these measurements.

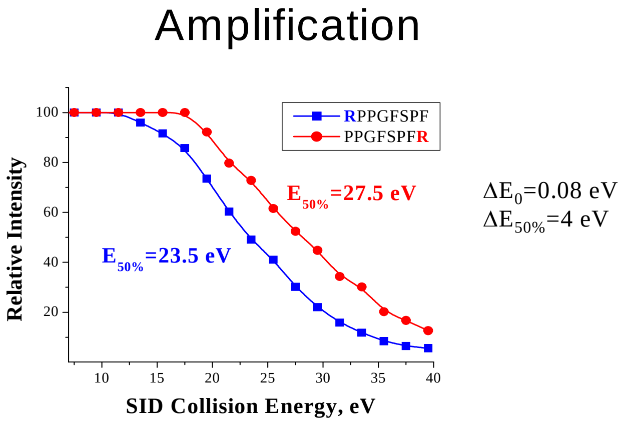


Fig. 1. Energy shift in dissociation spectra

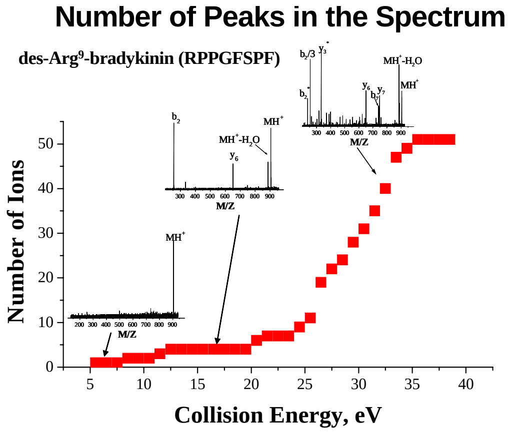


Fig. 2 Number of mass peaks as a function function of collision energy

Shattering of Ions on Surfaces..A second important discovery is that with increasing kinetic energy and/or complexity of peptides a sharp transition in their kinetic behaviour is observed. Fig. 2 illustrates this phenomenon for an octapeptide molecular ion with about 400 internal degrees of freedom. This figure plots the total number of ions in the mass spectrum as a function of ion collision energy with a fluorinated self-assembled monolayer (SAM) surface. At the lowest energy, below about 12 eV, only the reflected protonated molecular ion is detected. At slightly higher energy, up to about 20 eV, the lowest energy dissociation channels are opened and typical RRKM kinetics are valid. At about 25 eV a sharp break in the curve is noted and extensive dissociation of the ion is observed. These fragments are all formed with no detectable time dependence—that is, they are formed instantaneously within our ability to investigate the time evolution of ions. We describe this phenomenon as "shattering" taking place on or very near the surface. A detailed analysis suggests that this is the principal kinetics mode for any class of mass spectrometer that detects ions on the sub-millisecond time scale, including most tandem instruments that have been used to study these phenomena to date.

The effect of changing the surface is shown in Fig. 3, a comparison of the SID mass spectra originating from impact on a very soft surface, a hydrocarbon SAM polymer, and a very hard surface, vapor deposited diamond. The added stiffness of the diamond surface exhibits the expected effect of increasing the efficiency of energy transfer into the ion. It is about twice as effective in energy transfer. An unexpected result is that the energy distribution function—the width of the energy transfer function—is much broader for diamond. This has the interesting consequence that a broad range of energy deposition, analytically desirable for opening a number of dissociation channels that are useful for structure determination, occurs simultaneously with increased energy transfer efficiency. Finally it is an especially robust surface with respect to damage by ion impact.

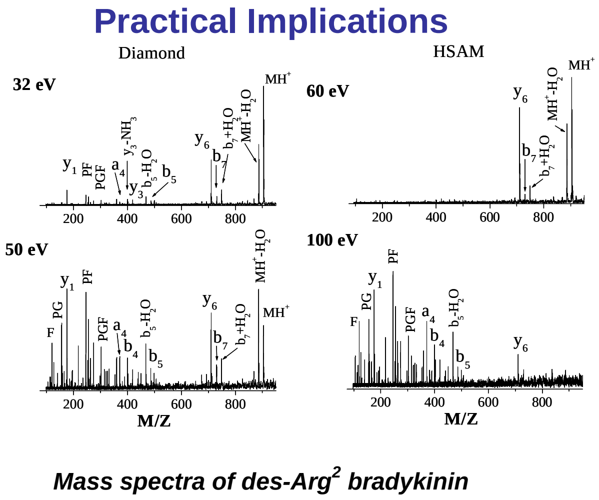


Fig.3. Mass spectra from hard and soft surfaces

Thermochemical Determinations from Dissociation of Proton-Bound Dimers. We used kinetic energy release distributions (KERDs) upon dissociation of proton-bound dimers along with Finite Heat Bath theory analysis to obtain relative proton affinities of monomeric species composing the dimer. The proposed approach allows accurate measurement of relative proton affinities based on KERD measurements for the compound with unknown thermochemical properties versus a single reference base. It also allows distinguishing the cases when dissociation of proton-bound dimers is associated with a reverse activation barrier, for which both our approach and the kinetic method become inapplicable. We examined dissociation of proton-bound alcohol dimers is a good example of competing reactions without reverse activation barriers and with equivalent entropy and dissociation of proton-bound dimers that contain diamines that represent a good test case for competing reactions with significantly different protonation entropies. Our results demonstrate both the success and challenges for thermochemical determinations using kinetic measurements.

Scattering Studies. Our first studies on our new scattering apparatus have examined the interaction of small molecular ions (acetone and ethanol) with SAM surface. These studies demonstrated an entirely new feature in SID dynamics, distinct in both angle and energy in which fragment ions are sharply distributed close to the surface parallel and only slightly endoergic. The dynamics of this feature are indistinguishable within experimental error from that observed for undissociated primary ions. Relative abundance of this mechanism increases in comparison with highly inelastic scattering as ion energy is increased. Since the scattering features and energy distributions for this process are essentially identical to that of the undissociated primary ethanol ions, we suggest that the same ion–surface collision dynamics result in formation of long-lived, excited primary ions which decompose after ions have passed through the energy analyzer.

Plans for future research on this project. Our efforts this year will explore in greater detail the results presented here. Our goals for the coming year are:

(1) Understand and quantify shattering of large floppy molecules on surfaces by combining time and energy-resolved experimental data with theoretical modeling using molecular mechanics simulations and the maximum entropy method. (2) Refine our present understanding of the factors governing energy transfer efficiency in collisions of complex ions with surfaces. (3) Install and test a high-transmission electrospray source on our scattering apparatus and investigate SID of selected peptides that we have already studied using FT-ICR to verify or challenge the kinetics and dynamics description deduced from the ICR experiments. (4) Initiate a study of proton affinities of selected amino acids, for which there is a large discrepancy between the experimental and theoretical values (for example, glutamine), and small alanine- and glycine-containing peptides, for which proton affinities are not established from the kinetic energy release distributions obtained upon fragmentation of the corresponding heterodimers.

Publications Acknowledging DOE Support – 2002-3

1. V. S. Rakov, E. V. Denisov, J. Laskin and J. H. Futrell. "Surface Induced Dissociation of the Benzene Molecular Cation." *J. Phys. Chem. A*, 106, 2781-2788(2002).
2. J. Laskin, E. Denisov and J. H. Futrell. "Fragmentation Energetics of Small Peptides from Multiple-Collision Activation and Surface-Induced Dissociation in FT-ICR MS." *Int. J. Mass Spectrom.*, 219, 189-201(2002).
3. J. Laskin and J. H. Futrell."On the Efficiency of Energy Transfer in Collisional Activation of Small Peptides." *J. Chem. Phys.*, 116, 4302-4310(2002).
4. J. Laskin, E.V. Denisov, A.K. Shukla, S.E. Barlow and J. H. Futrell. "Surface-Induced Dissociation in a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer: New Instrument Design and Evaluation." *Anal. Chem.*, 74, 3255-3261 (2002).
5. J. Laskin, T.H. Bailey, E.V. Denisov and J. H. Futrell. "On the Relative Stability of Singly Protonated des-Arg1 and des-Arg9 Bradykinins." *J. Phys. Chem. A*, 106, 9832-9836(2002).
6. V.J. Nesatyy and J. Laskin. " Dissociation of noncovalent protein complexes by triple quadrupole tandem mass spectrometry: comparison of Monte Carlo simulation and experiment." *Int. J. Mass Spectrom.*, 221, 245-262 (2002).
7. J.J. Hache, J. Laskin and J. H. Futrell. " Relative Proton Affinities from Kinetic Energy Release Distributions for Dissociation of Proton-Bound Dimers." *J. Phys. Chem. A*, 106, 12051-12057 (2002).
8. A. K. Shukla and J. H. Futrell, “A Beam Scattering Instrument for the Dynamics Studies of Surface-Induced Dissociation Processes”, Rev. Sci. Instrum., 74, 168-175 (2003).
9. T.H. Bailey, J. Laskin and J. H. Futrell. " Energetics of Selective Cleavage at Acidic Residues Studied by Time-and Energy-Resolved Surface-Induced Dissociation in FT-ICR-MS." *Int. J. Mass Spectrom.*, 222, 313-327(2003).

10. J. Laskin, T.H. Bailey and J. H. Futrell. " Shattering of Peptide Ions on Self-Assembled Monolayer Surfaces." *J. Am. Chem. Soc*., 125, 1625-1632 (2003).
11. J. Laskin and J. H. Futrell. " Collisional Activation of Peptide Ions in FT-ICR Mass Spectrometry." *Mass Spectrom. Rev*., 22, 158-181 (2003).
12. J. Laskin and J.H. Futrell. " Energy Transfer in Collisions of Peptide Ions with Surfaces." *J. Chem. Phys*., 119, 3413-3420(2003).
13. J. Laskin and J.H. Futrell. " Entropy is the Major Driving Force for Fragmentation of Proteins and Protein-Ligand Complexes in the Gas-Phase." *J. Phys. Chem. A*, 107, 5836-5839 (2003).
14. A. K. Shukla and J. H. Futrell, “Surface-Induced Dissociation of Acetone Cations from Self-Assembled Monolayer Surface of Fluorinated Alkyl Thiol on Au (111) Substrate at Low Collision Energies”, *Int. J. Mass Spectrom*., 228, 563-576 (2003).
15. A. K. Shukla, J. H. Futrell and A. D. Sen, “Dynamics of the Dissociative and Non-dissociative Scattering of Hyperthermal CS_2^+ from a Self-Assembled Fluoroalkyl Monolayer Surface on Gold Substrate”, *J. Chem. Phys*., 118, 11217-11225 (2003).
16. J. Laskin and J.H. Futrell. " Surface-Induced Dissociation of Peptide Ions: Kinetics and Dynamics." *J. Am. Soc. Mass Spectrom*., 2003, 14, 1340-1347 (2003).
17. J. Laskin. " Energetics and Dynamics of Peptide Fragmentation from Multiple-Collision Activation and Surface-Induced Dissociation Studies." *Eur. J. Mass Spectrom.,* 2003, in press.
18. J. Laskin and J.H. Futrell. "Activation of Large Ions in FT-ICR Mass Spectrometry." *Mass Spectrom. Rev*., accepted.
19. 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*., in press.
20. J. J. Hache, J. H. Futrell and J. Laskin. “Relative Proton Affinities from Kinetic Energy Release Distributions for Dissociation of Proton-Bound Dimers: 2. Diamines as a test case”. *Int. J. Mass Spectrom.,* submitted, October 2003.
21. J. Laskin, T.H. Bailey and J.H. Futrell. “Time-and Energy-Resolved Surface-Induced Dissociation in FT-ICR-MS: Fragmentation of Angiotensin and its Analogs”. *Int. J. Mass Spectrom.,* submitted, November 2003.

Fragmentation Chemistry of Peptide Ions as a Function of *N*-terminal Residue and Charge Carrier: $[M+H, Li, Na, K, or Cu^{(I)}]^+$

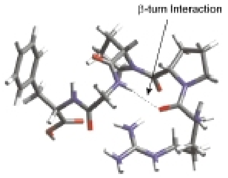
David H. Russell, PI
Dept. of Chemistry, Texas A&M University, 3255 TAMU, College Station, TX 77843-3255
Russell@mail.chem.tamu.edu
http://www.chem.tamu.edu/rgroup/russell/

Overall research goals. Our research is aimed at understanding reactivity and structures of gas-phase ions, issues that underlie the utility of mass spectrometry as a molecular probe. Our studies require extensive use of computational chemistry techniques and cutting-edge ion mobility and mass spectrometry experiments, including laser ionization/excitation, esp. matrix-assisted laser desorption ionization (MALDI) and laser-ion beam photodissociation, ion-neutral and ion-surface collisions, *e.g.,* collision-induced dissociation (CID) and surface-induced dissociation (SID), and the development of new instrumentation and analytical techniques.

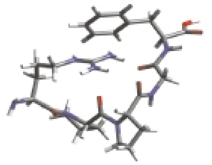
Research objectives for 2003-2004. Our current work is aimed at fundamental studies of ions formed by MALDI with emphasis on how various MALDI parameters, esp. sample preparation, matrix, matrix crystal morphology, and laser wavelength, affect the internal energies and structure(s) of the analyte ion. The studies are aimed primarily at protonated molecules, $[M + H]^+$ ions, and peptides attached to alkali and transition metal ions attached, esp. $[M + Na]^+$ and $[M + Cu]^+$ ions. In parallel with studies of gas-phase species we also use techniques such as H/D exchange measurements, circular dichroism, and solvent polarity to address questions related to solution phase structures. For example, recent data suggests that gas-phase peptide ion structures are very similar to structures in low dielectric solvents such as trifluoroethanol (TFE).[1]

Significant Achievements In our studies of $[M + H]^+$, $[M + \text{alkali metal}]^+$ complexes and $[M + Cu]^+$ ions we have demonstrated that intra-molecular charge-solvation plays an important role in determining the structure(s). For example, we observe multiple structures for bradykinin fragment 1-5 $[M + H]^+$ ions by ion mobility, due to different intra-molecular charge-solvation (see **Figure 1** for the two (2) different ion forms (labeled **a** and **b** in **Figure 2**). **Figure 2** contains a mobility plot of bradykinin fragment 1-5 (AA sequence RPPGF). The bottom left contains the SID fragment ion spectrum for the drift time range from 870 to 880 μsec, and the right is the SID fragment ion spectrum for the drift time range from 917 to 927 μsec. The structures shown in **Figure 1** were derived from extensive molecular dynamics simulations and comparisons of calculated and measured collision cross-sections. We have used these same approaches to study similar bradykinin fragments, specifically 1-6 and 1-7, which also have R as the N-terminal residue and each can exist as multiple structures. Conversely, gas-phase ions of bradykinin fragments 2-5, 2-6 and 2-7, which do not contain an N-terminal R, exist as a single structure. Similarly, peptide ions comprised of the sequence **X**VGVA**Z**G, where **X** represents a highly basic amino acid such as arginine (R), lysine (K), or histidine (H) and for comparison, the acidic amino acid aspartic acid (D) and **Z** is glycine (G), proline (P) or serine (S) can form structurally different ions that can be detected by fragmentation chemistry and ion mobility. The data shown in **Figure 3** illustrates the differences in fragment ion abundances for different charge sites. For example, H^+, Li^+ and Na^+ attach to both the N- and C-terminus, whereas K^+ and Cu^+ bind almost exclusively to the N-terminus.

Figure 1



This structure (σ = 163 Å^2) represents the most compact conformation of bradykinin fragment 1-5 ions formed from aqueous solvent systems and the only conformation arising from organic solvent systems.



This structure (σ = 168 Å^2) is only observed when aqueous solvent systems are used in the MALDI preparation.

Figure 2

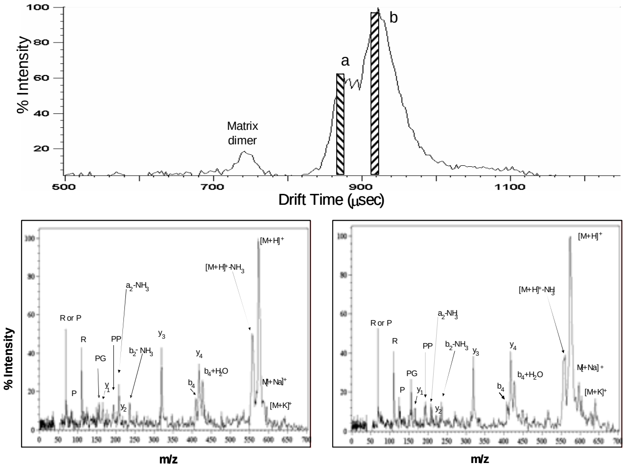
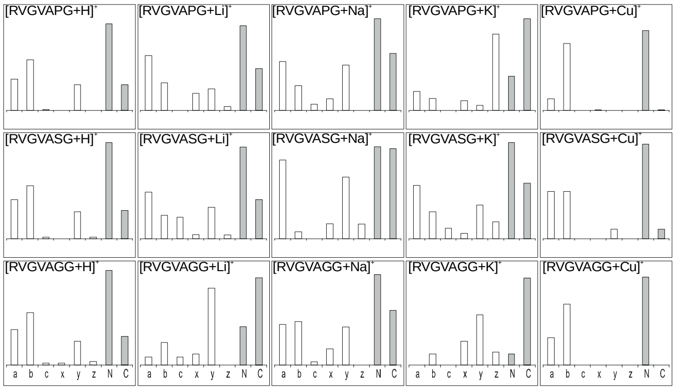


Figure 3



We have also used ion mobility-MS to separate and characterize peptide ions on the basis of secondary (2^o) ion structure, *i.e.,* peptide ions having high propensities for forming helical structures from random coil structures, and we have demonstrated that IM-MS is a highly unique tool for rapid screening of complex mixtures for the presence of phosphopeptides.[2] We have also demonstrated that this same technique can be used to characterize the structure(s) of $[M + H]^+$ and $[M + Na]^+$ ions of cyclic peptides, which can exist as either random coils or β-turn species.[3] Lastly, we have developed variable-temperature IM-MS (86-300 K) and demonstrated enhanced structural resolution of isomeric ionic species.[4] For example, we used VT-IM-MS to separate the various electronic states (^1S_o, ^3P_o, $^3P_1$, $^1D_2$, and $^3P_2$) of Kr^{2+} (**Figure 4**). We also used VT-IM-MS to re-investigate the energetics for interconversion of distonic radical cations of methanol (**Figure 5**) and separation of the keto and enol forms of acetone radical cations formed by EI of acetone as well as the McLafferty rearrangement of various methyl ketones.[5]

Figure 4

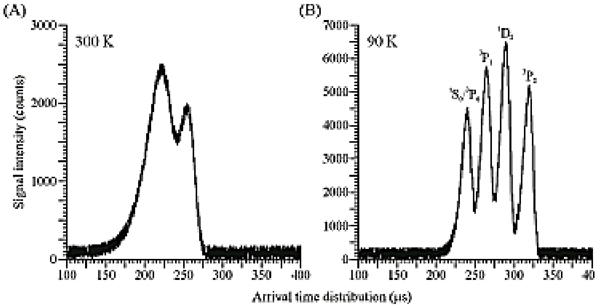
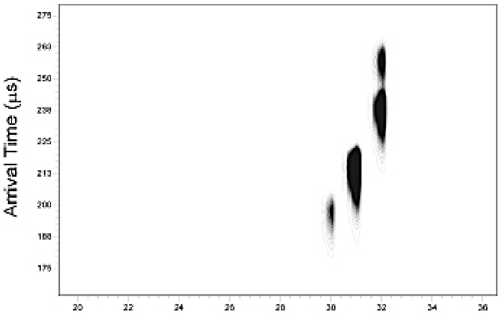


Figure 5



<u>Plans for future research on this project.</u> Our research plans for the next few years are aimed at expanding the use of tandem MS, IM-MS, and VT-IM-MS for studies of the chemistry and dynamics of gas-phase ions. Much of this work will be aimed at studies of ions formed by MALDI; however, we also developing instrumentation and computational chemistry capabilities for studies of multiply-charged ions formed by ESI. Some of the ESI work will emphasize comparisons of ion structures formed by MALDI vs. ESI; however, we also plan to develop independent studies of ions formed by ESI. For example, charge neutralization ion-ion reactions has been studied by McLuckey and co-workers, and this chemistry provides unique methods for synthesizing ionic species that cannot be easily generated by other ionization methods. We are also interested in probing whether lower charge states of peptides/proteins formed by charge-neutralization processes structurally similar to the structure of the initial ions or does the neutralization reaction yield a structurally different ion?

Publications Acknowledging DOE Support

---

[1] "Observation of Conserved Solution-Phase Secondary Structure in Gas-Phase Tryptic Peptides," B. T. Ruotolo, G. F. Verbeck, L. M. Thompson, K. J. Gillig, D. H. Russell *J. Am Chem. Soc.* **2002**, *124*, 4214-4215.

[2] "Distinguishing between Phosphorylated and Non-phosphorylated Peptides by Ion Mobility-Mass Spectrometry," B. T. Ruotolo, G. F. Verbeck, L. M. Thompson, A. S. Woods, K. J. Gillig, D. H. Russell *J. Proteo. Res.* **2002**, *1*, 303-306.

[3] "Ion Mobility-Mass Spectrometry Applied to Cyclic Peptide Analysis: Conformational Preferences of Gramicidin S and Linear Analogs in the Gas-Phase" B. T. Ruotolo, C. C. Tate, D. H. Russell *J. Am Soc. Mass Spectrom.* submitted.

[4] "Variable-Temperature Ion Mobility-Mass Spectrometry Studies of Electronic Isomers of Kr^{2+} and CH_3OH Radical Cations" G. F. Verbeck, K. J. Gillig, D. H. Russell *Eur. J. Mass Spectrom.* in press.

[5] "Separation of Conventional and Distonic Radical Cations of CH3X (X = OH, NH_2, and F) using Variable-Temperature Ion Mobility-Mass Spectrometry" G. F. Verbeck, C. E. Webster, M. B. Hall, D. H. Russell, submitted to *J. Phys. Chem.*

Mass Spectrometry of Nanocrystal and Cluster Compounds

T. Gregory Schaaff, PI
Chemical Sciences Division
Oak Ridge National Laboratory
1 Bethel Valley Rd. MS 6131
Oak Ridge, TN 37831-6131
schaaffg@ornl.gov

Overall research goals. Due to their inherent compositional and structural complexity, inorganic nanocrystal and cluster compounds represent a significant challenge for routine analytical chemical techniques, even those developed for other macromolecular systems. Accompanying this challenge resides a unique opportunity to expand mass spectrometry in new directions and gain yet another perspective on ionization and energy transfer phenomena in mass spectrometry not afforded by ions derived from traditional molecules. The goals of this area of research are to provide fundamental descriptions of ion processes during mass spectrometry experiments involving these unique nanometer-scale structures. In addition to enabling analytical chemistry to address the challenge of characterizing nanocrystal compounds, the unique structure and electronic properties associated with these emerging macromolecules permits the study of ion processes from a completely different perspective – well removed from traditional organic and biological mass spectrometry. Soft-ionization methods (e.g. MALDI and ESI) combined with unimolecular dissociation schemes (which have long been used for biologic and organic molecules) should allow for efficient molecular weight and structure determination in nanocrystal compounds when pursued to its maturity.

Specific objectives for 2002-2003. Utilize a unique class of gold-thiolate nanocrystal compounds to understand the ionization processes and gas phase ion chemistry inherent to ions derived from inorganic nanocrystal and cluster compounds. Specific goals were to: (i) determine fragmentation pathways occurring during ionization (ii) reduce fragmentation of nanocrystal compounds in matrix assisted laser desorption ionization and (iii) probe unimolecular dissociation of ions derived from nanocrystal and cluster compounds.

Significant Achievements

Ionization and fragmentation in MALDI of nanocrystal compounds. This section presents (among other things) progress toward the goal of enabling the comprehensive analysis of nanocrystal compounds by mass spectrometry, and illuminates some of the mechanisms and challenges inherent to ionization and energy transfer processes as applied to such macromolecular structures. The initial results presented below indicate mass spectrometry of these nanocrystal compounds can provide not only information regarding the structure of the nanocrystal compound, but also a different perspective on ion processes that occur during ionization and dissociation. Gold:thiolate nanocrystal compounds consist of large inorganic cores surrounded by a dense monolayer of thiolate ligands – conceptually, the 3-dimensional analog to self-assembled monolayers on gold (see Fig. 1). Since these nanocrystal compounds are simi-

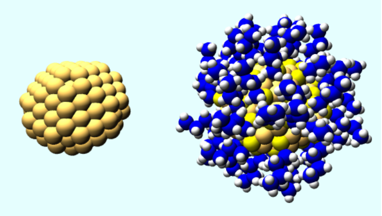


Fig. 1. Model of proposed Au_{144} nanocrystal core and $Au_{144}SC4_{56}$ nanocrystal compound. Au_{144} coordinates courtesy of Prof. Uzi Landman (School of Physics, Georgia Institute of Technology, Atlanta, GA.)

lar in size and structure to other macromolecules (e.g. proteins, DNA, polymers), it should be possible to determine their molecular weights using soft ionization methods developed for these biologic and organic molecules. Dilution of thermally labile macromolecules into organic matrix crystals allows the liberation of molecular-like ions into the gas phase upon irradiation of the co-crystallite with a pulsed UV laser.

Figure 2 shows mass spectra resulting from ionization of a gold:butanethiolate ($Au_{144}SC4_{56}$) nanocrystal compound under three different conditions. From high-fragmentation measurements, we observe ions consistent with the core-mass of the nanocrystal compound at m/z 28400 (Au_{144}) and the molecular weight as determined by elemental analysis at m/z 33350 ($Au_{144}SC4_{56}$). Two ionization regimes were determined for MALDI of the nanocrystal compounds (low- and high-fragmentation). From these initial studies, it appears that two crystalline species are present when the nanocrystal compounds are dispersed in the organic matrix.

The shot-to-shot evolution of the mass spectra can be seen in Figure 3. The initial few laser shots produce ions consistent with the gold-core of the nanocrystal compounds. After this initial ablation period (typically 10-20 shots), ions corresponding to the intact molecular assembly begin to appear. Finally, after removal of the initial layer of non-incorporated nanocrystal compounds, the only ions detected are those with m/z values in the range of the molecular weight of the nanocrystal compound.

The presence of these high mass ions allows insight into not only the ionization processes occurring with nanocrystal compounds, but also those ionization processes not observable with biologic, organic and polymeric compounds studied by MALDI. While this initial 'clean-up' period and subsequent matrix-effect has been postulated previously as a possible process in matrix-assisted laser desorption ionization, it has not been possible to directly observe this effect because no ions are formed from other macromolecules. Having the ability to determine both the core-size mass under one ionization condition and the intact assembly-mass under a different condition provides additional veracity to mass spectrometric measurements that cannot be readily realized through typical condensed-phase analytical methods (e.g. electron microscopy and x-ray diffraction).

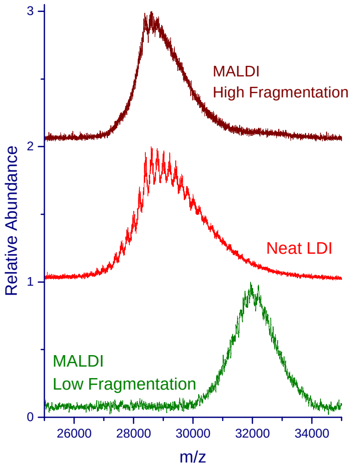


Fig. 2. Ionization of $Au_{144}SC4_{56}$ nanocrystal compounds. Under high-fragmentation MALDI and LDI of neat films, the laser-desorbed ions correspond to the approximate core-mass. Under low-fragmentation MALDI, the laser desorbed ions correspond to the molecular weight of the macromolecular assembly.

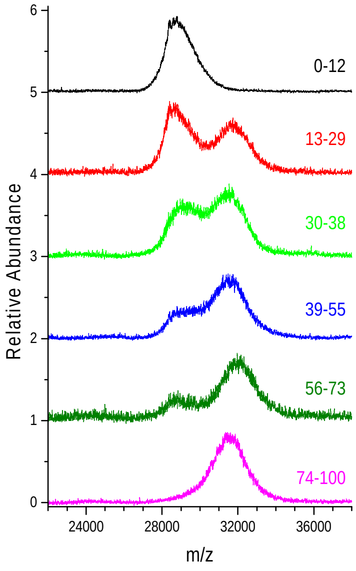


Figure 3: Shot-to-shot evolution of desorbed ions from MALDI of Au:SC4 nanocrystal compounds.

Metastable Ions – Beyond MW to Structure Determination

Unimolecular dissociation has long been a mainstay in determination of structure for ions derived from organic and biologic molecules. Metastable decay of ions (or post-source decay) occurs when ions fragment during their flight after ionization, producing product ions with different kinetic energy (i.e. loss of mass, $E=1/2mv^2$). Product ions were mass analyzed by employing a reflectron (or electrostatic ion mirror) in the time-of-flight measurement. Ions derived from the 22 kDa (Au-core mass) nanocrystal compounds were found to produce a grouping of product ions centered at m/z ~6000. Operating under the same conditions, ions derived from the 29 kDa nanocrystal compounds produce different groupings of product ions centered at m/z 8000, 15000 and 22000. While the mechanisms are not yet understood for the dissociation of these macromolecular ions, it is evident from these studies that the 22 kDa and 29 kDa nanocrystal compounds do not share the same general geometric structure in the gold core of the compounds.

Plans for future research on this project.

Initial studies described above have concentrated on laying the framework for expanding mass spectrometry to an increasingly important class of macromolecular structures. Future studies will concentrate on expanding similar measurements to other gold-based (and other metallic) nanocrystal compounds, as well as expanding the types of mass spectrometric measurements made on such nanocrystal compounds.

Expanding and Improving Ionization Techniques. Through work performed concurrent to this project, many gold:thiolate nanocrystal compounds have been isolated with core-masses ranging from 6 kDa to 190 kDa having both hydrophobic (e.g. n-alkanes, phenyl) and hydrophilic (e.g. cysteine-based peptides) tail groups incorporated into the ligands of the compounds. Expanding the studies described above will allow for a more general description of MALDI ionization processes prevalent in the gold:thiolate nanocrystal compounds (e.g. ionization efficiency, degree of fragmentation, etc. as a function of core-size and molecular weight). In addition, understanding MALDI and ESI ionization processes for gold-based nanocrystal compounds lays the foundation for enabling mass spectrometry as analytical technique for other types of nanocrystals (e.g. magnetic FePt, semiconductor CdSe) with similar size and structure. In addition to traditional MS analysis (e.g. being able to determine molecular weights and core-masses), generation of gas-phase ions allows for more sophisticated techniques for structure determination (e.g. unimolecular dissociation, gas phase reactions).

Unimolecular Dissociation. Studies of unimolecular dissociation for nanocrystal compounds will concentrate on continuing the study of post-source decay of ions generated by laser desorption ionization and expanding studies that allow for inducing dissociation in ions generated by MALDI and ESI. To date, unimolecular dissociation has only been observed for two Au:SR nanocrystal compounds out of the many compounds that have been isolated from previous and ongoing research. Probing all of these types of compounds through similar methodologies can provide extensive information about the internal structure of the compounds and possibly how the ligand shell influences the structure of the nanocrystal core. As a single example, the 29 kDa Au:SR nanocrystal compounds with R=C4, C6, C12 and C18 show slightly different x-ray diffraction patterns indicative of small perturbations in the structure of the gold core. Comparing the unimolecular dissociation of this group of nanocrystal compounds, it may allow for determination of how the structure of the compounds changes due to the ligand shell.

Publications Acknowledging DOE Support – 2002-3

1. Schaaff T. G., "Metastable ions produced by laser desorption of gold:thiolate cluster compounds", *Rapid Commun. Mass Spectrom.* 2003; **17**: 2567.
2. Schaaff T. G., "Laser desorption and matrix-assisted laser desorption ionization mass spectrometry of 29 kDa Au:SR cluster compounds", *Anal. Chem.* In press.

Ion Sampling and Transport in Plasma Source Mass Spectrometers

Paul B. Farnsworth, PI
Ross L. Spencer, CoPI
Jeffrey Macedone, Neil Radicic graduate research assistants
Andrew Mills, undergraduate research assistant
Department of Chemistry and Biochemistry
Brigham Young University
Provo, Utah 84602
paul_farnsworth@byu.edu

Overall research goals. Inductively coupled plasma mass spectrometry (ICP-MS) is the method of choice for trace elemental analysis in a wide variety of research and production laboratory settings. The technique provides impressive sensitivity and detection limits, but is also known for susceptibility to matrix effects. Matrix effects can negatively affect the accuracy of determinations by ICP-MS, particularly if the fundamental processes that cause changes in instrument response with changes in sample matrix are not well understood. Our overall goal in this project is to develop a fundamental understanding of the processes that control the transport of analyte ions from the ICP (the ion source) to the mass analyzer in an inductively coupled plasma mass spectrometer.

Specific objectives for 2003-2004. Our specific objectives for the first year of the project are to experimentally characterize the spatial distribution of ions across the 1-mm sampling orifice of an ICP mass spectrometer, to trace that distribution through the supersonic expansion of the hot plasma gases, and to determine the effects that changes in the spatial distributions have on the ion transmission efficiency through the first vacuum stage of the instrument. We are also preparing a detailed comparison of ion and atom temperatures and velocities in the first vacuum stage, and evaluating the behavior of both species against well-established models for supersonic expansions.

Significant Achievements

High resolution imaging of the sampling cone. We have constructed a mockup of the first vacuum stage of an inductively coupled plasma mass spectrometer that allows us to record monochromatic images of the 1-mm diameter sampling orifice with a spatial resolution of approximately 10 μm. Representative images for argon atoms and for barium ions are shown in figure 1. These images dramatically illustrate that a cylindrical section of the ICP several millimeters in diameter is drawn into the sampling cone, and that spatial variations within that cylindrical section are preserved and compressed to the 1-mm scale of the orifice. Inhomogeneities in the distributions of ions across the sampling orifice, and changes in those distributions have important implications for the efficiency with which ions are transported through the first vacuum stage of the instrument. Only the ions in the center of the distribution pass through the skimmer cone into the second vacuum stage of the interface. A higher percentage of ions in a peaked distribution will be passed to the second vacuum stage than will be passed for a flat distribution.

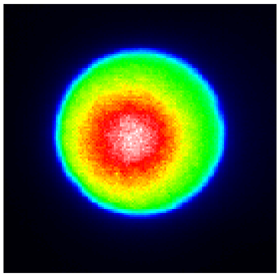


Figure 1a. Image of sampling cone at Ba II 614.2 nm emission wavelength.

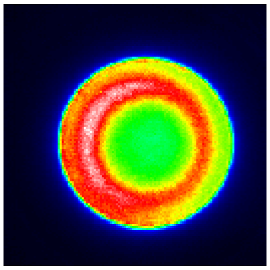


Figure 1b. Image of sampling cone at Ar I 842.5 nm emission wavelength.

Temperature and velocity mapping of argon atoms in the first stage expansion. We have constructed detailed maps of argon atom velocities and temperatures based on the Doppler shifts and Doppler widths of fluorescence excitation spectra, respectively. These maps will serve as a baseline against which we will compare the behavior of charged species. Any differences between the behaviors of neutral and charged species will point to areas where the models of the first-vacuum-stage expansion in an inductively coupled plasma mass spectrometer need revision.

Our measurements of temperatures and velocities of neutral species are consistent with established models of supersonic expansions, but they reveal features of the expansion that are ignored in the simplified treatments found in the ICP literature. For example, at 1 Torr, the pressure of our experiments, the mach disk is not a well defined shock structure located at the position predicted by simple formulas, but rather is spread over several millimeters.

Plans for future research on this project. We expect by the end of the first year on the project to have a solid understanding of analyte behavior in the first vacuum stage of the inductively coupled plasma mass spectrometer. With an understanding of how ions are presented to the skimmer cone and the second vacuum stage, we will be in a position to experimentally characterize and model ion transport through the second stage. Study of ion transport in the second vacuum stage will be the focus of our second year's effort.

Publications Acknowledging DOE Support - 2003-2004

We have just completed the fourth month of work on this project, and have not yet submitted papers acknowledging DOE support.

FUNDAMENTAL STUDIES OF THE INDUCTIVELY COUPLED PLASMA AND GLOW DISCHARGE

Gary M. Hieftje, PI
Gerardo Gamez and George Chan, Graduate Research Assistants
Indiana University Department of Chemistry
Bloomington, IN 47405
hieftje@indiana.edu
http://www.indiana.edu/~gmhlab/

Overall Research Goals. Plasmas have been established as very important tools in analytical spectrochemistry because they serve as sources of analyte atoms and ions for absorption, fluorescence, emission and mass spectrometry. Nevertheless, to make further advances in the analytical performance of plasma-based sources it is of utmost importance to have a complete understanding of the processes that occur in them. For example, inductively coupled plasma atomic emission spectrometry (ICP-AES) and mass spectrometry (ICP-MS) instruments have been commercially available for almost two decades, yet the ICP still suffers from sample-related matrix effects. That is, the presence of other constituents in a sample influences the signal that is obtained from a given analyte concentration. Commonly, these inaccuracies are ignored; at best they are minimized through use of tedious, time-consuming procedures such as matrix matching, internal standardization, and standard additions. A better approach, in our view, is to characterize the processes that occur in the ICP and to overcome the interferences on a rational basis. Another plasma that has gained popularity for direct analysis of solid samples is the glow discharge (GD). The GD also suffers from matrix effects, yet very few fundamental studies have been performed on some GD configurations and experimental conditions which hold analytical promise. A detailed picture of the plasma behavior can be developed by measuring the fundamental plasma parameters of gas-kinetic temperature, electron temperature and electron concentration. It is these parameters that are directly responsible for sample volatilization, analyte excitation and analyte ionization. Furthermore, the measurement of atom and ion number densities and emission intensities yields information on the spatial distribution of analyte and plasma-gas species within the discharge and about their excitation. The general goals of this project are to understand the behavior of key plasma species through high-powered plasma diagnostic tools (i.e. Thomson and Rayleigh scattering, laser saturated fluorescence, computer-aided tomography) in order to improve the analytical performance of plasma sources.

Specific Objectives for 2003-2004. The specific objectives are: (1) Characterize the spatial distribution of the electron number density, electron energy distribution function, and the gas-kinetic temperature in a direct-current GD; (2) Compare results of the experimental characterization of the dc GD to those of a theoretical computer model; (3) Study the influence of operating conditions on the effects of a mass spectrometer interface on the ICP; and (4) Characterize matrix effects in ICP-AES and utilize them to probe excitation mechanisms.

Significant Achievements

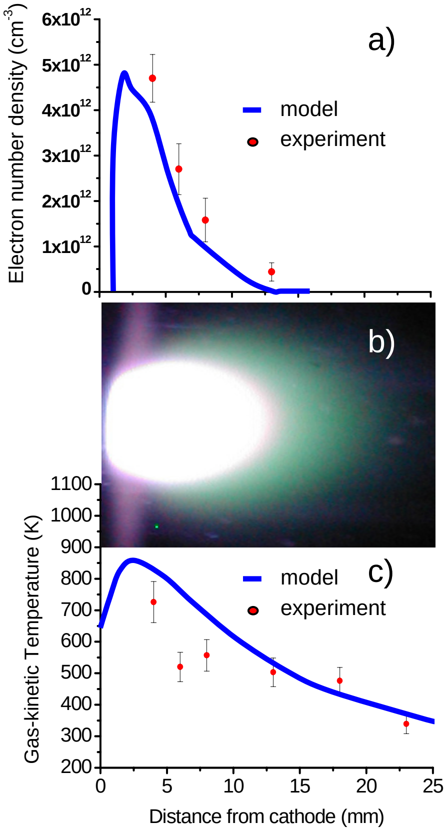


Fig 1. Experiment vs. model data comparison of DC GD: a) axial profile of n_e; b) image of DC GD (same scale as graphs); c) axial profile of T_g.

Direct Current Glow Discharge. Glow discharges (GD) have also gained popularity as AES and MS sources, but mostly for the direct analysis of solid samples. It is important to observe the electron properties of the GD to understand how the atoms, ions and their excited species are produced. Under some GD experimental conditions (especially pulsed) there have been very few studies to observe the electron properties. Other GD conditions have been widely studied (DC and RF) but with techniques that likely introduce errors in the calculated values or perturb the plasma. Laser scattering does not introduce such errors but due to the low scattering signals is difficult to implement. Recently, we designed an instrument that addresses such concerns. Further, we have measured successfully the gas-kinetic temperature and electron properties in a DC GD with laser scattering while studying the effects of the GD operating conditions. We have also compared these results with simulations from the most current numerical models of the GD in order to improve upon our understanding of it. We have learned that even though there is a good agreement between the trends in the measured and simulated data but there is still room for improvement. For example, the numerical model needs more precise input on the actual cathode temperature and, since obtaining this parameter is not a trivial task, this opens new areas where more research is needed.

Mass Spectrometer Sampler Effects on ICP. The ICP has also become very popular as an ion source for mass spectrometry (MS) and a great deal of research has been undertaken to clarify why the mass spectrum changes with plasma conditions. However, almost nothing has been done to determine whether and how an ICP-MS sampling interface influences the plasma itself. It was unclear whether the fundamental properties of the plasma upstream of the interface are affected, a surprising fact, considering the large 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 high-powered diagnostics techniques, we have found that the electron temperature, electron number density, gas-kinetic temperature, analyte number densities and even matrix effects are affected by the presence of the mass spectrometer interface. In addition, we have observed that the operating parameters of r.f. power and sampling depth exert an influence on such effects.

Matrix Effects in ICP-AES. It is also desirable to study how the matrix perturbs analyte excitation on an energy-level by level basis, because some matrix effects can be excitation-level specific. Also, fundamental mechanisms of matrix effects can be deduced if a complete picture of how the matrix perturbs different analyte excitation levels is obtained. For this purpose, the changes in emission intensity of a pool of spectral lines originating from different excitation levels are followed in the absence and presence of a matrix using an Echelle-grating spectrometer with a 2D imaging detector that yields complementary information to the Thomson scattering, Rayleigh scattering, and laser induced fluorescence studies. In this manner, a novel method to characterize charge-transfer excitation has been developed which can possibly be extendable to other atomic emission sources.

Plans for Future Research.

(1) Fundamental characterization of millisecond and microsecond pulsed glow discharges. This mode of operation is interesting because higher instantaneous powers can be applied to the glow discharge to yield better analytical figures of merit. In addition, time-resolved sampling of the GD can be used to obtain elemental, molecular, or structural information from a given sample. However, pulsed GDs have not been as widely studied as dc discharges; in fact, very little is known about their electron behavior. We plan to take advantage of the time-resolution capability of laser scattering techniques to study pulsed GDs. *(2) Fundamental study on the effect of trace-gas impurities in a GD.* It has been confirmed that addition of small amounts of gases such as H_2, N_2, O_2, or H_2O has a significant effect on the GD global and analytical characteristics. A similar effect has been noted with samples that generate such species in the discharge, i.e. TiH_2. *(3) Continue study of mass spectrometer sampler effects on ICP*. The ICP load-coil grounding configuration is known to influence the occurrence of a secondary discharge between the plasma and the tip of the mass spectrometer sampler. We will determine how the secondary discharge affects the ICP upstream from the sampling cone. Also, we will explore the influence of the thermal and electrical conductivity of the materials used to construct the MS interface. *(4) Investigation of analyte-matrix specific matrix effects and their interference mechanism in the ICP, as well as the fundamentals of charge-transfer excitation mechanism and Penning-ionization excitation mechanism in the ICP.*

Selected Publications Acknowledging DOE Support: 2003-2004 (total pub. in 2003-4: 9)

1. S. A. Lehn, M. Huang, K. A. Warner, G. Gamez, G. M. Hieftje, “Spatially resolved Ground-State Number Densities of Calcium and Strontium Ion in an ICP in Contact with an ICP-MS Sampling Interface,” *Spectrochim. Acta, Part B.*, **2003**, 58 (1647-1662).
2. G. Gamez, M. Huang, S. A. Lehn, G. M. Hieftje, “Laser-Scattering Instrument for Fundamental Studies on a Glow Discharge,” *J. Anal. Atom. Spectrom.*, **2003**, 18 (680-684).
3. G. Gamez, A. Bogaerts, F. Andrade, G. M. Hieftje, “Fundamental Studies on a Planar-Cathode Direct Current Glow Discharge Part I: Characterization via Laser Scattering Techniques,” *Spectrochim. Acta, Part B.*, **2004**, in press.
4. A. Bogaerts, R. Gijbels, G. Gamez, G. M. Hieftje, “Fundamental Studies on a Planar-Cathode Direct Current Glow Discharge Part II: Numerical Modeling and Comparison with Laser Scattering Experiments,” *Spectrochim. Acta, Part B.*, **2004**, in press.
5. G.C.-Y. Chan, G.M. Hieftje, “Using matrix effects as a probe for the study of the charge-transfer mechanism in inductively coupled plasma-atomic emission spectrometry,” *Spectrochim. Acta Part B*, **2004**, in press.

Fundamental Nebulization Processes and Analyte Transport in High-Temperature Plasmas

Akbar Montaser, PI
José Rámon Chirinos, María De Los A. Alvarez, Visiting Professors
Billy W. Acon, Kaveh Jorabchi, Kaveh Kahen, Su-Ann E. Murdoch, Cristina M. Nechita, Craig S. Westphal, Graduate Research Assistants
Gretchen M. Carpintero, Jonathan A. Levine, Ryan C. McCormick, Daniel E. Mittelberger, Undergraduate Research Assistants
Unique J. Luna, High School Student
Department of Chemistry
The George Washington University
725, 21st Street, NW
Washington, DC 20052
montaser@gwu.edu
http://home.gwu.edu/~montaser/

Overall Research Goals. In the current state of knowledge, intuition and guesswork play a major role in nebulizer design and plasma spectrometry. By all reasonable standards, the introduction of sample into plasmas and flames is the most serious bottleneck in atomic spectrometries. The principal goal of this research is to gain fundamental information for quantitative assessment, prediction, and, ultimately, control of the quality of the nebulizer aerosol used in plasma spectrometry. The research is centered on the exploration and development of novel direct injection micro- and nanonebulizers, new aerosol diagnostic techniques, and realistic predictive models, essential for analytical spectrometry with high-temperature plasmas. The long-range objective of this research is to expand the frontiers of analytical measurements at all concentration levels for a variety of chemical species in diverse samples. The fate of the sample aerosol is probed to understand and control the critical processes of direct liquid introduction and to obtain further insight into the complex nature of the interaction between aerosol and plasma. Ultimately, such an investigation allows predictions and improvements that would be impossible with only conventional knowledge. These studies are conducted to achieve the following general goals: (1) provide a better understanding of fundamental processes in nebulization for the purpose of improving elemental and isotopic ratio analysis, (2) enable improvements in the selectivity, sensitivity, precision, reliability, and ease of operation of speciation measurements, (3) reduce sample size requirements, toxic wastes, and the cost of analytical determinations, (4) decrease the size and cost of future analytical instruments, and (5) contribute to the preparation of trained scientists in spectrochemical analysis.

Specific Objectives for 2002-2003. Our specific objectives are: (1) development of low-cost nebulizers and plasma sources for direct injection nebulization; (2) exploration of aerosol generation and transport with new direct injection devices to improve aerosol properties for several measurement, particularly micro- and nano-separation using atomic emission and mass spectrometric detection techniques; (3) development of novel laser-based imaging techniques, centered on particle image velocimetry, particle tracking velocimetry, and optical patternation to map and contrast droplet size-velocity distributions in direct and indirect nebulization, and to trace individual droplets that survive the plasma; and (4) modeling droplet evaporation and coalescence and solid particle evaporation in argon inductively coupled plasma (Ar ICP) to ultimately predict and reduce the extent of matrix effects and other interferences on accuracy and performance.

Selected Significant Achievements

The general scope of our research and productivity is evidenced by the list of publications and patents catalogued in several documents.[1-17] Only selected studies are discussed below.

Direct Injection Nebulization with Demountable Devices. We seek to expand the domain of direct injection micronebulization by utilizing hybrid micro/nanonebulizers that enhance solution-gas interactions. The principal idea behind this aspect of research is that fundamental aerosol properties are greatly improved when the critical nebulizer dimensions are reduced in size. This simple concept suggests that it is possible to produce fluid nebulization and transport to the plasma with greater efficiency and reduced droplet size and droplet velocity distributions. As shown in Table 1, the demountable direct injection high efficiency nebulizer (d-DIHEN)[10,11] can be used at solution uptake rates of 1-10 μL/min, providing key analytical performance indices better than the conventional DIHEN and conventional nebulizer-spray chamber arrangements which consume 10 to 100 times more sample. The d-DIHEN is tunable, that is, it provides an adjustable solution capillary. This facilitates fundamental studies to improve operational characteristics of the micronebulizer, adjust and fine tune aerosol properties, and obtain superior analytical figures of merit in ICP spectrometries. In contrast to our previous devices, the DIHEN and the large bore-DIHEN (LB-DIHEN), the optimum position for the d-DIHEN nozzle is located 5 mm (rather than 2 mm) below the end of the torch intermediate tube for measurements in ICP mass spectrometry (ICPMS), thus reducing the chance of accidental nebulizer tip meltdown. Compared with the DIHEN, the d-DIHEN produces smaller droplets with narrower droplet size distribution and lower mean droplet velocities, characteristics important for improved sample-plasma interaction. Sensitivity, detection limits, and precision attained with the d-DIHEN are far superior to conventional nebulizer-spray chamber arrangements and other direct injection nebulizers, especially at low solution uptake rates (< 40 μL/min). In general, oxide ratios for the d-DIHEN and DIHEN are low at solution uptake rates of 10 μL/min or less. Above 10 μL/min, the d-DIHEN provides lower oxide ratios than the DIHEN. For example, the oxide ratio for Ce increases from 0.6% to 3.8% (d-DIHEN) and 0.5% to 7.6% (DIHEN) as the solution uptake rate is increased from 5 μL/min to 85 μL/min. Doubly charged ratios for Ba are also lower for the d-DIHEN at all solution uptake rates compared to the DIHEN. The cost of a d-DIHEN is approximately 10 times less than the conventional DIHEN. Additionally, if a d-DIHEN component is damaged, it can easily be replaced at a low cost, whereas comparable damage to the DIHEN may result in it being unusable. A related device was

	Solution Uptake Rate																	
	5 μL/min						10 μL/min						40 μL/min					
Isotope	d-DIHEN		DIHEN		LB-DIHEN		d-DIHEN		DIHEN		LB-DIHEN		d-DIHEN		DIHEN		LB-DIHEN	
^{7}Li	0.9	(5.8)	0.2	(8.1)	0.3	(15)	1.8	(3.7)	0.3	(6.5)	0.6	(11)	7.4	(2.2)	3	(2.5)	2	(2.4)
^{55}Mn	6.9	(3.6)	2	(5.8)	2	(17)	15	(2.5)	4	(5.3)	4	(13)	63	(2.2)	25	(1.2)	14	(3.6)
^{75}As	3.4	(4.1)	0.3	(6.2)	0.3	(15)	7.0	(3.0)	0.6	(4.7)	0.5	(14)	25	(1.7)	4	(1.3)	2	(3.2)
^{103}Rh	11	(3.8)	3	(7.1)	3	(17)	22	(2.5)	8	(5.2)	6	(13)	93	(1.6)	50	(1.6)	23	(2.6)
^{133}Cs	13	(3.3)	6	(9.1)	5	(15)	18	(2.2)	15	(4.9)	11	(13)	113	(1.8)	86	(1.4)	38	(2.5)
^{208}Pb	6	(4.2)	3	(7.6)	2	(15)	12	(1.8)	7	(5.7)	5	(12)	51	(1.6)	37	(0.9)	16	(2.6)
^{238}U	11	(3.6)	6	(6.8)	5	(14)	22	(2.1)	11	(5.0)	11	(12)	93	(1.6)	80	(0.9)	33	(2.0)

Table 1. Relative Sensitivities (MHz/ppm) and Precision (%RSD) Obtained for the d-DIHEN, DIHEN, and LB-DIHEN at Low Solution Uptake Rates and 1500 W. The nebulizer gas flow rate is 0.16, 0.17, and 0.25 L/min for the d-DIHEN, DIHEN, and LB-DIHEN, respectively. Actual solution uptake values for the DIHEN and LB-DIHEN are 5.6, 11, and 42 μL/min. The d-DIHEN is positioned 5 mm below the torch intermediate tube with the solution capillary extended 0.1 mm beyond the nebulizer gas nozzle. Values from Reference 10.

also explored for conventional nebulization with a spray chamber to allow adjustment of the solution capillary for optimization, or capillary replacement in the event of nebulizer clogging.

Direct Injection Nebulization with Short Torches & Conventional Micronebulizers. One drawback of the micronebulizers (including the DIHEN and LB-DIHEN) in addition to their high cost is a greater susceptibility to nebulizer clogging compared to conventional devices due to the smaller dimensions of the solution capillary and gas annulus area, a limitation that may completely damage the cited devices. With an LB-DIHEN, nebulizer clogging is reduced for the nebulization of slurries and solutions having high total dissolved solids, but analytical figures of merit are slightly worse than those of the DIHEN. Additionally, the close proximity of the nebulizer tip to the plasma increases the likelihood of accidental and gradual damage to the direct injection nebulizers. These drawbacks are eliminated with the d-DIHEN.[10,11] In an alternative approach, we radically simplified direct solution introduction by designing/constructing a short torch that can incorporate, for example, a conventional nebulizer. As shown in Figure 1, the short torch design consists of: (1) a custom-made torch with critical dimensions similar to conventional torches, except for the torch length, and (2) a Delrin adapter to support the nebulizer. The short-torch scheme is a universal approach in that it maintains the advantages of direct solution injection while reducing the nebulizer cost by using any of a wide range of less expensive, off-the-shelf nebulizers including micronebulizers. For example, sensitivity, detection limits, and precision obtained with the short torch-micronebulizer combination are comparable to those obtained using the DIHEN and d-DIHEN. Relatedly, oxide ratios obtained with the short torch-micronebulizer are similar to or slightly better than the results from the DIHEN, regardless of the solution uptake rate. Most importantly, the short torch design allows any conventional nebulizer to be used as a direct injection device.[13] These studies, still in progress, have the ultimate potential to make direct solution nebulization easy, low cost, and accessible to the entire plasma community, opening ample opportunities for other research groups worldwide to embark on this taxing field.

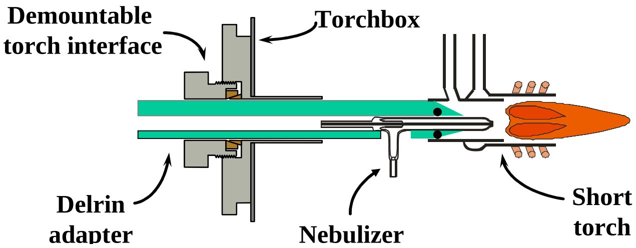


Figure 1. Short-torch design for using conventional nebulizers as direct injection devices.

New Aerosol Diagnostic Techniques for Plasma Spectrometry. Our prior research shows that the issue of aerosol transport efficiency becomes more critical at low solution uptake rates, especially if the analyst aims to achieve analytical performance indices better than those obtained with conventional nebulizer-spray chamber arrangements. At very low solution uptake rates (less than 100 μL/min), key aerosol properties are also more difficult to measure. Aerosol diagnostic techniques such as laser Fraunhofer diffraction and phase-Doppler particle analysis cannot probe the aerosol close to the nebulizer tip, measure droplets having a diameter less than 0.5 μm, or record the spray patterns quickly and easily. High-speed photography and optical imaging methods based on two-dimensional aerosol sizing are more amenable to such studies, and their applications will bring a wealth of information not previously possible. A perfect tool for an aerosol scientist (and an ICP spectroscopist) is a particle-sizing instrument that can provide real-time spatial information on the distribution of particle size, particle velocity, particle shape, droplet (or particle) temperature, and spray pattern in a single run and over a wide size range (or particle) temperature, and spray pattern in a single run and over a wide size range (0.01 to 100 μ). Certainly, this is one of the exciting waves of the future research in plasma spectrometry.

One of our major areas of investigation, at least since 1998, has been the direct observation of droplets in high-temperature plasmas, from the point of aerosol generation to the site of analytical measurements. Unfortunately, adequate funding was not available from DOE, and despite several proposals to the National Science Foundation, six proposals were declined thanks to the comments of one or two prominent reviewers with marginal expertise in the review field. With partial funding from DOE, we recently have been able to borrow resources such as the required laser, optics, and detector systems to arrive at a number of exciting results.[14,15] Briefly, three novel laser-based imaging techniques, centered on particle image velocimetry (PIV), particle tracking velocimetry (PTV), and optical patternation, are used for the first time to map and contrast droplet size-velocity distributions in direct and indirect nebulization, and to trace individual surviving droplets in the ICP. Two pulses of a laser sheet at a short time difference illuminate the flow field of the droplets or particles. A charge coupled detector (CCD) captures the Mie scattering signal, providing two nearly simultaneous images of the droplets or particles. Cross-correlation of the corresponding images yields a two-dimensional velocity map of the aerosol. For droplet size mapping, laser induced florescence (LIF) and Mie scattering images are captured simultaneously by two CCDs. The resulting size distribution image is then scaled by a point calibration method via PDPA. Our analysis of data thus far reveals four major findings: 1) the central region of the aerosol cone, both from the nebulizer-spray chamber arrangement and a DIHEN, consists of fast, fine droplets as compared to slow, large droplets in the fringes of the spray; 2) the spray chamber acts as a momentum filter as it removes droplets having large sizes and high velocities; 3) less than 30% of the droplets introduced in the plasma by the DIHEN remains in the central channel contributing to analytical signal with the rest entering the Eddy current region of the ICP, causing plasma instabilities, and increased noise and interferences; and 4) droplets having axial velocities of 15 m/s or higher are more likely to survive beyond the analytical zone of the plasma, resulting in local cooling effects in the analytical zone of the ICP. These new observations are critical in 1) the design of the next-generation direct injection devices for lower sample consumption, higher sensitivity, improved analytical precision, and reduced matrix effects in high-efficiency elemental and isotopic ratio measurements; and 2) developing smart plasma spectrometers.

Modeling Aerosol Fate in Plasmas. Computational techniques to determine the fate of the aerosol in an ICP are an integral part of our research because they are important for predicting complex desolvation, vaporization, atomization, excitation, and ionization processes, providing a theoretical basis for our experimental results. Briefly, a new numerical model was developed to consider droplet coalescence along with transport, heating, and desolvation in an Ar ICP.[16,17] The direct simulation Monte Carlo (DSMC) method and the Ashgriz-Poo model were used to compute droplet-droplet interactions and to determine the outcome of droplet collisions, respectively. Molecular dynamics (MD) simulations supported the use of the Ashgriz-Poo coalescence model for small droplet coalescence. Simulations predicted spatial maps of droplet number and mass densities (Figure 2) within an Ar ICP for a conventional nebulizer-spray chamber arrangement, a DIHEN, and an LB-DIHEN. The primary findings were: (1) even at

1500 W, the collisions of the droplets in the plasma lead primarily to coalescence, particularly for direct aerosol injection; (2) the importance of coalescence in a spray simulation exhibits a complex relationship with the gas temperature and droplet size; (3) DIHEN droplets penetrate further into the Ar ICP when coalescence is considered; and (4) droplets from a spray chamber or the LB-DIHEN coalesce less frequently than those from a DIHEN. While 99% of droplets desolvate within the first 30 mm segment of the plasma for the nebulizers studied, solid particle evaporation, atomization, excitation, and ionization must occur before the analyte is detected. Our future simulation studies are aimed to: (1) address such processes; (2) consider droplet coalescence within the spray chamber; (3) evaluate the effect of droplet desolvation and evaporation on the physical properties of the ICP; (4) address the verification issues; and (5) utilize improved and more realistic initial droplet velocity and diameter distributions. In this regard, the challenging task is to apply the optical imaging techniques discussed above to obtain experimental maps of aerosol properties in the plasma.

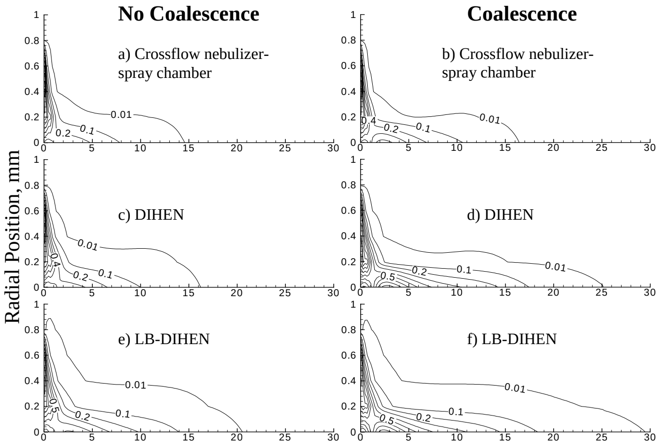


Figure 2. Droplet mass densities within the Ar ICP for the crossflow nebulizer-spray chamber (a,b; normalized to 4.0 kg m^{-3}), DIHEN (c,d; normalized to 10.0 kg m^{-3}), and LB-DIHEN (e,f; normalized to 13.0 kg m^{-3}) nebulizers, at the analytical conditions outlined in Table 1 of 2003 modeling manuscript, without (a, c, e) and with (b, d, f) coalescence. Contour lines represent fraction of initial aerosol remaining in the plasma.

Plans for Future Research. Our efforts in the coming year will expand and explore in greater detail the results presented and listed in the manuscripts. The specific projects to pursue will include:

(1) investigation of new micro- and nano-flow nebulizers for plasma mass spectrometry, with emphasis on µHPLC and CE applications especially for limited biological samples and toxic wastes; (2) exploration of aerosol generation and transport from novel micro- and nano-nebulizers; (3) modeling aerosol generation to predict aerosol properties; (4) probing the fate of droplets from the point of production to the site of analytical measurements in the plasmas; (5) further development and applications of imaging diagnostic tools for rapid elucidation of three-dimensional spray structure and properties; and (6) developing high efficiency plasma sources and new diagnostic tools to measure plasma properties.

Publications Acknowledging DOE Support – 2002-2003

1. J. R. Chirinos, K. Kahen, S. E. O'Brien and A. Montaser, Mixed-Gas Inductively Coupled Plasma Atomic Emission Spectrometry Using a Direct Injection High Efficiency Nebulizer, Anal Bioanal Chem 372: 128-135 (2002).

2. C. S. Westphal, J. A. McLean, B. W. Acon, L. Allen, and A. Montaser, Axial Inductively Coupled Plasma Time-of-Flight Mass Spectrometry Using Direct Liquid Sample Introduction, J. Anal. At. Spectrom. 17, 669-675 (2002).
3. S. E. O'Brien, J. A. McLean, B. W. Acon, B. J. Eshelman, F. Bauer, and A. Montaser, The Determination of Memory Prone Elements Using a Direct Injection High Efficiency Nebulizer with Inductively Coupled Plasma Mass Spectrometric Detection, Appl. Spectrosc. 56, 1002-1008 (2002).
4. S. F. Boulyga, J. L. Matusevich, V. P. Mironov, V. P. Kudrjashov, L. Halicz, I. Segal, J. A. McLean, A. Montaser and J. S. Becker, Determination of ^{236}U/^{238}U Isotope Ratio in Contaminated Environmental Samples Using Different ICP-MS Instruments, J. Anal. At. Spectrom, 17, 958-964 (2002).
5. K. Kahen, A. Strubinger, J. R. Chirinos, and A. Montaser, Direct Injection High Efficiency Nebulizer-Inductively Coupled Plasma Mass Spectrometry for Analysis of Petroleum Samples, Spectrochim. Acta, 58, 397 - 413 (2003).
6. S. E. O'Brien, J. R. Chirinos, K. Jorabchi, K. Kahen, M. E. Cree, and A. Montaser, Investigation of the Direct Injection High Efficiency Nebulizer for Axially and Radially Viewed Inductively Coupled Plasma Atomic Emission Spectrometry, J. Anal. At. Spectrom. 18, 910 - 916 (2003).
7. S. E. O'Brien, B. W. Acon, S. F. Boulyga, J. S. Becker, H.-J. Dietze, and A. Montaser, Reduction of Molecular Ion Interferences in Hexapole Collision Cell in Direct Injection Nebulization – Inductively Coupled Plasma Mass Spectrometry, J. Anal. At. Spectrom. 18, 230 – 238 (2003).
8. C. S. Westphal, J. A. McLean, S. J. Hakspiel, W. E. Jackson, D. E. McClain, and A. Montaser, Determination of Depleted Uranium and Uranium Isotope Ratios in Biological Samples with Direct Liquid Sample Introduction-Inductively Coupled Plasma Mass Spectrometry, Submitted to Appl. Spectrosc. (2003).
9. K. Jorabchi and A. Montaser, Effect of Secondary Discharge on Plasma Gas Temperature and Analytical Figures of Merit in Atmospheric-Pressure Helium Inductively Coupled Plasma Mass Spectrometry, Submitted to Spectrochim. Acta, Part B (2003).
10. C. S. Westphal, K. Kahen, W. F. Rutkowski, and A. Montaser, Demountable Direct Injection High Efficiency Nebulizer for Inductively Coupled Plasma Mass Spectrometry, Spectrochim. Acta, Part B (2004), in Press.
11. A. Montaser, C. S. Westphal, K. Kahen, and W. F. Rutkowski, Demountable Direct Injection High Efficiency Nebulizer for Inductively Coupled Plasma Mass Spectrometry, US Patent Application, 2003; pending.
12. S. E. O'Brien, K. Kahen, J. R. Chirinos, M. E. Ketterer, D. D. Hudson, and A. Montaser, Aerosol Diagnostic and Analytical Studies of a Demountable Concentric Nebulizer for Inductively Coupled Plasma Mass Spectrometry, J. Anal. At. Spectrom (2004), in Press.
13. A. Montaser, C. S. Westphal, and K. Kahen, Short Torch Design for Direct Liquid Sample Introduction Using Conventional Nebulizers for Plasma Spectrometry, US Patent Application, 2003; pending.
14. K. Kahen, K. Jorabchi, C. Gray, and A. Montaser, Spatial Three-Dimensional Mapping of Droplet velocity and Size in Direct and Indirect Nebulization, in preparation for Anal. Chem. (2003).
15. K. Jorabchi, K. Kahen, C. Gray, and A. Montaser, Insitu Visualization and Characterization of Aerosol Droplets in an Inductively Coupled Plasma, in preparation for Anal. Chem. (2003).
16. C. M. Benson, S. F. Gimelshein, D. A. Levin, J. Zhong, and A. Montaser, Simulation of Droplet Heating and Desolvation in an Inductively Coupled Plasma – Part II: Coalescence in the Plasma, Spectrochim. Acta. 58, 1453-1471 (2003).
17. C. M. Benson, D. A. Levin, J. Zhong, S. F. Gimelshein, and A. Montaser, A Kinetic Model for the Simulation of Aerosol Droplets in a High-Temperature Environment, J. Fluid Mech. In press (2003).

2004 DOE/BES Analysis Program
Contractors' Meeting

Abstracts
Session 3

Measurements of Mass Transport Rate Through Well-Defined Nanoscopic Tubes

Richard M. Crooks, PI
Li Sun, Research Scientist
Takashi Ito, Jinhua Dai, Postdoctoral Research Associates
Ronald Henriquez, Graduate Research Assistant
Department of Chemistry
Texas A&M University
P. O. Box 30012
College Station, TX 77842-3012
crooks@tamu.edu
http://www.chem.tamu.edu/rgroup/crooks

Overall Research Goals

Because of their unique geometric, mechanical, and chemical properties, carbon nanotubes have been suggested for a wide range of applications. We prepared the first example of single-pore membranes based on multiwall carbon nanotubes (MWNT) and then demonstrated their use as pores for Coulter nanoparticle counters for analytical applications as well as for studying transport phenomena through nanoporous media. Our research focuses on two main goals. The first goal is to develop Coulter counters that can characterize individual solution-phase particles and biomacromolecules in the 2-100 nm size range. Such a counter provides a means for studying the intrinsic distribution of a particular property of interests. The second goal is to understand the interactions between particles/molecules and the interior surface of the nanopore. These two goals are closely related to each other, and progress toward either one is important for developing a chemically-selective device that can discriminate between individual molecules.

Specific Objectives for 2003-2004

During the last year we successfully demonstrated that Coulter counters based on single-MWNT membranes can simultaneously measure the size and surface charge of individual nanoparticles and their concentrations. Our specific objectives for the coming year are: (1) to compare the MWNT-based Coulter counter to other techniques in order to validate the measured nanoparticle size and surface charge; (2) to apply the MWNT-based Coulter counters to monitoring nanoparticle surface chemistry, i.e., determination of the apparent surface pK_a of COOH-terminated polymer nanoparticles.

Significant Achievements

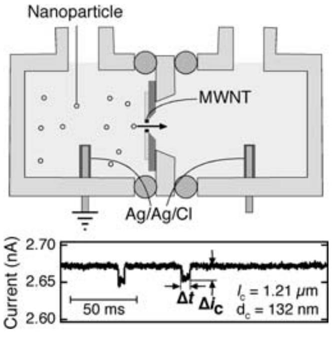


Fig. 1. Schematic illustration of a MWNT-based Coulter counter (top) and typical time course data (bottom).

Data Validation for MWNT-based Coulter counters. In our previous reports (*J. Am. Chem. Soc.* **2000**, *122*, 12340.; *Anal. Chem.* **2003**, *75*, 2399.), we fabricated a single nanopore membrane of 130 - 160 nm in diameter (d_c) and ca. 1 µm in thickness (l_c) by slicing an epoxy block containing a single MWNT. Such a nanopore can be used as a resistive-pulse Coulter counter to detect polymer nanoparticles (28-100 nm in diameter) that electrophoretically pass through the channel (Fig. 1). The diameter (d_s) and electrophoretic mobility (μ) (or effective surface charge, Q) of each nanoparticle can be obtained from the height (Δi_c) and width (Δt) of each resistive pulse and the nanoparticle concentration can be determined from the signal counting frequency. As an analytical technique, the reproducibility and accuracy of data are important, and thus we tried to study them using two types of polymer nanoparticles having similar diameters (ca. 60

nm) but different numbers of surface COOH groups (IDC-PS: 120, Bangs-PS/PA: 24220).

Very similar d_s and μ data were obtained for both types of nanoparticles when independently prepared MWNT-containing membranes were each fabricated from the same MWNT (Table). This demonstrates that the MWNT-based counter reproducibly provides these data without calibration once the diameter of the MWNT is known.

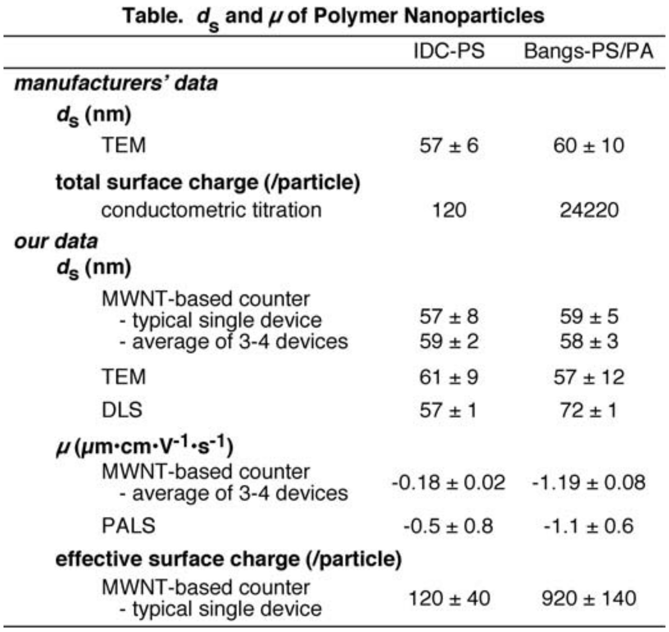


Table. d_s and μ of Polymer Nanoparticles

	IDC-PS	Bangs-PS/PA
manufacturers' data		
d_s (nm)		
TEM	57 ± 6	60 ± 10
total surface charge (/particle)		
conductometric titration	120	24220
our data		
d_s (nm)		
MWNT-based counter - typical single device	57 ± 8	59 ± 5
- average of 3-4 devices	59 ± 2	58 ± 3
TEM	61 ± 9	57 ± 12
DLS	57 ± 1	72 ± 1
μ (μm·cm·V^{-1}·s^{-1})		
MWNT-based counter - average of 3-4 devices	-0.18 ± 0.02	-1.19 ± 0.08
PALS	-0.5 ± 0.8	-1.1 ± 0.6
effective surface charge (/particle)		
MWNT-based counter - typical single device	120 ± 40	920 ± 140

The accuracy of the d_s determination was evaluated by comparing those obtained via transmission electron microscopy (TEM) and dynamic light scattering (DLS) (Table). All the techniques give ca. 60 nm as d_s for IDC-PS, suggesting that the d_s data obtained via the MWNT-based counter are accurate. Slight differences in d_s values, e.g., the larger d_s obtained for Bangs-PS/PA via DLS (ca. 72 nm), possibly reflects differences in the nature of each technique (Fig. 2). TEM measures the size of dried nanoparticles, and DLS measures the hydrodynamic diameter from diffusion data for suspended particle ensembles. DLS is affected by a swelled polymeric surface layer that is hydrodynamically impermeable during Brownian diffusion, while the MWNT-based Coulter counter detects only the effective volume of a polymer mass and cannot detect the swelling acrylic acid shell through which a current can flow under a strong electric field. The above comparison indicates that these three methods give complementary information about the particle diameter.

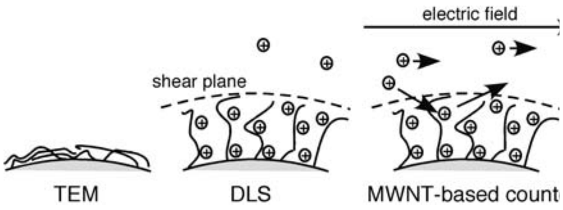


Fig. 2. Schematic illustration of different detection nature of the three techniques.

The accuracy of the μ determination was validated by comparing to results obtained from phase analysis light scattering (PALS) (Table). The average μ values are comparable to each other, indicating that the μ determination via the MWNT-based counter is accurate. The MWNT-based counter gives more precise data than PALS, due to the larger electric field inside the MWNT sensing channel.

These results indicate that MWNT-based counters provide a means for determining the d_s and μ of individual suspended nanoparticles accurately and reproducibly without calibration once MWNT diameter is known. These characteristics originate from negligible immobile surface charges inside the channel and the uniform cylindrical structure of the channel over its full length.

Application of the MWNT-based Coulter counters for monitoring nanoparticle surface chemistry. MWNT-based counters could be applied for discrimination of individual nanoparticles having similar sizes but different surface charges, and for monitoring the surface chemistry of nanoparticles. The former was shown last year (*Anal. Chem.* **2003**, *75*, 2399.). As an example of the latter experiments, the apparent surface pK_a of nanoparticle having very small surface charge (IDC-PS) was determined from

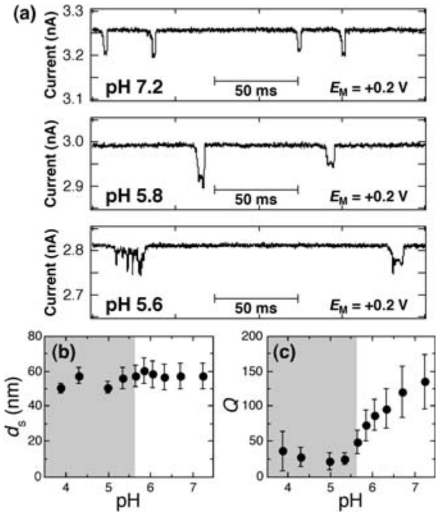


Fig. 3. (a) Typical Coulter counting signals of IDC-PS at three different pHs. (b, c) Effect of pH on (b) d_s and (c) Q. Obtained with a MWNT-based Coulter counter (d_c = 132 nm, l_c = 0.96 μm) in 0.1 M KCl, 10 mM phosphate buffer and 0.1% Triton X-100.

measurements using MWNT-based counters at several pHs in the range of 4 to 9. Fig.3a shows Coulter counting signals of IDC-PS at three different pHs. As the pH decreases from 7.2 to 5.6, the width of the signal becomes larger. At pHs lower than 5.6 (shown in grey in fig. 3b and c), clustering of signals is observed. Fig. 3b and c shows the pH dependence of d_s and Q of IDC-PS. Whereas d_s is very similar at the pHs examined (Fig. 3b), Q decreases with decreasing pH (Fig. 3c), which reflects the decrease in the effective surface charge of the nanoparticles due to the protonation of their surface COOH groups. The clustering of signals at lower pH probably suggests that, because of their very slow electrophoretic motion, the particles are attached to the channel surface and/or entrance during transport through the channel. From Fig. 3c, the apparent surface pK_a of the nanoparticles can be estimated to be about 5.8. This result indicates that this MWNT-based counter is suitable for studies in colloid surface science.

Plans for Future Research

Our efforts in the coming year will extend and explore in greater detail the results presented here. In particular our goals are:

(1) Study of colloid surface chemistry using MWNT-based Coulter counters. We are trying to use this device to study various chemistries on nanoparticle surfaces. *(2) Applications of MWNT-based Coulter counters for biosensing.* We are ready to detect biological samples such as viruses and DNA. *(3) Addition of chemical selectivity to MWNT channels by their chemical modification and understanding of mass transfer behavior in such a channel.*

Publications Acknowledging DOE Support – 2003-4

1. T. Ito, L. Sun, and R. M. Crooks, “Electrochemical Etching of Individual Multiwall Carbon Nanotubes”, *Electrochemical Solid-State Lett.* **2003**, *6*, C4-C7.
2. T. Ito, L. Sun, and R. M. Crooks, “Simultaneous Determination of Size and Surface Charge of Individual Nanoparticles Using a Carbon Nanotube Coulter Counter”, *Anal. Chem.* **2003**, *75*, 2399-2406.
3. T. Ito, L. Sun, and R. M. Crooks, “Observation of DNA Transport through a Single Carbon Nanotube Channel Using Fluorescence Microscopy”, *Chem. Commun.* **2003**, 1482-1483.
4. J. Dai, T. Ito, L. Sun, and R. M. Crooks, “Electrokinetic Trapping and Concentration Enrichment of DNA in a Microfluidic Channel”, *J. Am. Chem. Soc.* **2003**, *125*, 13026-13027.
5. T. Ito, L. Sun, M. A. Bevan, and R. M. Crooks, “Unique Characteristics of Carbon Nanotube-Based Coulter Counter as a Tool to Measure Diameter and Electrophoretic Mobility of Nanoparticles”, in preparation for *Langmuir*.
6. T. Ito, L. Sun, and R. M. Crooks, “Carbon Nanotube-Based Coulter Nanoparticle Counter”, in preparation for *Acc. Chem. Res.*

Chemical Analysis at Nanodomains: Composition, Structure, and Function Relationships

Marc D. Porter - Principle Investigator
Heather Bullen - Postdoctoral Research Associate
David Keller, Lisa Ponton, and Sebastian Donner - Graduate Research Associates
Ames Laboratory - USDOE and Department of Chemistry
Iowa State University
Ames, Iowa 50011
mporter@porter1.ameslab.gov

Research goals. Structure and environment in nanodomains dictate catalytic efficiency, energy conversion, electronic device performance, immune system response, and chromatographic resolution. For these and other areas to flourish, however, advances in the basic underpinnings that affect structure-function relationships and approaches that can quantitatively probe these relationships at unprecedented levels of detail are needed. As part of this integrated program at the Ames Laboratory - USDOE, this project is aimed at the development of fundamental insights into structure-function relationships at the length scale central to the performance of electrochemical and chromatographic interfaces.

Objectives for 2002-03. The 2002-03 objectives include: a) development of the capability to utilize chromatographic retention for the determination of interfacial excess (Γ), surface charge (q^m), and surface tension (γ) at carbon-based materials; b) design, construction, and testing of a system to perform separations under potential control as a function of temperature; c) use this system to quantify both the enthalpy and entropy of adsorption for model analytes; and d) establishment of the ability to correlate these macroscopic observables with microscopic observables by probing interfacial interactions with atomic force microscopy (AFM) and single molecule spectroscopy (SMS).

Significant Achievements. *1)* We have developed novel experimental and theoretical constructs for probing key thermodynamic properties of electrified interfaces. Our approach takes advantage of a separation technique that combines electrochemistry and liquid chromatography: electrochemically modulated liquid chromatography or EMLC. In EMLC, a conductive stationary phase (e.g., glassy carbon (GC) or porous graphitic carbon (PGC)) also functions as a working electrode. Changes in the potential applied (E_{app}) to this dual-purpose packing alter the surface charge density of the packing, which changes retention. With this capacity, we can utilize retention time to quantitatively determine Γ, γ, and q^m, providing insights into interfacial processes beyond those at the traditional mercury-electrolyte interface.

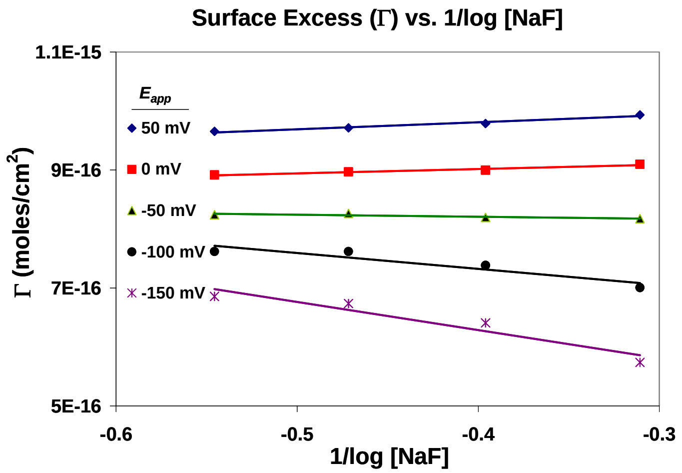


Fig. 1. Dependence of Γ for tosylate anion on E_{app} as a function of NaF supporting electrolyte concentration at a PGC stationary phase (reference electrode: Ag/AgCl/sat'd KCl).

Fig. 1 presents an example of such data using a PGC stationary phase. It plots the dependence of Γ for tosylate anion at five different values of E_{app} as the NaF supporting electrolyte concentration is systematically changed. These plots yield two interesting observations. First, Γ at a constant NaF concentration increases as E_{app} becomes more positive. Second, the plots evolve from having a strong negative slope at the more negative values of E_{app} to a small positive slope at the more positive values of E_{app}. These observations reflect the location (+0.1 to -0.2 V) of the potential of zero (*pzc*), and arise from the competition between tosylate and supporting electrolyte.

2) Construction and testing of a system to perform EMLC separations as a function of temperature has been completed. With this capability, we can potentially determine both the enthalpy and entropy of adsorption. Preliminary studies have already changed the picture of how the interactions of a few types of analytes change with E_{app}. For example, the retention of aromatic sulfonates increases as E_{app} increases. This trend is consistent with expectations based on changes in Γ. That is, the more positive E_{app}, the greater the excess of positive surface charge density and the greater the retention of anionic or donor-type species. These data, however, show that the retention of these organic anions is entropically and not enthalpically driven. The enthalpy of the system actually *increases* as E_{app} decreases, which is opposite that of conventional expectations. In contrast, the entropy of the system undergoes a strong decrease as E_{app} becomes more negative. These findings therefore argue that solvation plays a major role in dictating the extent of retention. We are presently addressing how to accurately describe and determine the volume of the stationary phase in order to quantify these entropic changes.

Future research plans. *1)* The next step in exploiting the capabilities to characterize adsorption thermodynamics at electrified interfaces will examine processes involving simple cations (e.g., K^+, Na^+, Li^+, Cs^+, Ca^{2+}, Mg^{2+}) and anions (e.g., F^-, NO_3^-, OH^-, Cl^-, Br^-, SO_4^{2-}, ClO_4^-, and PF_6^-). These species are among the most studied in the arena of electrified interfaces, and are the subject of a vast literature on electrocapillary phenomena. We should be poised to quantitatively extract the potential dependence of Γ, γ, and q^m, yielding in-depth macroscopic details of this important class of electrified interfaces. To realize this goal, we are working with R. Houk, another member of the Ames Laboratory team, to utilize either inductively coupled plasma or electrospray mass spectrometry as a means for the low level detection of these model ionic species.

2) We have begun to apply AFM as a tool for the characterization of electrical interfaces by examining the distance dependence of the interactions between a chemically modified probe tip and GC surface as a function of E_{app}. The goal is to develop fundamental correlations between the microscopic findings from the EMLC experiments with the observed interactions at a much smaller length scale. Our preliminary findings are in agreement with the reports of others, and show that the repulsive force between the tip and surface becomes detectable at a separation of ~30 nm when E_{app} is sufficiently removed from the *pzc*. The next step is to detail the extent in which such interactions vary as a function of electrolyte composition and concentration and tip composition, with the ultimate goal being to test the established models of the electrical double layer.

3) In an effort to extend the correlation between macroscopic and microscopic observables, we have examined the construction of optically transparent carbon electrodes. To this end, we have begun to evaluate the literature preparation of carbon materials from pyrolyzed photoresist as a means to fabricate films at thicknesses sufficiently thin to be optically transparent, and yet remain effectively conductive to function as an electrode. Our first set of results is shown in Fig. 2, which plots the transmittance from 270 to 700 nm for four different film thicknesses. As expected, the transmittance increases as wavelength increases, and the conductivity decreases as thickness decreases. Importantly, these films also function effectively as electrode materials, showing quasi-reversible electron transfer kinetics for $Fe(CN)_6^{4-/3-}$. The next step will pursue an integrated series of experiments by combining AFM characterizations of interfacial interactions with those based on SMS, an approach heavily utilized in by E. Yeung group at the Ames Laboratory.

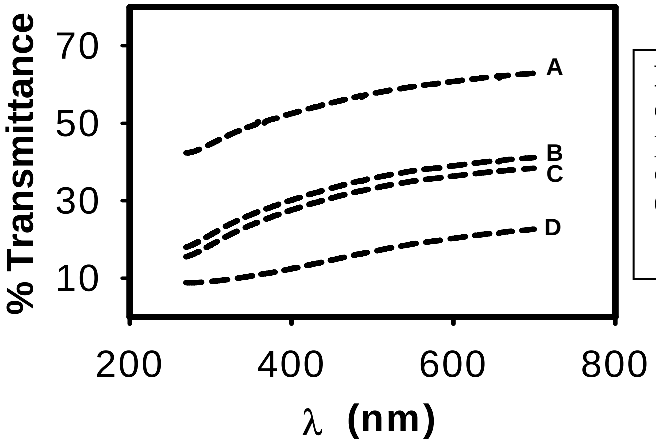


Fig. 2. Transmittance and conductivity dependence on thickness of pyrolyzed photoresist. A) thickness: 13 nm, conductance: 0.11 $\Omega^{-1}cm^{-1}$; B) 39 nm, 0.24 $\Omega^{-1}cm^{-1}$; C) 60 nm, 0.29 $\Omega^{-1}cm^{-1}$; and D) 79 nm, 0.50 $\Omega^{-1}cm^{-1}$.

Publications Acknowledging DOE Support in 2002-3.
Y. Melikhov, S. J. Lee, D. C. Jiles, D. H. Schmidt, M. D. Porter, and R. Shinar, “Microelectro magnectic Ferrofluid-Based Actuator,” J. Appl. Phys. **2003**, 93, 8438-40.

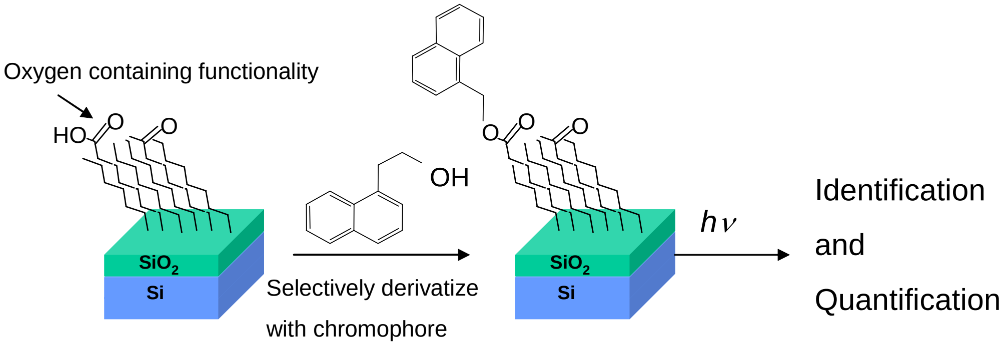
W. He, S. J. Lee, D. C. Jiles, D. H. Schmidt, M. D. Porter, and R. Shinar, “Design of High-Magnetic Field Gradient Sources for Controlling Magnetically Induced Flow of Ferrofluids in Microfluidic Systems,” J. Appl. Phys. **2003**, 93, 7459-61.

N. M. Grubor, R. Shinar, R. Jankowiak, M. D. Porter, and G. J. Small, “Design Optimization of a Biosensor Chip for DNA-Carcinogen Adducts with Low-Temperature Fluorescence Detection,” Biosensors and Bioelectronics, **2003**, 19, 547-56.

Fluorescence Labeling of Surface Species (FLOSS) a Key to Understanding the UV Photoreactivity of Alkylsiloxane SAMs

Eric Borguet, PI
Stephane Petoud, Collaborator
Jason Cross, Post-doctoral Research Associate
Tao Ye, Graduate Research Associate
Eric A. McArthur, Undergraduate Research Associate
Department of Chemistry and Surface Science Center University of Pittsburgh, Pittsburgh, PA 15260
borguet@pitt.edu
www.pitt.edu/~borguet

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 demonstrate that covalent attachment of fluorescent molecules could enable the identification and quantification of low concentrations of surface species. The surface functionalization of materials 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 show that by covalent fluorescent labeling of surface species (FLOSS), the inherent sensitivity of fluorescence spectroscopy can be exploited to identify and quantify concentrations of functional groups on surfaces (Figure 1 and 2) as low as 10^{11} molecules/cm^2. FLOSS enables the identification of intermediates in the UV photoreactivity of octadecylsiloxane (ODS) self-assembled monolayers (SAMs). IR and XPS measurements were inconclusive suggesting low concentrations, if any, hypothetical oxygen containing intermediates at the surface. FLOSS showed that the UV phototransformation of the ODS SAM in ambient does introduce up to a few percent of a monolayerof CHO, OH, and COOH groups, consistent with inconclusive results from more traditional surface technique.

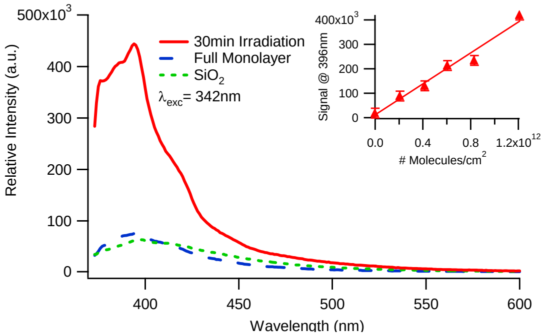


Figure 1 Emission spectra of 1-pyrenemethylamine reacted with 30 minute UV irradiated ODS SAM (**Solid**), unirradiated ODS SAM (**Dashed**) and SiO_2 (**Dotted**). Inset: calibration plot. Aldehyde groups are are detected on UV irradiated SAM but not on neat siloaxane SAM nor on bare SiO_2.

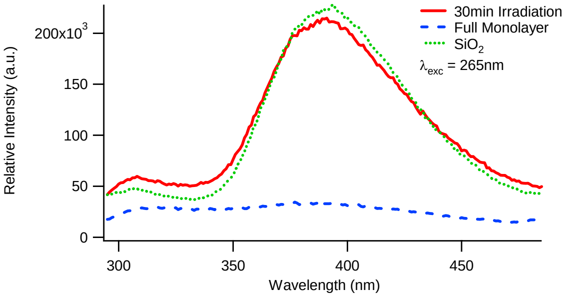


Figure 2 Emission spectra of triphenylmehylchloride reacted with 30 minute UV irradiated ODS SAM (**Solid**), Unirradiated ODS SAM (**Dashed**) and SiO_2 (**Dotted**). –OH groups are detected on bare SiO_2 and on UV irradiated SAM but not on neat siloxane SAM.

“Significant Achievements”

We have developed a novel method sensitive to surface bound chemical functional groups as low as 10^{11} molecules/cm^2 by specific covalent attachment of fluorescent chromophores. This enables the intermediates of the UV photochemistry of alkylsiloxane Self-assembled monolayers to be identified. A significant advantage of this method is its ability to probe surface concentrations in the 10^{-4}-10^{-2} ML range. Moreover, FLOSS does not require a UHV environment commonly needed for highly sensitive surface techniques such as XPS or SIMS.

“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.

“Publications Acknowledging DOE Support”

Ultrafast time-evolution of the Nonlinear Susceptibility of Hot Carriers at the Ge(111)-GeO_2 Interface as Probed by SHG
Arthur McClelland, Vasiliy Fomenko, and Eric Borguet, Journal of Physical Chemistry (in press, 2004).

Fluorescence Detection of Surface Bound Intermediates Produced from UV Photoreactivity of Alkylsiloxane SAMs
Eric A. McArthur, Tao Ye, Jason Cross, Stéphane Petoud and Eric Borguet, Journal of the American Chemical Society (in press, 2004).

2004 DOE/BES Analysis Program
Contractors' Meeting

Abstract
Plenary Lecture 2

Ion Mobility: The Method and Its Applications to Problems in Materials and Biochemistry

Michael T. Bowers
Department of Chemistry and Biochemistry
University of California
Santa Barbara, CA 93106-9510

The use of ion mobility based methods for investigating the structure and energetics of macromolecular systems is approaching maturity. In this talk the method will be briefly described and its synergistic interaction with theoretical modeling studies emphasized. Examples will be chosen from systems under active study by our research group. Possible topics include oligophenyl vinylenes, polyoligomeric silsesquioxanes (POSS), oligonucleotides, and several peptide/protein systems.

2004 DOE/BES Analysis Program
Contractors’ Meeting

Abstracts
Session 4

The Dynamics and Thermodynamics of Gaseous Macro-ions

Scott A. McLuckey, PI
Ravi Amunugama, Postdoctoral Research Associate
Kelly A. Newton, Paul A. Chrisman, Min He, Harsha P. Gunawardena, Graduate Research Assistants
Department of Chemistry
Purdue University
560 Oval Drive
West Lafayette, IN 47907-2084
mcluckey@purdue.edu
http://www.chem.purdue.edu/mcluckey

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. Furthermore, ion/ion chemistry also appears to provide a novel means for the synthesis of macro-molecular 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.

Specific objectives for 2003-2004: The specific objectives for this year include the following: (1) Establish a working paradigm for the phenomenology observed in the ion/ion reactions in which both reactants carry multiple charges. (2) Establish a strategy for the selective insertion of metal ions into polypeptides and proteins. (3) Establish a strategy for the selective removal of metal ions from cations with both excess protons and metal ions. (4) Establish strategies for the efficient inversion of ion charge states in either polarity direction.

Significant Achievements

Ion/ion reactions in which both reactants carry multiple charges. Last year we modified an instrument that allowed us to study for the first time the reactions of oppositely charged ions in which both reactants were multiply charged. Our initial studies involved the reactions of multiply protonated proteins with multiply-deprotonated proteins. We observed the formation of complexes of the ions as well as products arising from a range of numbers of transferred protons. Both observations are, in a sense, remarkable. Complex formation without fragmentation is remarkable given the high degree of energy expected to be released upon mutual neutralization. Partial proton transfer is remarkable given the fact that it is energetically preferred to undergo complete proton transfer. We have examined the kinetics associated with the reactions and compared them with several kinetic schemes based on various candidate models for describing the phenomenology. We have found that one, in particular, accounts well for the observed behavior. This scheme involves the formation of a long-range orbiting complex that collapsed eventually to a chemically bound complex. However, based on the shape of the orbit of the complex (i.e., the degree of its eccentricity) proton transfer reactions over a relatively long distance can occur thereby giving rise to partial proton transfer products.

Metal Ion Insertion. We have established a strategy for the insertion of metal ions into polypeptides, shown generically in Reaction (1) for a doubly protonated molecule and a +1 oxidation state metal:

$$MH_2^{2+} + MetalL_2^{-} \rightarrow (M+Metal)^{+} + 2HL \qquad (1)$$

Reactions of this type have been demonstrated for Na^+ and Ag^+ and an analogous process has been demonstrated for +2 oxidation state metals such as Ca^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, and Cu^{2+}. It appears that the overall strategy is general in the sense that we have been successful in inserting every type of metal ion thus far attempted. However, Reaction (1) is usually not the exclusive process. A variety of other reactions have also been observed depending upon the nature of the peptide, the identities of the ligands, the metal identity and its oxidation state, and the total charge of the ion. We have recently established a paradigm in which all of the observed reaction types can be rationalized. We are currently focusing attention on the role of the ligand because the ligand appears to be a key variable in determining the efficiency with which Reaction (1) is observed.

Metal Ion Removal. We have also established a strategy for the removal of a metal ion from polypeptide ions with mixed excess metals and protons, shown generically in Reaction (2) for a doubly charged species with one metal ion and one excess proton:

$$(M+H+Metal)^{2+} + L^{-} \rightarrow (M+H)^{+} + MetalL \qquad (2)$$

The nature of the ligand is key to determining the efficiency with which Reaction (2) occurs relative to the competitive process of proton transfer. Most ligands studied to date favor proton transfer. We are examining the roles of proton versus metal ion affinities of various ligands to identify highly selective reagents for metal ion removal. We have identified highly selective reagents for proton removal and a limited number of reagents with a degree of selectivity for metal ion removal.

Charge Inversion. We have begun the study of ion/ion reactions that lead to the inversion of the polarity of ions of interest. This capability has several potentially useful analytical applications. For example, the use of two consecutive charge inversion steps can lead to a net increase in the charge state of an ion in the gas phase. This can be highly desirable when the charge states of the ion formed by the ionization method do not give rise to satisfactory structural information upon dissociation. We have demonstrated the sequential charge inversion process and observed that it is possible to increase the charge state of an ion by this approach. We are currently examining the chemical characteristics of reagent ions used for charge inversion that give rise to either the most clustering or the least clustering. Clustering can either be desirable or undesirable depending upon the application.

Plans for future research on this project.

In addition to a continuation of the studies mentioned above, we also plan in the coming year the following initiatives:
(1) Modify an existing apparatus for improved reagent ion mass selection capability. We are currently limited in the specificity with which we can simultaneously define the positive and negative reactants. (2) We are currently examining the factors that affect the fragmentation, or lack thereof, associated with macro-ion/ion reactions. (3) We will establish the factors that give rise to an upper mass limit associated with collision induced dissociation of high mass ions and their complexes in the quadrupole ion trap and relate them to models for ion trap collisional activation.

Publications Acknowledging DOE Support – 2002-3:

1. K.A. Newton, S.A. McLuckey, "Gas-Phase Peptide/Protein Cationizing Agent Switching via Ion/Ion Reactions." *J. Am. Chem. Soc.*, **2003**, 125,12404-12405.
2. M. He, S.A. McLuckey, "Two Ion/ion Charge Inversion Steps to form a Doubly-protonated Peptide from a Singly-protonated Peptide in the Gas Phase." *J. Am. Chem. Soc.*, **2003**, 125, 7756-7757.
3. J.M. Wells, P.A. Chrisman, S.A. McLuckey, "Formation and Characterization of Protein-protein Complexes *in Vacuo*." *J. Am. Chem. Soc.*, **2003**, 125, 7238-7249.
4. B.J. Engel, P. Pan, G.E. Reid, J.M. Wells, S.A. McLuckey, "Charge State Dependent Fragmentation of Gaseous Protein Ions in a Quadrupole Ion Trap: Bovine Ferri-, Ferro-, and Apo-cytochrome *c*." *Int. J. Mass Spectrom.*, **2002**, 219, 171-187.
5. J.M. Wells, P.A.. Chrisman, S.A. McLuckey, "Dueling Electrospray: Instrumentation to Study Ion/Ion Reactions of Electrospray-generated Cations and Anions." *J. Am. Soc. Mass Spectrom.,* **2002**, 13, 614-622.
6. K.A. Newton, S.A. McLuckey, "Generation and Manipulation of Sodium Cationized Peptides in the Gas phase." *J. Am. Soc. Mass Spectrom.*, In press.
7. K.A. Newton, M. He, R. Amunugama, S.A. McLuckey, "Selective Cation Removal From Gaseous Polypeptide Ions: Proton versus Sodium Ion Abstraction via Ion/Ion Reactions." *Phys. Chem. Chem. Phys.*, Submitted.
8. H.P. Gunawardena, S.A. McLuckey, "Synthesis of Multi-unit Protein Hetero-complexes In the Gas Phase via Ion/Ion Chemistry. *J. Mass Spectrom.*, Submitted.

Physicochemical Processes in RF Quadrupole Ion Traps*

Douglas E. Goeringer, PI
Larry A. Viehland, Collaborator (Chatham College)
Organic and Biological Mass Spectrometry Group
Oak Ridge National Laboratory
4500-S MS-6131
Oak Ridge, TN 37831-6131
goeringerde@ornl.gov

*This activity is part of ERKCC42: Sampling, Ionization, and Energy Transfer Phenomena in Mass Spectrometry.

Overall research goals. Key to the remarkable versatility of mass spectrometric methods is the ability to manipulate gas-phase ions via a myriad of physical and/or chemical processes. The radio-frequency (rf) quadrupole ion trap, as deployed in a configuration designed for mass analysis, has emerged as one of the foremost devices for analytical mass spectrometry. Despite the progress achieved in development of the ion trap for that application, the detailed understanding of the physicochemical processes occurring in its multiple collision environment necessary for further advancement is lacking. Thus, this research addresses theoretical and experimental studies aimed at increasing this understanding. The knowledge gained should enhance existing ion trap mass spectrometry and ultimately enable its current capabilities to be surpassed. At the same time, the insights resulting from the studies will likely enable accurate manipulation of ion temperatures and internal energies, thereby enhancing the utility of ion traps as a tool for investigation of fundamental ion chemistry. In addition, the fundamental understanding gained for the quadrupole ion trap should be directly applicable to the rf linear ion trap, which has all the capabilities of a quadrupole trap while exceeding its performance in other areas.

Specific objectives for 2003-2004. Our specific goals are to: (1) adapt classical kinetic theory to the multiple collision environment of the rf quadrupole ion trap; and (2) develop expression(s) for ion energies (temperatures) during trapping in the presence of buffer gas by solving the resulting Boltzmann equation.

Significant Achievements

Adaptation of kinetic theory. The kinetic theory of ion transport in gases focuses on application of the Boltzmann equation, an integro-differential equation that describes the effects of applied forces and collisions on the ion distribution function. The advantage of using the Boltzmann equation to describe ion motion is that it treats collisions with the same level of sophistication and detail as is used to treat the time- and space-dependent electric fields. Consequently, ion transport coefficients and kinetic energy can be calculated numerically from knowledge only of the ion-neutral interaction potential energy. For a Boltzmann treatment of ion traps that is as straightforward as possible, we made the assumptions: (1) motion of the ions in a trap is a superposition of motion of the ion swarm through the apparatus and the motion within the swarm, and (2) the dependence of the ion distribution function upon velocity and position within the swarm can be separated, with all of the position dependence carried by the ion number density and all of the velocity dependence carried by a reduced distribution function.

Solving the Boltzmann equation. For general ion-neutral systems, most techniques for solving linear kinetic equations, such as the Boltzmann, in the hydrodynamic regime are moment methods or other special cases of the method of weighted residuals. However, because the electric fields in ion traps vary strongly with both position and time, the Boltzmann equation needs to be solved without requiring hydrodynamic conditions, that is where all of the time and space dependence of the ion behavior is carried by the ion number density and its (assumed small) spatial gradients. If a non-hydrodynamic modification of this approach were used to study ion traps, practical difficulties would arise. Standard three-temperature treatment of the Boltzmann equation, however, does not suffer from these difficulties. The essence of multi-temperature kinetic theory of gaseous ion transport is to use an ion temperature in the basis functions, rather than the gas temperature. This allows the transport coefficients to be calculated accurately at high fields. Thus, we extended the kinetic theory to apply to ion traps using four temperatures: the gas temperature and three ion temperatures, one for each Cartesian axis in the trap. The resulting system of coupled differential equations was solved using standard techniques, thereby producing expressions that provide an *ab initio* way to describe the ion kinetic energies and other properties by a series of successive approximations.

Plans for future research on this project. Our efforts in the coming year will: *(1) Extend the theory to the situation where ion kinetic energy is increased via resonance excitation of secular oscillations.* Resonance excitation is the primary method used in ion trap mass spectrometers to carry out tandem mass spectrometry. *(2) Address the effects of having mixed, rather than pure, buffer gas.* What are the important parameters affecting the choice of buffer gas(es).

Publications Acknowledging DOE Support – 2002-3

1. G. P. Jackson, F. L. King, D. E. Goeringer, D. C. Duckworth, "Gas-Phase Reactions of U^+ and U^{2+} with O_2 and H_2O in a Quadrupole Ion Trap," *J. Phys. Chem. A.* **106** (2002) 7788-7794.
2. G. P. Jackson, F. L. King, D. E. Goeringer, D. C. Duckworth, "Collision-Induced Dissociation of Lanthanide Oxide Ions In Quadrupole Ion Traps: Effects of Bond Strength and Mass," *Int. J. Mass Spectrom.* 216 (2002) 85-93.
3. D.E. Goeringer, "Factors Influencing the Analytical Performance of an Atmospheric Sampling Glow Discharge Ionization Source as Revealed Via Ionization Dynamics Modeling" J. Amer. Soc. Mass Spectrom., 14, 1315-1326 (2003).
4. L.A. Viehland and D.E. Goeringer, "Kinetic Theory of RF Quadrupole Ion Traps I. Trapping of Atomic Ions in a Pure Atomic Gas," *J. Chem. Phys.*, accepted for publication.

Inorganic Mass Spectrometry with ICP and Electrospray Ionization Sources

R. S. Houk, PI
Fumin Li and Cory Gross, graduate research assistants
Ames Laboratory USDOE
Department of Chemistry
Iowa State University
Ames IA 50011
rshouk@iastate.edu

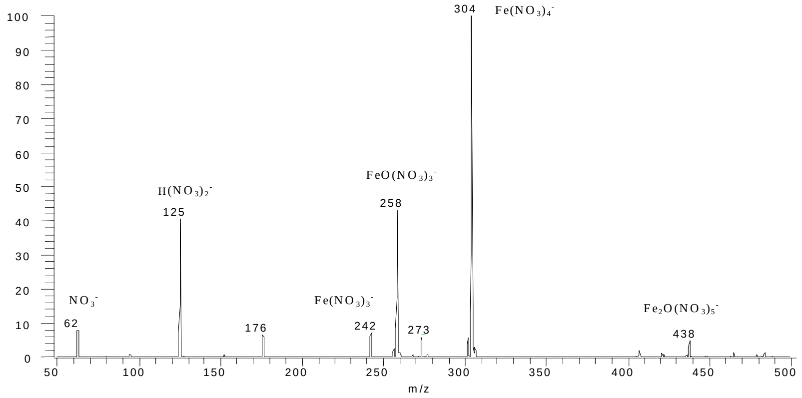
Overall research goals. This project has generated numerous useful techniques in elemental and isotopic analysis by ICP-MS, including several of direct use to the DOE. In recent years, BES research in analytical chemistry at the Ames Laboratory has been redirected into a common theme: chemical analysis at nanodomains. Several projects involving ICP and electrospray mass spectrometry pertinent to this theme are under investigation.

Specific objectives for 2002-2003.

-The use of complexation with counter ions to stabilize reactive species during electrospray and the subsequent ion extraction process.
-Controlled dissolution followed by ICP-MS for elemental quantification in thin sample layers.
-Electrochemical removal of trace elements from blank solutions to improve detection limits.

Significant Achievements

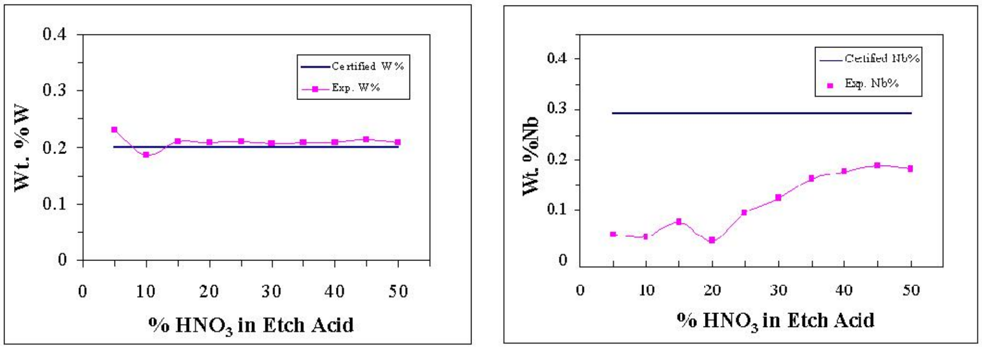
Electrospray of Counter Ion Complexes. Solutions containing metal cations with an excess of nitrate anions, usually from nitric acid, are ionized by electrospray in negative ion mode. $M(NO_3)_x^-$ ions are seen for many elements M under a single set of conditions. Elements in +2 and +3 oxidation states that usually react with water or solvent during ion extraction are observed intact. An example for Fe^{3+} is shown below.



ESI mass spectrum of 50 ppm Fe in 25/75 water/methanol solvent with 0.05% HNO_3. The major ions are $Fe(NO_3)_4^-$ (m/z 304), $FeO(NO_3)_3^-$ (m/z 258) due to in-source fragmentation, and some $Fe^{II}(NO_3)_3^-$ (m/z 242) from reduction of $Fe^{III}(NO_3)_4^-$.

Collision-induced dissociation has been used to investigate the structure and properties of these ions. There is evidence that the type of ion extraction system (i.e., a long, heated capillary vs. a short aperture) affects the types of ions observed. The eventual objective is to stabilize reactive molecular species such as intermediates in catalysis.

Controlled Dissolution. The usual dissolution process for ICP-MS puts all the sample into solution. The amount of sample is determined from the weight before dissolution. Given the high dynamic range of ICP-MS devices, it should be possible to determine both major elements and trace elements, in different dilutions if necessary. ICP-MS could then be used to determine the composition of discrete layers of the sample, rather than the whole material, using standard solutions for calibration. This concept is already widely used in the semiconductor industry, where the purity of silicon is measured routinely by vapor-phase decomposition. Experiments that investigate whether this idea can be extended to other materials, ones where the sample matrix cannot be evaporated away, will be discussed. Work on both simple, single-matrix materials, like pure metals, and multicomponent materials like steel will be presented. The key point is whether the matrix and analytes are removed at the same rates. As shown below for steel, some elements like Mn are removed consistently with the Fe matrix, while other elements like Nb are underrepresented in the solutions.



Comparison of measured and certified values for concentrations of W and Nb in steel etched with aqueous nitric acid at the indicated concentrations.

Electrochemically Modulated Chromatography (EMLC) for Reducing Blanks and Improving Detection Limits. The detection limit in ICP-MS is generally limited by atomic ions in the background for all the elements of interest. One common source of these ions is very low levels of the elements in the blank solutions used. For certain measurements where the blank is not used to correct for such contaminants, like analysis of high-purity acids, it may be possible to reduce the elemental concentration in the blank by electrochemical deposition. These experiments are related to previous work in stripping voltammetry and in electrodeposition of analytes for ICP-MS (Caruso, Van Berkel, Duckworth and co-workers), except that it is the blanks that are subjected to electrodeposition, not the samples. The expertise of M. Porter in EMLC is key here. Initial experiments indicate that certain metals can be removed at carbon cathodes, although issues of generality and other aspects of cleanliness remain.

Research Activities Planned

The studies mentioned above will continue. New directions include the following:
a) Use of micronebulizers as a general method to generate nanoparticles, and study of the sizes and morphology of the particles by AFM (collaboration with M. Porter)
b) Characterization of both solids and liquid layers with lateral resolution pertinent to catalyst arrays (collaboration with E. Yeung).
c) Determination of the volume of stationary phase in EMLC by direct measurement of electrolytes (collaboration with M. Porter).

Publications Acknowledging DOE Support – 2002-03

1. Y.-i. Sung, H. B. Lim* and R. S. Houk, "Diagnostic Studies of a Low-Pressure ICP in Argon Using a Double Langmuir Probe," *J. Anal. Atomic Spectrom*. 2002, 17, 565-569.

2. R. S. Houk, "Elemental Speciation by ICP-MS with High Resolution Instruments," in Handbook of Elemental Speciation, R. Cornelis, Ed., Wiley, 2003, p. 379-416. Peer reviewed.

3. E. T. Luong, R. S. Houk, "Determination of Carbon Isotope Ratios in Amino Acids, Proteins and Oligosaccharides by ICP-MS," *J. Amer. Soc. Mass Spectrom*., 2003, 14, 295-301.

4. F. Li, M. D. Byers and R. S. Houk, "Tandem Mass Spectrometry of Metal Nitrate Ions Produced by Electrospray Ionization," *J. Amer. Soc. Mass Spectrom*., 2003, 14, 671-679.

5. F. Li and R. S. Houk, "Controlled Dissolution for Analysis of Sample Layers by ICP-MS: A Feasibility Study," *Appl. Spectrosc*., submitted (2004).

6. T. Hasan, D. Gazda, M. D. Porter and R. S. Houk, "On-Line Cleanup of Blanks for ICP-MS by EMLC," *Anal. Chem*., submitted 2004.

Abstract S4-4

Mass Spectrometry of Room Temperature Ionic Liquids*

Douglas C. Duckworth, PI
Glen P. Jackson, Postdoctoral Research Associate
Gary Van Berkel, Co-PI
Sheng Dai, Co-PI
Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6375
duckworthdc@ornl.gov
*This effort is part of FWP ERKCC42: Sampling, Ionization, and Energy Transfer Phenomena In Mass Spectrometry

Overall research goals. To investigate and characterize electrospray mass spectrometry for determining the composition and contents of room temperature ionic liquids (RTIL). Fundamental understanding of electrospray processes involved in the generation of ions from RTILs is required if the composition of newly-synthesized RTILs and any dissolved ionic species — impurities, additives, extractants, catalysts —are to be determined. A full understanding of the electrospray process for RTILs will support DOEs missions in a number of areas including catalysis, synthesis, separations, electrochemistry, and electrical energy storage by providing definitive characterization of RTIL media that is not possible using existing techniques.

Specific objectives for 2003-2004: (1) Identify analytical characteristics of ES mass spectra of RTILs; (2) Characterize ES-MS spectra of mixed cations or mixed anions; (3) Investigate ES-MS response for ions dissolved within RTILs; (4) Utilize the unique properties of RTILs to perform fundamental investigations of the ES process and enhance analyte response.

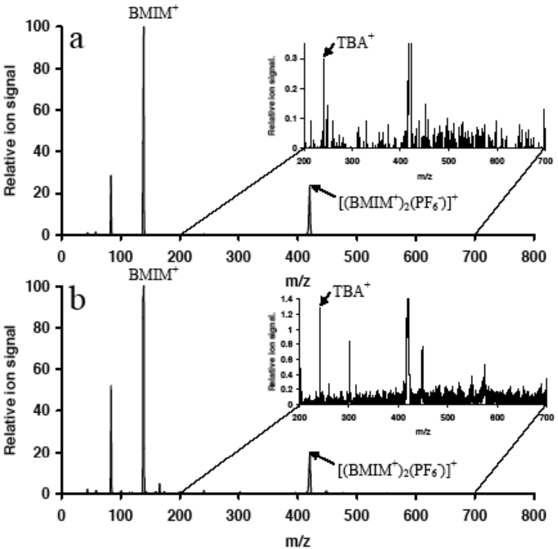


Fig.1 ES mass spectrum of BMIM-PF$_6$ containing 2 x 10^{-4} M TBAI, a) matrix electrosprayed without dissolution, b) RTIL matrix dissolved to 2 x 10^{-4} in methanolic solution.

Significant Achievements *Electrospray of Undiluted Ionic Liquids*. Figure 1 shows a mass spectrum obtained from an undiluted and unpurified sample of BMIM-PF$_6$ containing 4 x 10^{-4} M tetrabutylammonium iodide (TBAI). Clearly evident is the BMIM$^+$ cation signal at m/z 139 and the trimolecular cluster [(BMIM)$_2$PF$_6$]$^+$ at m/z 424. Figure 1(b) shows the same sample dissolved to 2 x 10^{-4} M BMIM-PF$_6$ in the methanolic solution (final concentration of TBA$^+$ ≈ 1 x 10^{-7} M). In general, the two spectra show the same major ions in similar relative abundance; absolute ion signals were also similar. Closer inspection of the baseline of the two spectra, shown in the insets, reveals interesting differences. The spectrum for the undissolved RTIL displays considerably less chemical noise and shows the TBA^+ peak at ~0.3% of the base peak height, whereas the baseline for the dissolved RTIL shows significant ion signal at nearly every mass and a TBA^+ peak at 1.3 % of the base peak height. In this example, dissolution of the RTIL matrix provides better absolute signal response for the dissolved "impurity" ions at the expense of higher background noise. Calculation of the signal-to-noise ratio for the two methods (dilution versus no dilution) gave very similar results.

ES of Mixed RTILS. Our initial investigations towards analyzing mixtures of undiluted RTILs using ES-MS generated gas-phase ion signals that were not always representative of the condensed-phase molar ratios. These observations could provide insight into the molecular binding properties of each cation and anion in the mixture and could provide a combinatorial-like approach to determining the properties of future ionic liquids.

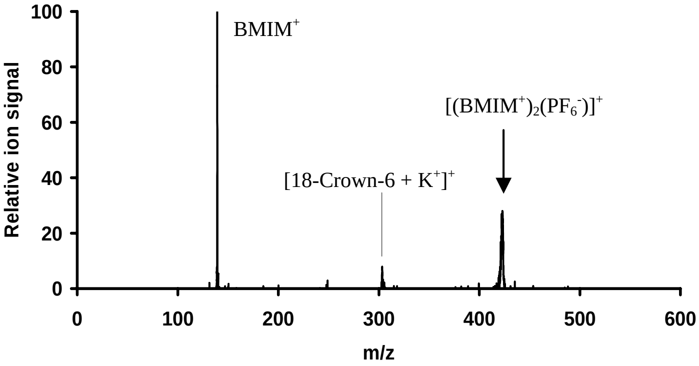


Fig. 2 ES-MS spectrum of undiluted BMIM-PF_6 containing 18-Crown-6. Potassium is present as an impurity in this experiment and was not deliberately added.

ES of Dissolved Crown Ether Complexes. We have been able to identify ionic 'impurities' deliberately added at ~10^{-4} M concentrations and crown-ether/metal ion complexes dissolved at ~10^{-3} M concentrations. Figure 2 provides an example of the ability to detect a crown ether/metal ion complex from undiluted ES-MS of an ionic liquid. The ability to detect extractant/metal ion complexes dissolved in the ionic liquid could greatly facilitate the development of more efficient extractants that could be used to decontaminate liquid waste at DOE sites.

ES Analysis of Back-Extracted RTIL. In liquid-liquid extractions of aqueous solutions using RTILs, some RTIL undesirably back-extracts into the aqueous phase. ES-MS has been applied successfully to the determination of $BMIM^+$ in the aqueous phase using PMIM-Tf_2N as an internal standard. The aqueous phase saturated with 1.5×10^{-2} M $BMIM^+$, in agreement with UV-VIS absorption measurements.

Plans for future research on this project. Research plans in the coming year include:

(1) Analytical Characterization. Studies will assess the analytical potential of ES-MS for neat RTILs, dissolved species (e.g., crown ethers, calixarenes, catalysts, metal ions), and solvent impurities (e.g., water). *(2) Mechanistic studies of molecular ion formation in the undiluted RTIL ES process.* Understanding the ES ionization process involving undiluted RTILs, including electrochemical charge compensation considerations, will assist in the optimization and extension of this analytical approach. RTILs have very unique properties that may provide new insight into the ES process. For example, RTILs have

little vapor pressure, so that small droplets formed in the electrospray plume cannot desolvate *via* evaporative means as conventional solvents do. *(3) Comparison of Gas- and Condensed-Phase Composition.* Investigations will compare the observed relative gas-phase and condensed-phase abundances. Present results show that the cation-anion binding affinity, which affects melting temperature and viscosity in the condensed phase, seems to correlate strongly with clustering tendencies observed in the mass spectra. Judicious selection of ionic liquid mixtures of known properties will be used to study the relationship between condensed-phase molar ratios and gas-phase ion ratios under a variety of electrospray conditions. *(4) Analyte Signal Enhancement.* Future studies will also address the ability to study minor constituents dissolved in RTIL phases and how these signals can be preferentially enhanced over the RTIL matrix ions. One method to be investigated is to use zwitterionic compounds as the matrix solvent. The medium would consist of sum-neutral-charge molecules with separate positively and negatively charged moieties within each molecule. Neutral compounds such as this, which do not readily accept protons in solution, are known to be 'invisible' to ES-MS. Thus, the use of zwitterions as the ionic liquid solvent could suppress ion signal from the matrix so that charged ions dissolved within this matrix would dominate the spectra.

Publications Acknowledging DOE Support – 2002-3

1. Glen P. Jackson and Douglas C. Duckworth "Electrospray Mass Spectrometry Of Undiluted Ionic Liquids", *Chemical Communications,* **2004,** DOI:10.1039/B314754A
2. G. P. Jackson, , D. C. Duckworth, J. K. Gibson, "Gas-Phase Reactions of Bare and Ligated Uranium With Sulfur Hexafluorides and Water", *J. Phys. Chem. A.*, in press.
3. G. P. Jackson, F. L. King, D. C. Duckworth, "Efficient Polyatomic Interference Reduction in Plasma-Source Mass Spectrometry Via Collision Induced Dissociation," *J. Anal. At. Spectrom.*, 18 (2003) 1026 – 1032.
4. G. P. Jackson, R. G. Haire, D. C. Duckworth, "A New Glow Discharge Source with Enhanced Ion Extraction for Small Non-Conductive Samples and Atmospheric Sampling," *J. Anal. Atom. Spectrosc.*, 18(6) (2003) 665-669.
5. G. P. Jackson, J. K. Gibson, D. C. Duckworth, "Gas-Phase Reactions of Bare and Oxo-Ligated Actinide and Lanthanide Cations with Pentamethylcyclopentadiene in a Quadrupole Ion Trap Mass Spectrometer," *Int. J. Mass Spectrom.* 220 (2002) 419-441.
6. G. P. Jackson, F. L. King, D. E. Goeringer, D. C. Duckworth, "Gas-Phase Reactions of U^+ and U^{2+} with O_2 and H_2O in a Quadrupole Ion Trap," *J. Phys. Chem. A.* 106 (2002) 7788-7794.
7. G. P. Jackson, F. L. King, D. E. Goeringer, D. C. Duckworth, "Collision-Induced Dissociation of Lanthanide Oxide Ions In Quadrupole Ion Traps: Effects of Bond Strength and Mass," *Int. J. Mass Spectrom.* 216 (2002) 85-93.

Electrostatic and Electrochemical Processes in Electrospray*

Gary J. Van Berkel, PI
Keiji G. Asano, ORNL Research Staff
Vilmos Kertesz, and Michael J. Ford, ORNL Postdoctoral Research Associates
Michael C. Granger , Electrochemist, ESA, Inc (Chelmsford, MD)
Chemical Sciences Division
Oak Ridge National Laboratory
P.O. Box 2008/Bldg 4500S
Oak Ridge, TN 37831-6131
*This effort is part of Field Work Proposal ERKCC42: Sampling, Ionization, and Energy Transfer Phenomena in Mass Spectrometry

Overall Research Goals. Advances in ionization sources, particularly those advances providing the ability to ionize new classes of compounds or produce new types of ions, lead to major revolutions in the applications of mass spectrometry (MS). This central role of ionization in furthering mass spectrometry is the reason that within the scope of our program we have several different but often interrelated ionization investigations ongoing. We discuss here just those ionization studies that deal with electrostatics and electrochemistry of electrospray (ES) ionization. The occurrence of electrochemical reactions at the emitter electrode of the ES ion source, as normally configured in ES-MS, is required for the device to sustain the production of charged droplets and gas-phase ions. These electrochemical reactions alter the composition of the solution electrosprayed. As such, the electrolytic processes can and do influence the nature and distribution of the ions observed in the ES mass spectrum under certain analysis scenarios. We have shown through numerous publications that the electrolytic reactions in the emitter can involve the emitter itself, solvent species and additives, or the analytes of interest. Our goal is to understand and then utilize this electrochemical process for analytical benefit in ES-MS.

Specific Objectives for 2003-2004. (1) Design and test a floated three electrode ES emitter cell that enables “dial-in” control of the electrochemical reactions in an ES emitter. (2) Use the floated emitter cell to better study the electrochemical processes in the ES ion source and exploit this understanding for analytical benefit in the application if ES-MS.

Significant Achievements.

Electrochemical Processes Inherent in Electrospray - Floated Three Electrode Emitter Cell. We have been able to gain our most control to date over the inherent electrochemistry occurring at the emitter electrode of an ES ion source by incorporating a three-electrode controlled-potential electrochemical cell into the controlled-current ES emitter circuit. Two different basic cell designs were investigated to accomplish this control, viz., a planar flow-by working electrode and porous flow-through working electrode design, each operated with a potentiostat floated at the ES high voltage Figure 1. The indole alkaloid reserpine, which is often used to test the specifications of ES-MS instrumentation, was used as a model compound. With the proper cell counter electrode configuration and adjustment of the working electrode potential, it was found that reserpine oxidation could be “turned off” at flow rates as low as 2.5 µL/min as well as at flow rates as high as 30 - 40 µL/min. Just as important, it was also possible to “turn on” essentially 100% oxidation of reserpine in this flow rate range. The results presented show that the geometry of the counter electrode along with parameters that might affect mass transport of analytes to this electrode are critical in controlling the electrochemical reactions in the emitter cell. With this new tool in place we can now investigate a varied suite of analytes to

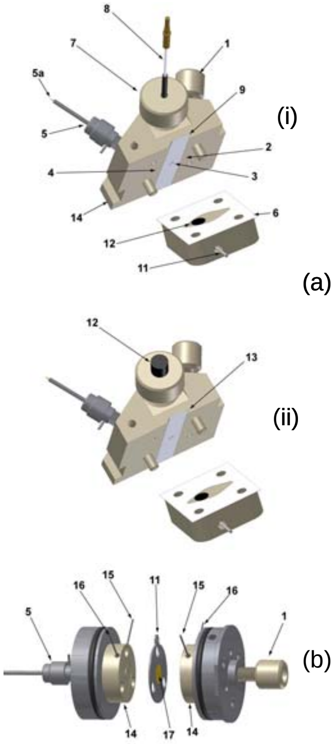


Figure 1. Flow cell schematics of (a) a planar flow-by electrode cell employing (i) Ag/AgCl reference electrode or (ii) a Pt quasi-reference electrode, and (b) a porous flow-through electrode cell.

assess the ability to enhance their ES –MS response or avoid detrimental consequences to the analysis brought about by the electrochemiatry.,

<u>Plans for Future research on this project.</u> Other than the three electrode emitter cell, we will continue to study new single and dual electrode emitter designs.

Porous Flow-through Electrode Electrospray Emitter. Our work has shown that progression from a simple tubular electrode emitter to a planar, flow-by electrode geometry increases the efficiency of hetereogenous redox reactions of the analytes. We expect that a porous flow through design for the emitter electrode might have a more dramatic effect on analyte electrolysis efficiency as the flow rate through the system is increased. However, purely on the basis of calculated surface-to-volume ratio, neither our planar emitter electrode designs or the flow-through electrode arrangement would appear to be better that the other. This assumes of course that the total physical area of the electrodes can be utilized for a particular reaction. This is not a certainty because the ES system is a controlled current device and the interfacial potentials at the electrode are known to decrease in an exponential fashion from the spray side of the electrode back upstream.

One practical goal of this fundamental investigation is to demonstrate an electrode emitter geometry that provides 100% electrolysis efficiency at solution flow rates of 40-50 µL/min thereby allowing coupling of the emitter system with microbore chromatography. These flow rates are needed so that the dead volumes from the bore-throughs, etc. in the device does not cause band broadening. Operation with lower flow rates would require more complicated machining processes or expensive and less versatile microfabricated devices.

Coupled with microbore chromatography,such a system can be used to enhance analyte signals from species not particularly amenable to ES-MS analysis. ES-MS is most successfully used for the analysis of analytes that are either ionic in solution or that are readily ionized in solution by manipulation of solution chemistry (e.g., pH). We will start our investigations with separations and ionization of our ferrocene-tagged natural products and expand to other neutral compounds like nickel and vanadyl porphyrins, which we have studied extensively in our BES funded program. These neutral compounds are important in petroleum prospecting and play a role in catalyst poisoning during petroleum refining. We will also investigate the reduction in negative ion mode ES of simple primary alcohols and aldehydes (not typically amenable to ES-MS) to ES-active carboxylic acids. The electrochemical processes in negative ion mode ES have not been investigated to any extent.

Planar Flow-By Electrode Capacitive Electrospray Ion Source. We recently patented the concept of a planar flow-by electrode capacitive ES ion source. Using a capacitor effect, we conceive that this device will be able to separate ions in a liquid solution passing through it into two separate streams of liquid, one enriched in positively charged ions and the other enriched in negatively charged ions. The charged solutions will exit the device through narrow channels that are positioned opposite suitably biased electrodes. As the solutions exit the channels they each generate a charged droplet spray plume of the same polarity as that of the excess ions in the respective solutions. The charged droplets produced will give rise to gas-phase ions and these ions are transported to the inlet region of another device, such as a mass spectrometer, for analysis. Compared to normal ES ion sources, this source will provide for higher ionization efficiencies, because of the high degree of charge separation obtained, resulting in enhanced detection levels in ES-MS. A normal ES ion source operates at no better than about 50% separation. Maximum gas-phase ion production will occur when positive and negative ions are completely separated. In addition, this device should generate charged spray plumes without the need for a high voltage electrode. Also, this device provides a means to generate and analyze gas-phase ions of opposite polarity from the same sample simultaneously.

We will build the first prototype of this device and begin to explore the operational parameters to reach the potential of the device. Some of the initial questions to address both theoretically and operationally include: What is the proper combination of channel width, channel length and electrode length and material? What should be the cycle time of the capacitor charge/discharge cycle and how will this vary with solution flow rate? What is the best shape for the spacing gasket at the outlet end of the channel/electrode length? Would multiple units in series increase the charge separation efficiency?

Publications Acknowledging DOE Support – 2002-3.

1. Van Berkel, G. J.; Asano, K. G.; Granger, M. C. "Controlling Analyte Electrochemistry in an Electrospray Ion Source with a Three Electrode Emitter Cell," *Anal. Chem.*, in press.
2. Van Berkel G. J.; Llave, J. J.; Apadoca, M. F.; Ford, M. J. "Rotation Planar Chromatography Coupled On-Line with Atmospheric Pressure Chemical Ionization Mass Spectrometry," *Anal. Chem.* in press.
3. Van Berkel, G. J. "An Overview of Some Recent Developments in Ionization Methods for Mass Spectrometry," *Eur. J. Mass Spectrom.*, 9, 539-562 (2003).
4. Van Berkel G.J.; Asano, K. G.; Kertesz, V. "Enhanced Study and Control of Analyte Oxidation in Electrospray Using a Planar-Electrode Emitter," *Anal. Chem.*, **74**, 5047-5056 (2002).
5. Ketesz, V.; Deng, H.; Asano, K. G.; Hettich, R. L.; Van Berkel, G. J; "*N*-Phenyl-1,4-Phenylenediamine and Benzidine Oxidation Products Identified Using On-Line Electrochemistry/Electrospray Fourier Transform Mass Spectrometry," *Electroanalysis*, **14**, 1027-1030 (2002).
6. Kertesz, V.; Van Berkel, G. J. "Surface-Assisted Reduction of Aniline Oligomers, "*N*-Phenyl-1,4-Phenylenediamine and Thionin in Atmospheric Pressure Chemical Ionization and Atmospheric Pressure Photoionization," *J. Am. Soc Mass Spectrom.*, **13**, 109-117 (2002).
7. Kertesz, V.; Dunn, N. M.; Van Berkel, G. J. "Electrochemistry/Electrospray Mass Spectrometry Study of Cesium Uptake in Nickel Hexacyanoferrate Films," *Electrochimica Acta*, **47**, 1035-1042 (2002).
8. Van Berkel, G.J.; Asano, K.G.; Kertesz, V. "Enhanced Study and Control of Analyte Oxidation in Electrospray Using a Planar-Electrode Emitter," Anal. Chem., 74, 5047-5056 (2002).

Surface Ionization Mass Spectrometry

James E. Delmore, PI
A. D. Appelhans, J. E. Olson, K. B. Johnson
Department of Chemistry
Idaho National Engineering and Environmental Laboratory
Idaho Falls, Idaho 83415-2208
Jed2@inel.gov, ada2@inel.gov, olsje@inel.gov, johnkb2@inel.gov

Overall Research goals: Surface ionization has been known and used since the 1920's, and while the more simple processes have been understood for many years, the vast majority of surface ionization processes that are not at all understood. Early representations of surface ionization were as a Saha-Langmuir process, which is a highly simplistic representation of the thermodynamics and is extremely naive for all but a few very simple instances. In reality, the vast majority of ionization processes occurring on a hot filament are driven to a great extent by chemistry, as well as by the thermodynamics. This program has been working to gain insights into these chemistry issues so as to be able to improve and expand applications. Most of these applications have been split between isotope geochronology, nuclear science and engineering, environmental monitoring and national security. The goal of this program is to be able to gain sufficient understandings of the more important of these ionization processes so as to be able to improve and expand the applications.

Specific Objectives for 2003-2004: Our specific objectives for this time frame pertain to understanding and improving thermal ionization processes for three elements that have long lived isotopes that will be major factors in determining the ability to license long term geologic storage of the by-products of nuclear power. The isotopes of interest are ^{99}Tc (2.13E5 half life), ^{129}I (17E6 half life) and ^{135}Cs (2.3E6 half life). None of these isotopes are very practical to measure by radiochemistry due to weak emissions and long half lives. All are practical to measure by mass spectrometry, although mass spectral interferences limit applicability of ICP-MS. Thermal ionization is viable for each of these elements but is in need of significant improvements. There are two activities that are underway and one that is planned for this time frame. The first is a miniaturized version of a multiple filament assembly that concentrates ion production much closer to the ion optic center of the mass spectrometer. The second activity underway is development of understanding of Cs ionization from zeolites for applicability to measuring Cs 133/135/137 ratios. The third activity, which will start later in the year, is research into ionization of Tc as the pertechnate ion. There is an older analytical technique for Tc that is highly trouble prone. Since we have already made major strides in understanding perrhenate ionization mechanisms (see below about our chemically reactive ion emitter studies), we will conduct research into pertechnate ionization to determine if the mechanisms are the same, and if not, what are the differences. If Tc can be made into a chemically reactive ion emitter similar to how we have succeeded with perrhenate, this should allow development of a robust analytical method.

Significant Achievements:

Current studies: Iodine: Preliminary studies indicate that the negative ion signal from iodine is increased approximately five fold with the miniaturized dual filament assembly over the signal obtained by the traditional triple filament technique. This is thought to be due to more efficient reflection of iodine onto the ionizing filament, as well as to keeping ion production in close proximity to the ion optic center of the mass spectrometer. This technology is not restricted to iodine, and should be applicable to any element that is thermally ionized using existing double and triple filament ion sources.

Cesium: When Cs is ionized from the appropriate zeolite rather than from a refractory metal filament, the ionization temperature is reduced from 1550°C to 900°C. On the other hand, ionization of the major traditional interference for Cs, Ba, is totally suppressed to levels well below E-9 as measured on our dual detector triple sector mass spectrometer. The hydrocarbon background is also suppressed to E-9 levels. This technique is close to the point where it can be used for environmental surveillance programs. When ICP/MS is applied to Cs measurements at these extreme ratios, Ba is always detectable at some level, illustrating the need to selectively ionize Cs and not Ba. Zeolites accomplish this level of discrimination.

Studies completed in the past 12 months: Chemically reactive ion emitters: We have pioneered chemically reactive ion emitters with development of a new design perrhenate ion emitter. We have demonstrated that an ongoing solid state chemical reaction, taking place under high vacuum, can produce hundreds of nanoamperes of perrhenate ion current for hundreds of hours. An important feature of these emitters is the requirement to develop a chemical system that produces and stabilizes the species on the surface of the emitter in the same ionic form in which it is to be emitted. This is the first literature reference that we are aware of where such a chemically reactive ion emitter produces a useful intensity ion beam. This works so well that it is already being used in several ion guns for SIMS studies. It also opens possibilities for explosive ion emitters, where an explosive type chemical reaction is used to produce high intensity ion beams for brief periods.

Molten glass ion emitters: We have demonstrated that the old “silica gel” technique for producing ions from a variety of elements that have high ionization potentials is really nothing more than a technique for producing a molten glass with the element to be ionized dissolved in the glass. This has always been an “artsy” technique that either worked or did not work, with little understanding of the fundamentals. Now that there is a basic understanding of the technique, it is possible to both de-bug existing applications and to develop new types of molten glass matrices. This work has been ongoing for several years and was completed this past year.

Plans for future work: Identification of chemically reactive ion emitters with high current outputs opens a number of potential opportunities. It is improbable that the perrhenate ion emitter we have developed is the only possibility. Since rhenium and technetium have such similar chemistries, we plan to pursue the possibility of producing Tc ion beams by a similar technique for analytical applications. Several other possible systems are under consideration, starting with tri- and tetroxide metal species. We are also conceptualizing possible explosive ion emission processes and are considering several systems, but are not yet at the point of proposing actual experiments. The concept starts with a mixture on a solid surface that is highly reactive at elevated temperatures, but nominally stable at a preparatory temperature that is not below the maximum temperature at which the material might possibly be exposed up to the point of detonation. When the ion beam is needed, the emitter is flash heated at a very rapid rate to produce a highly intense but short lived ion beam. There are a number of possible applications of such devices if the science can be developed to the point where they can be adequately controlled.

A computer model of a radically new magnet geometry for a sector mass spectrometer has been developed that offers a large increase in dispersion between masses. We plan to construct a miniaturized version of this instrument analyzing Li (masses 6 and 7) to demonstrate the concept. This design has been extensively modeled in full 3D, and we have found no flaws up to this point. If this instrument concept proves valid, and all indications are that it is, it could become the predominant instrument design for isotope ratio measurements within several years.

Publications Acknowledging DOE/BES Support, 2002-2003

1. K. D. Johnson, J. E. Delmore and A. D. Appelhans, “High intensity perrhenate anion (ReO_4^-) emitters,” International journal of mass spectrometry, 229 (2003) 157-166
2. J. E. Delmore, G. F. Kessinger, D. A. Dahl and J. E. Olson, “High temperature Langmuir vaporization mass spectrometer, ”International journal of mass spectrometry, 225 (2003) 1-10
3. G. F. Kessinger and J. E. Delmore, “High temperature chemistry of molten glass ion emitters,” International journal of mass spectrometry, 213 (2002) 63-80

Ion Motion and Ion Excitation in the Quadrupole Ion Trap Mass Spectrometer: Simulation and Experiment

R. Graham Cooks, PI
Robert J. Noll, research scientist
Zoltan Takats, post-doctoral research associate
Lianming Wu, Sergio Nanita, Wolfgang Plass, Brandy Young, graduate research assistants
Chemistry Department, Purdue University, 560 Oval Drive, West Lafayette, IN 47906
cooks@purdue.edu, http://www.chem.purdue.edu/cooks

Overall research goals

Detailed understanding of trapped ion motion—employing both simulations and experiments—is sought in order to improve ion trap mass spectrometer performance and develop new applications. Fundamental understanding of ion thermochemistry and ion/molecule reactivity and its application, especially in the further development of the kinetic method. Extension of the scope of mass spectrometry to the quantitative analysis of mixtures of chiral compounds using the kinetic method; understanding of the basis of this convenient, simple new method. Extension of the kinetic method to quantitative analysis of mixtures of other isomers. Characterization of energy transfer in inelastic collisions, including collisions of ions with surfaces as well as gas phase collisions; this process underpins ion activation itself a central aspect of modern mass spectrometry. Characterization of heavy atom kinetic isotope effects in halogenated compounds of relevance to ozone chemistry. Clusters of amino acids, especially the octamer of serine, including its reactivity and structure and its possible role in early earth processes that led to homochiral living organisms.

Specific objectives for 2003-2004

1. Kinetic method: a) Examination of the possibility of using alkali-metal bound dimeric clusters in chiral and isotopic analysis. b) Fundamental studies on the origin of non-linearity in kinetic method plots. c) Relative stability of hetero/homo Ca^{+2} bound sugar dimers.
2. Isotope effects: explanation of the large, inverse heavy atom isotope effect observed in $CHCl_4^-$ and related ions.
3. Serine: Generation of the serine octamer at atmospheric pressure as part of an overall attempt to study the chemistry of this system outside the mass spectrometer.
4. Ion trap simulations: a) Extension of the multiparticle simulation program ITSIM to allow fields of arbitrary symmetry to be characterized and ion motion (and mass spectra) to be simulated. b) Full incorporation of inelastic collisions and fragmentation processes into the ITSIM suite of programs.

Significant Achievements

Quantitative Chiral Analysis and Resolution of Isomers by the Kinetic Method

Quantitative determination of enantiomeric excess (ee) is of growing importance in drug development and searches for extraterrestrial homochirality. Mass spectrometry is providing a new, simple method of performing this experiment via the kinetic method. The method is based on the competitive dissociation of singly-charged transition metal-cluster ions, $M(ref)_2(A)^+$ (M = transition metal, ref = reference ligand, A= A_S or A_R, the chiral analyte) in an ion trap mass spectrometer, to yield either $M(ref)(A)^+$ or $M(ref)_2^+$. Recorded by tandem mass spectrometry, the logarithm of the fragment ion abundance ratio $(M(ref)(A_R)/(M(ref)_2) / (M(ref)(A_S)/M(ref)_2)$, is linear with ee. Analytes include amino acids, α-hydroxy acids, nucleosides, sugars, amino alcohols, and oxazolidinones. In newer work, only one multidentate reference ligand is used to form the metal ion complex, simplifying dissociation kinetics so that only the reference ligand or the analyte can be lost. Metal-ligand and ligand-ligand interactions in these complexes are easier to optimize. Hence, improved chiral recognition can be more readily obtained. Several types of chiral compounds have shown improved chiral selectivity and quantification accuracy.

The approach has also been extended to multiple analytes (amino acids) in mixtures, in which the minor enantiomer is only a few percent. For the systems chosen, %ee's could be measured down to less than 2% ee with relative errors of 3.0% ~ 7%. This novel mass spectrometric method shows great promise for chiral mixture analysis without chromatographic separation. It also has potential importance in extra-terrestrial searches for life based on the connection of life with homochirality.

Ternary mixtures have also been successfully studied, by using two 3-point calibration curves. Applicable to higher mixtures of optical isomers, it may allow rapid and accurate chiral quantification of multiple chiral-center drugs and their metabolites. As increasing numbers of synthetic peptides are developed for pharmaceutical applications, it becomes of interest to apply the kinetic method to the resolution of positional (e.g., GGA vs. GAG) and isobaric (GGL vs. GGI) peptides. Different divalent transition metal ions, including Ca(II) and Fe(II), have been used as the central metal ions to achieve isomeric distinction and quantification.

Serine Cluster Ions and Homochirogenesis

A unique feature of the amino acid serine is its ability to form a stable octamer with strong preference for homochirality. Serine octamer might have been involved in mechanisms that led to the origin of homochirality; the exclusive existence of L-amino acids and D-sugars in living systems. A novel ion source based on sonic spray ionization, SSI, (an ionization method milder than ESI) was built. It employs a simple pneumatic spray operated at extremely high nebulizing gas flow rates, showing an order of magnitude better signal intensity than ESI and excellent signal-to-noise ratios. Under SSI conditions, >99% of the signal corresponds to ions of type $(Ser_8H_n)^{+n}$. Mixtures of different amino acids with serine yield chirally dependent incorporation of cysteine, threonine, phenylanine, asparagine and tyrosine in the homochiral serine octamer.

We, as well as others, have suggested several structures for the serine octamer, based on tandem mass spectrometry, ion mobility measurements, and quantum mechanical calculations. Recently we reported experimental hydrogen/deuterium (H/D) exchange data which demonstrate the existence of two different conformations of serine octamers. The conformers, which undergo H/D exchange at significantly different rates, can be differentiated easily by mass analysis. Sonic spray ionization has been coupled to a hybrid ion mobility time-of-flight mass spectrometer and used to study serine clusters as part of an ongoing collaboration with the research group of Prof. D. E. Clemmer at Indiana University. The joint work has already lead to the discovery of very large (nanometer scale) serine clusters as well as the formation of chirally-enriched serine octamers; the latter could potentially have played a role in accumulating an excess of the L-serine enantiomer during homochirogenesis.

Chiral enrichment

Recent studies have uncovered the ability of serine to form chirally-enriched octamers from non-racemic solutions, even in the absence of any other chiral reagent. Moreover, the dissociation of chirally-enriched octamers regenerates monomeric serine with chiral composition skewed in the opposite sense compared to the enantiomeric composition of the original solution.

The results suggest a prebiotic scenario where octamers of both chiralities might have coexisted, their abundances being drastically influenced by slight changes in the enantiomeric composition. Disruption of such a delicate equilibrium may have accumulated L-serine as part of a cascade of events leading to the exclusive existence of L-serine in living systems.

Chiral transmission to sugars and other compounds

Mixtures of serine and simple sugars in solution were analyzed by SSI-MS, uncovering the selective formation of the magic number cluster $(\mathrm{Serine}_6+\mathrm{Glucose}_3+\mathrm{Na})^+$. There is a strong preference for the formation of those cluster ions that contain L-serine and D-glucose (and vice versa) over LL or DD combinations. The homochiral serine octamer also reacts uniquely with other species of biochemical importance, forming magic number clusters with glyceraldehyde (simplest C_3 sugar), phosphoric acid, and transition metal ions. We believe that the favored L-serine/D-glucose clusters might have been involved in the transmission of chirality from an initial chiral molecule (serine) to the sugars just as chiral transmission from serine to other amino acids by substitution in the serine octamer has been previously suggested. A possible scenario involves serine separating into homochiral octamers (and higher clusters) in concentrated aqueous solutions; the serine octamer might serve in turn as a site for essential prebiotic reactions, including the binding of C_3 sugars and their dimerization.

Heavy atom secondary isotope effects

A recently discovered heavy-atom intramolecular kinetic isotope effect (KIE) in the unimolecular decomposition of chloroform/Cl^- adducts into chloride ions and chloroform neutrals is of immense interest due to the inverse (<< 1) nature atypical of isotope effects and the unprecedented magnitude (0.026). A triple-quadrupole mass spectrometer was used to mass-select, collisionally activate, and mass-analyze fragments, thus allowing measurement of a KIE from the relative abundances. The KIE was measured for $HC^{35}Cl_3{}^{37}Cl^-$ and compared to that of the individual isotopomers ($DC^{35}Cl_3{}^{37}Cl^-$, $DC^{35}Cl_2{}^{37}Cl_2^-$, $HC^{35}Cl_2{}^{37}Cl_2^-$) and the net KIE (i.e. the KIE resulting from the dissociation of all isotopomers).

ITSIM: Ion Simulations

The ITSIM program, written in this laboratory, allows multi-particle simulations of ions in ion trap mass spectrometers. The main goal is to improve ion trap performance and develop new types of ion trap instruments. The ability to compute fields of any arbitrary shape will allow the extension of the method to ion traps and arrays of traps of new geometry, including the orbitrap mass analyzer and linear quadrupole.

Plans for future research

Extension of the quantitative method of chiral analysis is planned especially to a broader selection of analytes and sample types, and new combinations of metal ions and reference ligands. We plan to examine closely the small non-linearities in some of the kinetic method data and to connect this to dissociation kinetics. Studies of homochirogenesis, especially with regard to serine octamer and transmission of chirality to other classes of biochemically relevant compounds will emphasize the chemistry of the octamer outside the mass spectrometer and the characterization of the second isomer recently observed. Efforts to broaden the scope and applicability of ITSIM, including alternate ion trap geometries of arbitrary symmetry, and full modeling of internal energy distribution upon inelastic collision, will also be undertaken.

Publications Acknowledging DOE Support, 2002-2003

[1] Li, H.; Plass, W. R.; Patterson, G. E.; Cooks, R. G. Chemical Mass Shifts in Resonance Ejection Experiments in the Quadrupole Ion Trap; *J. Mass Spectrom.* **2002,** *37*, 1051-1058.

[2] Plass, W. R.; Li, H.; Cooks, R. G. Theory, Measurement and Application of Chemical Mass Shifts in RF Quadrupole Ion Traps; *Int. J. Mass Spectrom.* **2003,** *228*, 237-267.

[3] Augusti, R.; Zheng, X.; Turowski, M.; Cooks, R. G. Kinetic Isotope and Collision Energy Effects in the Dissociation of Chloride and Bromide Adducts of Aliphatic Alcohols, Benzaldehyde and 2,4-Pentanedione; *Aust. J. Chem.* **2003,** *56*, 429 -436.

[4] Wu, L.; Denault, J. W.; Cooks, R. G.; Drahos, L.; Vekey, K. Alkali chloride cluster ion dissociation examined by the kinetic method: heterolytic bond dissociation energies, effective temperatures, and entropic effects; *J. Am. Soc. Mass Spectrom.* **2002,** *13*, 1388-1395.

[5] Tao, W. A.; Clark, R. L.; Cooks, R. G. Quotient Ratio Method for Quantitative Enantiomeric Determination by Mass Spectrometry; *Anal. Chem.* **2002,** *74*, 3783-3789.

[6] Tao, W. A.; 31A, R. G. C. A.-. Chiral Analysis by Mass Spectrometry; *Anal. Chem.* **2003,** *75*, 25A - 31A.

[7] Zheng, X.; Augusti, R.; Tao, W. A.; Cooks, R. G. In *Encyclopedia of Mass Spectrometry*; Gross, M., Caprioli, R., Eds.; Jonh Wiley and Sons: Chichester, England, **2002;** Vol. 5, Chemistry and Physics of Gaseous Ions (ed. P.B. Armentrout).

[8] Wu, L.; Tao, W. A.; Cooks, R. G. Ligand and Metal Ion Effects in Metal Ion Clusters Used for Chiral Analysis of alpha-Hydroxy Acids by the Kinetic Method; *Anal. and Bioanal. Chem.* **2002,** *373*, 618-627.

[9] Augusti, D. V.; Carazza, F.; Augusti, R.; Tao, W. A.; Cooks, R. G. Quantitative Chiral Analysis of Sugars by Electrospray Ionization Tandem Mass Spectrometry Using Modified Amino Acids as Chiral Reference Compounds; *Anal. Chem.* **2002,** *74*, 3458-3462.

[10] Wu, L.; Tao, W. A.; Cooks, R. G. Kinetic Method for Simultaneous Chiral Analysis of Different Amino Acids in Mixtures; *J. Mass Spectrom.* **2003,** *38*, 386-393.

[11] Wu, L.; Clark, R. L.; Cooks, R. G. Chiral Quantification of D-, L-, and meso-Tartaric Acid Mixtures Using a Mass Spectrometric Kinetic Method; *Chem. Commun.* **2003,** *137*, 136-137.

[12] Wu, L.; Cooks, R. G. Chiral Analysis Using the Kinetic Method with Optimized Fixed Ligands: Application to Oxazolidinone Antibiotics; *Anal. Chem.* **2003,** *75*, 678-684.

[13] Wu, L.; Lemr, K.; Aggerholm, T.; Cooks, R. G. Recognition and Quantification of Binary and Ternary Mixtures of Isomeric Peptides by the Kinetic Method: Metal Ion and Ligand Effects on the Dissociation of Metal-Bound Complexes; *J. Am. Soc. Mass Spectrom.* **2003,** *14*, 152-160.

[14] Takats, Z.; Nanita, S. C.; Schlosser, G.; Vekey, K.; Cooks, R. G. Amino Acid Clusters Formed by Sonic Spray Ionization; *Anal. Chem.* **2003,** *75*, 1514-1523.

[15] Takats, Z.; Nanita, S. C.; Schlosser, G.; Vekey, K.; Cooks, R. G. Atmospheric Pressure Gas-Phase H/D Exchange of Serine Octamers; *Anal. Chem.* **2003,** *75*, 6147 - 6154.

[16] Myung, S.; Julian, R. R.; Nanita, S. C.; Cooks, R. G.; Clemmer, D. E. Formation of Nanometer Scale Serine Clusters by Sonic Spray; *J. Phys. Chem.* Submitted.

[17] Nanita, S. C.; Takats, Z.; Myung, S.; Clemmer, D. E.; Cooks, R. G. Chiral Enrichment of Serine via Formation and Dissociation of Octameric Cluster Ions; *Angew. Chem. Int. Ed.* submitted.

[18] Takats, Z.; Nanita, S. C.; Cooks, R. G. Serine octamer reactions: indicators of prebiotic relevance; *Angew. Chem. Int. Ed.* **2003,** *42*, 3521-3523.

2004 DOE/BES Analysis Program
Contractors' Meeting

Abstracts
Session 5

Oriented Polymer Nanostructures: New insights into intramolecular structure and photophysics of conducting polymers

Michael D. Barnes, Sub-Task PI
Adosh Mehta, Postdoctoral Research Associate
Chemical Sciences Division, MS-6142 Oak Ridge National Laboratory
Oak Ridge, TN 37831-6142
Pradeep Kumar, Graduate Research Assistant
Department of Chemistry
University of Tennessee, Knoxville, TN 37996-1600
e-mail: barnesmd1@ornl.gov

Overall research goals. The objective of this program is to advance the state of the art of high sensitivity and/or high specificity laser-based chemical measurements to further our understanding of chemical systems in confined geometries. These laser techniques are applicable to a broad range of fundamental chemical measurement problems in fields encompassing environmental monitoring, process control, materials analysis, and biotechnology. The general research theme emphasizes optical probes of microdomains and interfaces with specific focus on nonlinear optical processes at planar interfaces, and effects of molecular confinement on enhancement of fluorescence properties for ultrasensitive detection.

Specific objectives for 2002-2003. The growing interest in nanoscale species in the role of fluorescent reporters or markers has fueled enormous effort in the study of new materials and methodologies for ultrasensitive imaging and photonics-based information processing applications. However, in these and related applications contexts, there are important fundamental scientific questions related to effects of confinement and intermolecular interactions on photophysical properties of the fluorophore. In our group, we have focused on questions of molecular confinement on length scales ranging from a few nanometers to several micrometers to explore ways in which photophysical properties of fluorescent species can be controlled or modified to enhance their functionality in a chemical analysis context. Our specific objective was to use microdroplets as a materials processing technique for polymeric systems where the effect of three-dimensional confinement leads to interesting nanoscale and microscale structures.

Significant Achievements. In conventional solvent-cast thin films, conjugated polymers may assume a broad range of configurations which give rise to significant heterogeneity in photophysical properties. Our goal was to explore effects of 3-D confinement on the structural and photophysical properties of single molecules of conjugated polymers using microdroplet techniques combined with novel optical imaging and scanning probe techniques. Our experiments combine atomic force microscopy and high-resolution fluorescence imaging to probe the morphology and orientation of MEH-PPV (poly[2-methoxy-5-(2’-ethyl-hexyloxy)-1,4-phenylene vinylene]) nanoparticles formed from

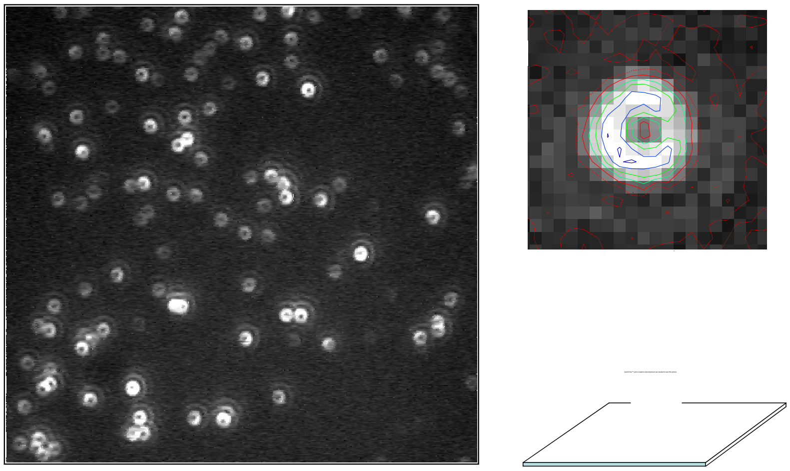


Figure 1. Fluorescence of single MEH-PPV molecules isolated from microdroplets excited using an intraobjective (1.4 N.A. 100x) total internal reflection (TIR) geometry. The top-right panel shows a close-up of a selected emission pattern from the z-oriented sample superimposed with a simulated image from classical electrodynamics. Bottom right shows a structural simulation consistent with dipole orientation and polarization anisotropy measurements.

micrometer -sized liquid droplets of dilute solution. We used ink-jet printing methods to isolate single conducting polymer chains in microdroplets of solution - typically less than 5-µm initial diameter that evaporate en route to the coverglass substrate. The MEH-PPV used in our experiments was obtained commercially (H. W. Sands Corp. OPA9576). Figure 2 shows a high-resolution fluorescence image (each pixel corresponds to ≈30 nm real-space distance) from isolated single MEH-PPV molecules. The toroidal spatial intensity patterns we observe derive from the fact that emission is forbidden at angles along the optical axis for z-orientation of the transition dipole, resulting in the central intensity node for each nanoparticle fluorescence image. Since the transition moment for poly (phenylene vinylenes) is nearly collinear with the conjugation axis, the observation of uniform z-orientation implies a high degree of intramolecular organization, a conclusion supported by polarization anisotropy measurements.

In addition to the novel orientation, these species have significantly enhanced spectral and photophysical properties relative to the same kinds of molecules in solvent-cast thin films. Figure 2 (top) shows a typical fluorescence signal vs. time from an individual CN-PPV nanoparticle under modest illumination intensity. Note that the abscissa scale is in hours; a typical single-molecule fluorescence transient from a thin film sample persists for less than a minute under similar conditions. We also observe considerable spectral narrowing (10 – 15 nm fwhm) as well as a significant red shift (≈ 0.2 eV relative to peak emission in the bulk) that is also attributed to a high degree of intramolecular order.

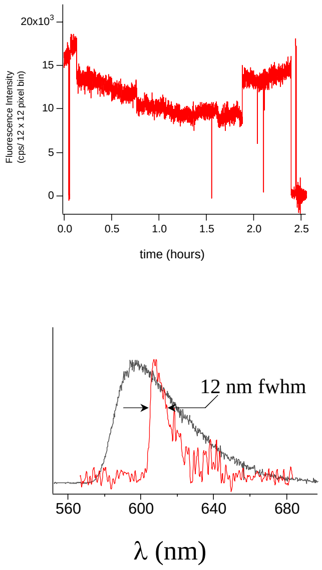


Figure 2. Top: Typical fluorescence signal as a function of time from a single z-oriented CN-PPV nanostructure under ≈ 1 kW//cm^2 illumination intensity at 514.5 nm. Bottom: Comparison of emission spectra from bulk CN-PPV (gray) and z-oriented nanostructure (red).

Plans for future research on this project. There are interesting questions regarding numbers of oriented structures and symmetries on the coherent radiation from such a system. How does the interaction between 2 (or more particles depend on interparticle distance and configuration (linear or folded symmetries, for example)? How is the interaction manifested in terms of spectral or time-domain properties? Such questions were considered theoretically by Dicke 50 years ago and lie at the heart of nanoscale photonic information processing schemes using these kinds of materials. We will use a combination of time-resolved photon correlation, pump-probe, and single-molecule spectroscopy methods to answer these questions. We can use polymer nanostructure samples that have a random distribution of particle separations to search for interesting multi-particle geometries at small (≤ 1 transition wavelength) spacings. Alternatively, we will explore methods to actively "write" particle configurations using nanoparticle manipulation methods.

Publications Acknowledging DOE Support – 2002-3

B. G. Sumpter, D. W. Noid, and M. D. Barnes, "Recent Developments in the formation, characterization, and simulation of micron and nanoscale droplets of amorphous polymer blends and semi-crystalline polymers," *Polymer* **44**, 4389-4403 (2003). [Feature Article]

A. Mehta, P. Kumar, M. Dadmun, J. Zheng, R. M. Dickson, T. Thundat, B. G. Sumpter, and M. D. Barnes, "Oriented cylindrical nanostructures of a semiconducting polymer: Polarization evidence for highly ordered individual macromolecular st,ructures" *Nanoletters* **3**(5), 603-607 (2003).

P. Kumar, A. Mehta, M. Dadmun, J. Zheng, L. Peyser, R. M. Dickson, T. Thundat, B. G. Sumpter, and M. D. Barnes, "Observation of narrow-bandwith spontaneous luminescence from oriented conjugated polymer nanostructures," *J. Phys. Che,m.* B **107**, 6252-6257 (2003). [Letter to the Editor]

A. Mehta, T. Thundat, V. Chhabra, R. Bhargava, A. P. Bartko, R. M. Dickson, and M. D. Barnes, "Size-correlated imaging and spectroscopy of rare-earth doped nanocrystals," *Applied Optics* **42**, 2132-2139 (2003).

M. D. Barnes, K. Runge S. M. Mahurin, A. Mehta, B. Hathorn, B. G. Sumpter, and D. W. Noid, "Photonic Molecules: New Challenges in Materials and Optics for Manipulating Photons at Micron Length Scales," *Materials Today* (invited) **5**, 15 (2002)

A. Bartko, L. Peyser, R. M. Dickson, A. Mehta, R. N. Bhargava, and M. D. Barnes, "Observation of dipolar emission patterns from isolated Eu^{3+}:Y_2O_3 nanocrystals," *Chemical Physics Letters* **358** (5-6): 459-465 (2002).

S. Mahurin, A. Mehta, B. Hathorn, K. Runge, B. G. Sumpter, D. W. Noid, and M. D. Barnes, "Photonic polymers: A new class of photonic wire structure from intersecting polymer-blend microspheres," *Optics Letters* **7** (8): 610-612 (2002).

B. Hathorn, B. G. Sumpter, D. W. Noid, M.D. Barnes "Molecular Dynamics Simulations of Nanoparticle Collisions: Internal Reorganization and Translation-vibration coupling", *Macromolecules* **35**, 1102 (2002).

B. Hathorn, B. G. Sumpter, D. W. Noid, M.D. Barnes, "Molecular dynamics simulation of collinear polymer nanoparticle collisions: Reaction and scattering", *J. Phys. Chem. B*. **105**, 11468 (2002).

B. Hathorn, B. G. Sumpter, D. W. Noid, M.D. Barnes "Molecular Dynamics Simulation of Nanoparticle Collisions: Orbital Angular Momentum Effects", *Polymer* **43**, 615 (2002).

M. D. Barnes, S. Mahurin, A. Mehta, B. G. Sumpter, and D. W. Noid, "Three-dimensional photonic molecules from sequentially linked polymer-blend microspheres," *Physical Review Letters*, **88** (1): art. no. 015508 (2002).

Triple Resonance Ionization: From Ultra-trace Isotope Analysis to High Precision Spectroscopy

Bruce A. Bushaw, PI
Chemical Sciences Division
Pacific Northwest National Laboratory
P.O. Box 999, MS K3-58
Richland, WA 99352
bruce.bushaw@pnl.gov

Collaborators. K. Wendt and A. Schmidt, *University of Mainz,* W. Nörtershäuser, *GSI-Darmstadt,* K. Blaum, *CERN-Geneva,* G. W. F. Drake, *University of Windsor,* L. Pibida, *NIST-Gaithersburg,* F. Roughead, *USDA-Grand Forks*

Overall research goals. This program investigates laser-induced ionization spectroscopy with emphasis upon simultaneously obtaining high selectivity and high sensitivity, as is needed for detection and investigation of ultra-rare isotopes that often occur at levels $<10^{-10}$ with respect to their more abundant neighbors. Measurement of such isotopes has a wide range of applications, e.g., monitoring trace radioisotopes in the environment and remediation processes, signature isotopes as indicators of specific nuclear processes, low-dose medical isotope tracers, and fundamental studies in atomic and nuclear physics. This project uses excitation with cw single-frequency lasers to avoid duty cycle limitations that occur when pulsed lasers are coupled with continuous atomization sources. The high resolution also provides optical isotopic selectivity and laser linewidth ≤ atomic resonance width maximizes efficiency and signal-to-background. Recent emphasis has been on developing triple-resonance ionization mass spectrometry methods for ultra-trace analysis. Examples are measurement the long-lived radioisotope ^{41}Ca with detection limits in the low attogram range and abundance sensitivity (relative to the major stable isotope ^{40}Ca) approaching 10^{-13} [1], and triple-resonance autoionization of Gadolinium [2], which has been applied to quantification of the MRI contrast enhancement agent Gd-DTPA in spatially correlated cancerous tissue samples [3]. In developing the spectroscopic bases for these analytical methods, it has been found that high-precision coordinated control of multiple single-frequency lasers can make significant contributions to fundamental studies of atomic electronic and nuclear structure. Such studies can then be used to improve and optimize analytical approaches.

Specific Objectives for 2003-2004. (1) Measure and understand high-resolution spectra of rare earth elements near their ionization limits, including bound Rydberg levels and autoionization levels. This is continuing work for Gadolinium and complementary studies on Samarium were initiated. The objective is to understand observed narrow autoionizing levels that can lead to saturated photoionization with low-power cw lasers. (2) Improve laser control systems for precision spectroscopic measurements and greater reliability in analytical application. (3) Demonstrate improved spectroscopic precision with measurements of 2S-3S transition energies, hyperfine structure, and isotope shifts in Lithium and compare results with recent theoretical calculations. (4) Precise measurement of the ionization energy of ^{7}Li. This uses the capability for precise long-range scanning and is another important test for recent theoretical work, for which existing experimental values are too imprecise.

Significant Achievements

Accurate determination of rare earth ionization potentials. High resolution spectra of bound Rydberg series of Gadolinium were obtained using triple-resonance excitation followed by drifted *rf*-field ionization. Resolution was sufficient to resolve and assign complex fine structure. Limit analysis for three different series, which included corrections for weak perturbations yielded a ^{160}Gd ionization limit of 49601.5142(8) cm^{-1}[4]. This is more than a two order of magnitude improvement over previous values. Further, combining this with other derived spectroscopic constants allows calculation of the 112 analyzed Rydberg level energies with average accuracy of 2x10^{-4} cm^{-1}. Similar results were recently obtained for ^{154}Sm, improving the ionization energy accuracy by nearly 4 orders of magnitude.

Autoionization of Gadolinium. Understanding the bound Rydberg series of Gd (above) allowed assignment of autoionizing series converging to the first excited state of the ion. From these, other 'interloping' resonances were separated and examined in detail with lineshape (lifetime), isotope shift, and hyperfine structure studies. Resonances previously shown capable of saturated cw photoionization were assigned as arising from mixing between different $J = 7$ autoionizing Rydberg series converging to the first and second excited states of the ion [2]. It is expected that similar structures and saturable resonances can be found for other elements that have ground-level fine structure.

Hyperfine structure and isotope shifts in the 2S-3S two photon excitation of ^{6,7}Li. Measurements of isotope shifts and hyperfine structure in the 2*S*-2*P* and 2*S*-3*S* transitions of Lithium [5], have improved precision of some of the atomic parameters by up to 3 orders of magnitude, resolved discrepancies in several existing measurements, and serve as a stringent test for accuracy of recent theoretical calculations in Hylleraas coordinates that include relativistic and higher-order QED corrections. These measurements, and the comparison with theory, serve as a baseline test for current efforts at accelerator-online mass separator facilities to measure the nuclear charge distribution of the short-lived ^{8,9,11}Li radioisotopes.

Ionization potential of ^{7}Li. In addition to the energies of the 2*P* and 3*S* states of lithium, the ionization energy is a fundamental property obtained from the theoretical calculations; however, existing experimental values trace back to classical atomic emission measurements made in the 1940's with uncertainty more than an order of magnitude larger than the recent theoretical work. Thus, the triple-resonance Rydberg excitation and convergence analysis developed for Gd and Sm has also been applied to ^{7}Li and the principal ^{2}P series has been observed out to $n > 300$ (Fig.1). Convergence

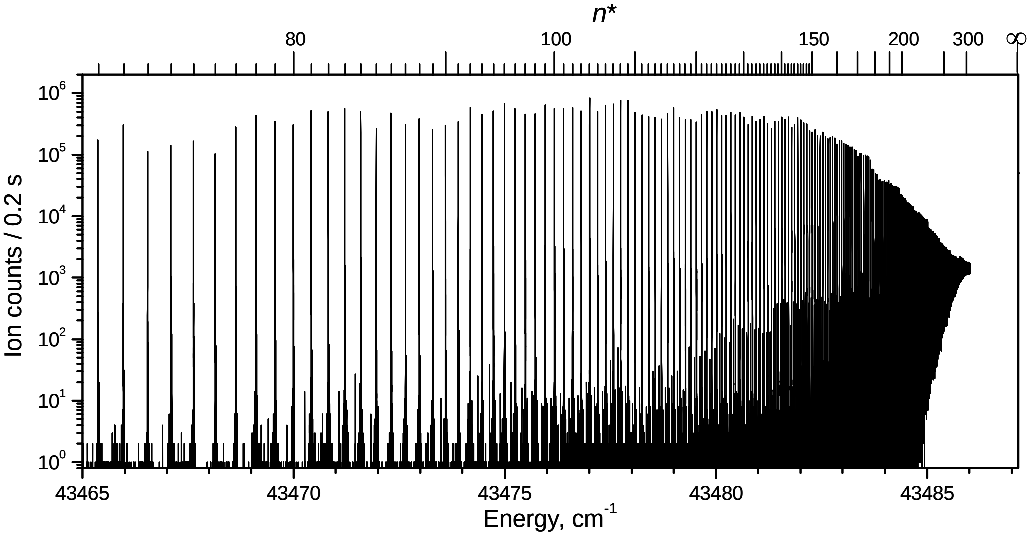


Fig. 1. $1s^2np\ ^2P$ Rydberg spectrum of ^{7}Li obtained by triple-resonance excitation with single-frequency lasers and drifted *rf*-field ionization.

analysis determines the ionization energy with an accuracy of 2×10^{-4} cm^{-1}, which is now somewhat better than theory. The remaining discrepancy between experiment and theory of ~0.001 cm^{-1} is currently being evaluated in terms of QED corrections of order α^4.

Plans for future research

(1) Spectroscopic studies of electronic structure of atoms near the ionization limit. This work will continue with samarium, which has a wide range of stable isotopes and several long-lived radionuclides of interest. Accurate measurements of the isotope shift of the ionization energy is needed for accurate prediction/optimization of shifts and selectivity in Rydberg and autoionizing levels, and are also of fundamental interest. (2) *Demonstrate detection of ^{41}Ca used as biomedical tracer isotope*. Triple-resonance detection methodology developed under this program will be tested for measurement of ^{41}Ca used as a long-term tracer in human biokinetic studies. Work will be done in collaboration with the USDA's Grand Forks Human Nutrition Laboratory, and will evaluate required preparation chemistry, reproducibility, and sensitivity for measuring ^{41}Ca in urine samples. (3) *Investigate triple-resonance ionization for determination of Uranium isotopes*. This work will be done in collaboration the University of Mainz and will concentrate on optimizing the detection of ^{236}U, which can be an important signature of nuclear activity, but cannot be adequately detected at trace levels by radiochemical methods because of long half-life ($t_{1/2} = 2.3 \times 10^7$ y) or by direct mass spectrometry because of interference from ^{235}UH$^+$.

Publications Acknowledging DOE Support

1. B. A. Bushaw, W. Nörtershäuser, P. Müller, and K. Wendt, "Diode-laser-based resonance ionization mass spectrometry of the long-lived radionuclide ^{41}Ca with $< 10^{-12}$ abundance sensitivity", *J. Radioanal. Nucl. Chem.* **247**, 351-356 (2001).
2. B. A. Bushaw, W. Nörtershäuser, K. Blaum and K. Wendt, 2003. "Studies of narrow autoionizing resonances in gadolinium", *Spectrochim. Acta B* **58**, 1083-1095 (2003).
3. K. Blaum, C. Geppert, W. G. Schreiber, J. Hengstler, P. Müller, W. Nörtershäuser, K. Wendt, and B. A. Bushaw, "Trace determination of gadolinium in biomedical samples by diode-laser-based multi-step resonance ionization mass spectrometry", *Anal. Bioanal. Chem.* **372**, 759-765 (2002).
4. B. A. Bushaw, K. Blaum, and W. Nörtershäuser, "Determination of the ^{160}Gd ionization energy", *Phys. Rev. A* **67**, 022508 (2003).
5. B. A. Bushaw, W. Nörtershäuser, G. Ewald, A. Dax and G. W. F. Drake, "Hyperfine Splitting, Isotope Shift, and Level Energy of the 3*S* States of ^{6,7}Li", *Phys. Rev. Lett.* 91, 043004 (2003).

Vibrational Spectroscopy of Chromatographic Stationary Phases

Jeanne E. Pemberton, PI
Christopher J. Orendorff, Zhaohui Liao, Piotr Macech, Graduate Research Assistants
Department of Chemistry
University of Arizona
1306 East University Boulevard
Tucson, AZ 85721
pembertn@u.arizona.edu
http://www.chem.arizona.edu/profile/profile.php?fid_call=pemb

Overall Research Goals: Chromatographic separations play a central role in Department of Energy (DOE)-supported fundamental research related to energy, biological systems, the environment, and nuclear science. This research has as its goal the development of an understanding of the molecular basis of retention in reversed-phase liquid chromatography (RPLC) and the fabrication of new stationary phase materials with tailorable retention characteristics based on this understanding. Raman spectroscopy figures prominently in our efforts to understand the molecular basis of retention in RPLC due to its exquisite sensitivity to subtle changes in rotational and conformational order of alkyl-containing systems.

Specific Goals for 2002-2003: Specific objectives for this phase of the research were: 1) correlation of the spectroscopic response of two high-density octadecylsilane (C18) stationary phases, TFC18SF and MFC18 (stationary phases provided by our collaborator, Dr. Lane C. Sander at NIST), with surface coverages of ~6.5 and 3.5 μmol m^{-2}, respectively, with their chromatographic performance, 2) development of alkylsilane-modified silica substrates suitable for emersion spectroscopy in order to investigate the interfacial mobile phase structure relevant to chromatography, and 3) fabrication and characterization of new, tailorable, high-density stationary phases showing shape selectivity using an organically-modified sol-gel approach. Advances in each of these three areas were realized and are described briefly below.

Significant Achievements:

Correlation of Surface Raman Spectroscopy with Chromatographic Performance of C18 Stationary Phases. Studies completed during the past year include the first attempt to correlate the chromatographic performance of stationary phase materials with molecular structural information about conformational and rotational order of the stationary phase alkylsilane. These combined chromatographic and spectral data offer unique insight into retention mechanisms for a series of solutes separated on a high-density stationary phase (TFC18SF, surface coverage ~6.5 μmol m^{-2}) and a low-density stationary phase (MFC18, surface coverage ~3.2 μmol m^{-2}). Studies were performed on a series of weakly retained aromatic solutes including toluene, anisole and aniline using 100% methanol, 75:25 methanol:water and 50:50 methanol:water mobile phases. For these weakly retained solutes, *k*' values are smaller and H values are larger on TFC18SF relative to MFC18. Smaller values of *k*' (i.e. poorer solute retention) are a result of fewer interaction sites available and limited free volume within the high surface coverage stationary phase. Similarly, larger H values result from free volume restrictions within the phase where solute mobility is hindered by nearly crystalline alkyl chains of TFC18SF as compared to the more liquid-like alkyl chains of MFC18. Spectral data provide structural information for these stationary phases under chromatographic conditions; these data have been used to ascertain molecular interaction information for these systems.

Solute interactions with TFC18SF are somewhat different than with MFC18, in general, because of the high density of alkyl chains on TFC18SF, restricting significant analyte partitioning. However, intercalation or partitioning of solutes into the distal ends of the alkyl chains is believed to occur from subtle rotational disorder imparted to these phases for aniline and anisole solutes in methanol/water mobile phases. While this view of partitioning is different from the idea of cavity formation deep within alkyl chains, it is a more partitioning-like interaction than a classical adsorption or solvophobic interaction.

Results from these Raman spectroscopic and chromatographic studies lend credence to the view that solute/stationary phase interactions occur predominantly at the stationary phase/mobile phase interface and support the idea of solute partitioning as a retention mechanism in which the stationary phase is actively involved in a manner that depends on the free volume of the stationary phase. However, partitioning in these systems is very subtle and these data suggest that, even for hydrophobic solutes on low coverage phases, intercalation does not take place into deep cavities formed within the alkyl chains.

Silica Substrates for Emersion Spectroscopy. Substantial progress has been made in developing a suitable platform for external reflection-based emersion spectroscopies on ultrathin silica films formed by sol-gel methods on Au. (Emersion refers to the process of first establishing the structure of a solid-liquid interface by immersing the substrate into the appropriate solution followed by careful removal or emersion of that intact interface from the bulk solution for bulk-solution-free vibrational spectroscopic probing.) Adhesion and wetting control functions are facilitated on Au surfaces through electrochemical fabrication of a hydrous Au oxide layer onto which an ultrathin silica layer is spin-coated as shown by the schematic in Figure 1. After cleaning the Au surface, a uniform layer of Au_2O_3 (~3 ML thick) is grown on the Au by application of a potential greater than ~1.2 V (vs SCE) in acidic media. This layer is hydrated if grown for a sufficient time and provides a suitable substrate for ultrathin silica deposition. In combination, the hydrous Au oxide and silica layers are sufficiently thin (total film thickness as thin as ~4-10 nm) that the underlying Au substrate is still accessible to the incident radiation, thereby allowing reflection based spectroscopic methods to be used.

Ellipsometry experiments on the emersion of these thin silica films from pure water have been completed and emersed water layers ranging from ~5-9 nm have been observed. Past work on the emersion of SAM-modified metals from water results in layers ranging in thickness from ~0.3 nm for hydrophobic $-CH_3$-terminated SAMs to ~2.5 nm for hydrophilic –COOH-terminated SAMs. This success now makes possible the study of interfacial solvent structure at alkylsilane-modified silica surfaces relevant in RPLC.

Fabrication of Shape-Selective Stationary Phases using a Modified Sol-Gel Approach. A new approach to the fabrication of RPLC stationary phase materials has been successfully developed that allows creation of stationary phases of variable surface coverage based on a single reaction scheme. Phases were characterized by various analytical techniques to determine their physical properties. The presence of a solution modifier in a conventional organically-modified sol-gel preparation results in useful chromatographic supports of varying bonding densities that can be controlled using only one set of relatively simple reaction conditions. All phases were prepared without special pretreatment or purification of reagents or silica substrates under ambient conditions. Phases fabricated from C18 precursors give stationary phase materials with surface coverages that are similar to those of commercially-available C18 columns (~3-4 μmol m^{-2}). The chromatographic performance of the phases prepared by this route exhibit separation efficiencies also comparable to those of commercially available C18 phases for a series of substituted aromatic solutes. High surface coverage phases exhibit a high degree of shape selectivity in solute retention, analogous to phases of comparable surface coverage prepared by conventional routes.

Plans for Future Research on This Project: During the next year, each of the efforts described above will be advanced through the steps described below. Additional stationary phases will be investigated in order to further our molecular understanding of the relationship between stationary phase structure and solute retention. Specifically, a series of docosylsilane (C22) stationary phases are targets as are C18 stationary phases on fluorescence-free silica supports that will allow access to other spectral regions containing other vibrational modes. Emersion vibrational spectroscopy experiments on a series of C18-modified ultrathin silica films will be undertaken to define mobile phase structure at the alkylsilane interface. Finally, further elaboration of our new stationary phase fabrication approach involving organically-modified sol-gels in the presence of solution modifiers will be performed. Specifically, the role of the nature of the solution modifier will be investigated.

Publications Acknowledging DOE Support

1. M.W. Ducey, C.J. Orendorff, J.E. Pemberton, L.C. Sander, *Anal. Chem.*, 2002, 74, 5576-5584. “Structure-Function Relationships in High-Density Octadecylsilane Stationary Phases by Raman Spectroscopy: 1. Effects of Temperature, Surface Coverage and Preparation Procedure.”
2. M.W. Ducey, C.J. Orendorff, J.E. Pemberton, L.C. Sander, *Anal. Chem.*, 2002, 74, 5585-5592. “Structure-Function Relationships in High-Density Octadecylsilane Stationary Phases by Raman Spectroscopy: 2. Effects of Common Mobile Phase Solvents.”
3. C.J. Orendorff, M.W. Ducey, J.E. Pemberton, L.C. Sander, *Anal. Chem.*, 2003, 75, 3360-3368. “Structure-Function Relationships in High-Density Octadecylsilane Stationary Phases by Raman Spectroscopy. 3. Effects of Highly Ordering Solvents.”
4. C.J. Orendorff, M.W. Ducey, J.E. Pemberton, L.C. Sander, *Anal. Chem.*, 2003, 75, 3369-3375. “Structure-Function Relationships in High-Density Octadecylsilane Stationary Phases by Raman Spectroscopy. 4. Effects of Model Aromatic Solutes and Bases.”
5. C.J. Orendorff, M.W. Ducey, J.E. Pemberton, *J. Phys. Chem. A*, 2002, 106, 6991-6998. “Quantitative Correlation of Raman Spectral Indicators in Determining Conformational Order in Alkyl Chains.”
6. C.J. Orendorff, J.E. Pemberton, L.C. Sander, *Anal. Chem.*, to be submitted. “Solute, Solvent, and Stationary Phase Interactions of Reversed-Phase Liquid Chromatographic Systems Determined by Raman Spectroscopy.”
7. C.J. Orendorff, J.E. Pemberton, *Anal. Chem.*, to be submitted. “Alkylsilane-Based Stationary Phases via Controlled Solution-Modifier Techniques: Synthetic Approach, Characterization, and Chromatographic Performance.”

Characterization of Intermediates by Attenuated Total Reflectance Infrared Spectroscopy

Edward M. Eyring, PI
Brian C. Dunn, David Sommerfeld, Hua Huang, Postdoctoral Research Associates
Jonathan R. Marda, Ben Lai, Keri Fairbanks, Linda Quintero, Christine Fuentes, Undergraduate Research Assistants
Department of Chemistry
University of Utah
315 S 1400 E
Salt Lake City, UT 84112
eyring@chem.utah.edu

Overall Research Goals. The ability to directly observe intermediates during the course of a chemical reaction is an important step in illuminating reaction mechanisms. Traditionally, reaction rate investigations have relied heavily on detection of reactants, products, and intermediates using light in the ultraviolet (200-400 nm) or visible (400-800 nm) spectral regions. These regions provide little information about the chemical structure of intermediates. The mid-infrared spectral region (400 – 4000 cm^{-1}) can provide structural and bonding information, but it is not as easily adaptable to reaction rate measurements in solution. Previous attempts by other research groups to couple stopped-flow mixing with infrared detection have relied on thin-layer transmission cells for spectroscopic observation. Unfortunately, the thin-layer cells restrict the flow of solution and severely limit the minimum time required for the reaction mixture to flow through the system. The goal of this research is to design, construct, and test a stopped-flow system which uses Attenuated Total Reflectance (ATR) rather than transmission in order to eliminate the restriction in flow and maintain the short pathlength necessary for IR observation in aqueous solutions. After further refinement, the stopped-flow ATR system will be used to investigate a variety of chemical reactions in aqueous solution.

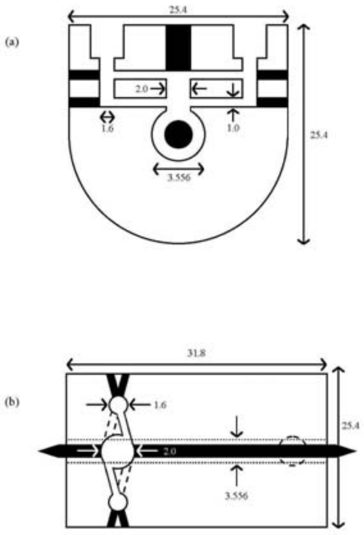


Fig. 1. (a) Horizontal cross-section of tangential mixing chamber. (b) Vertical cross-section showing tangential nature of flow channels

Specific Objectives for 2003-2004. Our objectives for this project are: to create a system capable of rapid mixing of two aqueous solution followed by observation of time-resolved mid-IR spectra in as short a time as possible; to evaluate the flow performance of the system; to test the system with a known rapid chemical reaction; to use the system to investigate the reactivity of hypervalent iron.

Significant Achievements. An ATR cell was constructed from Kel-F which included an integral tangential mixer. Figure 1 shows two cross-sections of the device. The ATR element is shown as the central feature in both drawings and the reacting solution flows around the element. The optical pathlength and flow cross-section are decoupled in this method. The optical pathlength is determined by the indices of refraction of the solution and the ATR element while the flow cross-section is determined by the distance from the ATR element to the inner wall of the flow channel. This design offers significant advantages over previous designs which use a thin-layer optical cell: (1) with a large flow cross-section, the flow can be significantly faster; (2) very little backpressure is induced during the flow pulse, therefore, inexpensive, off-the-shelf components can be used in the flow system; (3) there is no risk of damaging the optics during disassembly for cleaning; (4) the optical pathlength is sufficiently short to allow observation of the entire mid-IR spectrum including spectral regions near large water absorption peaks.

The flow performance of the system was evaluated by rapidly mixing methanol and water while simultaneously collecting mid-IR spectra. The IR spectrometer was configured to collect one complete spectrum (4000 to 800 cm^{-1}) every 30 ms. The time-resolved spectra (not shown) indicate that five spectra were collected during the mixing-filling process which corresponds to a 150 ms dead time. The simple modification of increasing the diameter of the flow channel would allow for a decrease in the dead time. However, this would cause an increase in the amount of reactant solution required per experiment.

The ability of the system to collect data during a chemical reaction was evaluated with a known chemical reaction: the basic hydrolysis of methylchloroacetate (MCA). A 0.10 M MCA solution was mixed with a 0.10 M NaOH solution, and spectra were collected every 50 ms. Figure 2 shows the result of this evaluation. Spectral data acquisition was initiated simultaneous with initiation of the flow, so the initial four spectra were recorded during the flow. Absorption peaks from MCA can be easily distinguished prior to reaction due to their constant height. After the flow is stopped, the reaction proceeds and the absorption peaks from MCA at 1744 cm^{-1} (C=O stretch), 1217 cm^{-1} (symmetric C-O-C stretch), and 1331 cm^{-1} (asymmetric C-O-C stretch) can be seen to decrease as a function of time while peaks from the reaction product at 1591 cm^{-1} (asymmetric O-C-O stretch) and 1397 cm^{-1} (symmetric O-C-O stretch) can be seen to increase as a function of time. These data demonstrate the applicability of the newly constructed system for observation of reactions in aqueous solution. While no reaction intermediates are observed in the test reaction, the data clearly indicate that short-lived species could be detected if they exist in sufficient concentration.

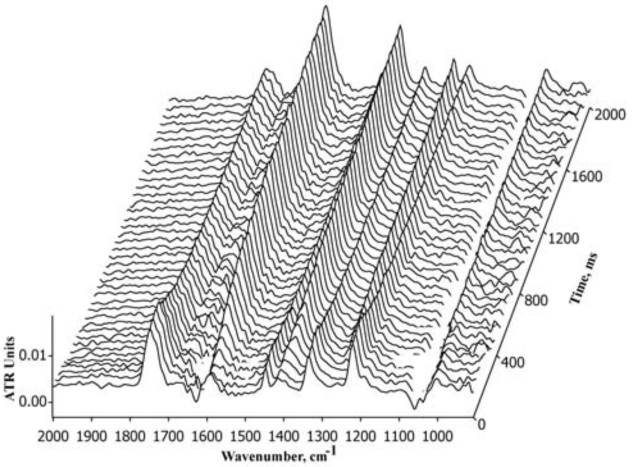


Fig. 2. Time-resolved IR spectra collected during the basic hydrolysis of methylchloroacetate. The first four spectra were collected during flow. The remaining spectra were collected after cessation of flow.

Most recently, the stopped-flow apparatus has been used to investigate the reaction between aqueous sulfite and acetone. Published reports indicate that the reaction proceeds via two parallel paths: one path with SO_3^{2-} reacting with acetone and the other path with HSO_3^- reacting with acetone. The results from one experiment appear in Fig. 3 in which 0.25 M acetone was reacting with 0.25 M total sulfite at pH 4.75. Our time-resolved IR data collected as a function of pH support the two parallel paths mechanism. In addition, the absorption peak at 1700 cm^{-1} due to the C=O bond in acetone was observed to decrease as a function of reaction time. This clearly indicates that the C=O bond is broken during the reaction. The change in the bonding around the central S atom in the SO_3^{2-} ion can be seen as the formation of new peaks at 1203 cm^{-1} and 1029 cm^{-1}.

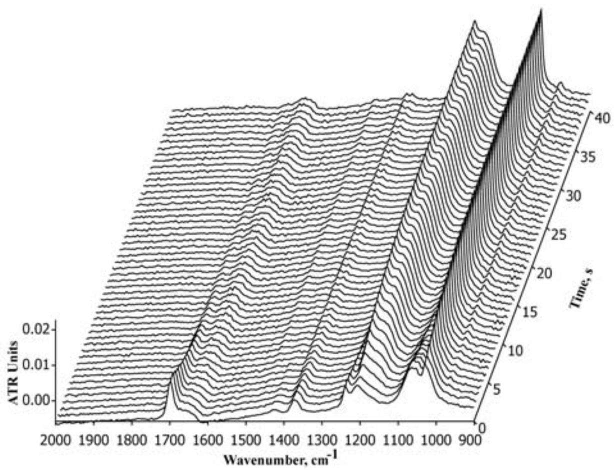


Fig. 3. Time-resolved IR spectra collected during the reaction of acetone and sulfite. The decrease in the peak at 1700 cm^{-1} indicates that the C=O bond of acetone is broken during the reaction. New peaks at 1203 cm^{-1} and 1029 cm^{-1} are attributed to the reaction product.

<u>Plans for future research</u>. Previous research from our group indicates the presence of a stable intermediate during the oxidation of phenol by Fe(VI). The intermediate has been detected using the stopped-flow mixing technique coupled with visible light detection. However, no structural information is available with visible spectroscopy. Using stopped-flow mixing with mid-IR light detection should allow for the observation of the intermediate and the IR spectral information should aid in identifying the intermediate. However, previous attempts at observing the oxidation of phenol by FeO_4^{2-} have been unsuccessful due to solubility limitations. As an alternative, it should be possible to simulate oxidation by FeO_4^{2-} using the oxidation by hydrogen peroxide catalyzed by Fe^{3+}. The structure of the oxidants are similar, and the reaction mechanisms are likely to be nearly identical.

<u>Publications Acknowledging DOE Support</u>.

1. B. C. Dunn, J. R. Marda, and E. M. Eyring, "Stopped-flow FT-IR Spectroscopy of Aqueous Solutions using Attenuated Total Reflectance," *Applied Spectroscopy*, **2002**, *56*, 751-755.
2. H. Huang, D. Sommerfeld, B. C. Dunn, C. R. Lloyd, and E. M. Eyring, "Ferrate(VI) Oxidation of Aniline," *Journal of the Chemical Society, Dalton Transactions*, **2001**, 1301-1305.
3. H. Huang, D. Sommerfeld, B. C. Dunn, E. M. Eyring, and C. R. Lloyd, "Ferrate(VI) Oxidation of Aqueous Phenol: Kinetics and Mechanism," *Journal of Physical Chemistry A*, **2001**, *105*, 3536-3541.

Abstract S5-5

Quantification of Interparticles Forces and Aggregation of Nanoparticles

Janos H. Fendler, PI
Department of Chemistry and Center for Advanced Materials Processing
Clarkson University
Potsdam, NY 13699-5814
fendler@clarkson.edu
http://www.clarkson.edu/~janoslab

Overall research goals. An understanding of the forces responsible for the adsorption and aggregation of particles is essential for the rational construction of nanostructured energy converting devices and sensors. Our overall research goal is to obtain such an understanding by a systematic investigation of the adsorption behavior of monodispersed carboxylated latex particles in aqueous electrolytes by different experimental techniques and to rationalize the obtained results by existing and new theories.

Specific objectives for 2003-2004. Our objectives are: (1) To develop infrared ellipsometry, both in the external and in the internal reflection modes, and use it to obtain values for the optical constants of the adsorbed particles. This will provide a direct means for assessing the thickness of the adsorbed layer of particles. Subsequently, we hope to perform ellipsometry concurrently with FTIR adsorption measurement, in real time, during the sedimentation. (2) To extend the adsorption measurements to different substrate surfaces and to different electrolytes. (3) Critically compare the results obtained by FTIR determination of the adsorption, with those obtained by studying the aggregation rate of particle dimers with time resolved stopped-flow simultaneous static and dynamic light scattering.

Significant Achievements

Unified treatment for reflection and absorption techniques for the characterization of adsorbed nanoparticles. We have derived a concise and unified treatment, in terms of a relatively simple multilayer model, for transmission localized surface plasmon resonance spectroscopy, T-LSPR; propagating surface plasmon resonance spectroscopy, P-SPR; polarization selective Fourier transform infrared reflection absorption spectroscopy, PS-FTIRRAS; polarization modulation Fourier transform infrared reflection absorption spectroscopy, PM-FTIRRAS; surface enhanced infrared reflection absorption spectroscopy, SEIRRAS and infrared ellipsometry (Figure 1). The model multilayer system for our discussion is shown in Figure 2. The sample consists of N parallel plate layers, where $,_j$ and d_j are the complex dielectric function and thickness of layer *j*, respectively. The first and the last layers are semi-infinite media. Light of polarization γ (γ = s or p) is incident from medium 1 at an angle $\mathbf{2}_1$ at the 1-2 interface. The system coordinates are described using a Cartesian system, where the z-axis is pointed along the direction of light transmission, and the plane of incidence is the xz plane. Any given layer *j* starts at the coordinate $z = z_{j-1}$, and ends at $z = z_j$, so that $d_j = (z_j - z_{j-1})$. The angle of the propagating light with respect to the z-axis in the jth layer is $\mathbf{2}_j$. The optical signal of the multilayer structure can be detected in the reflection geometry or in the transmission geometry. If layer 1 is optically denser than layer N, and if $\mathbf{2}_1$ is larger than the critical angle for total reflection, we have the situation corresponding to attenuated total reflection, ATR (the attenuation in ATR occurs in the optically absorbing layer(s) of the sample). The main optical properties of the system shown in Figure 2 can be described in terms of three sets of (interrelated) physical quantities: (I) Reflected optical fields in the incident medium 1 and transmitted fields in the final medium N; (ii) Total reflectance $R_{123...N}$ (ratio of reflected and incident fields) and transmittance $T_{123...N}$ (ratio of transmitted and incident fields) of the N-layer stack; (iii) Mean squared electric fields (light intensities) as functions of the z-coordinate within the individual layers.

Use of Attenuated Total Internal Reflection Fourier Transform Infrared Spectroscopy to Investigate the Adsorption of and Interactions Between Charged Latex Particles. Adsorption of 67 nm, 190 nm and 1,000 nm diameter carboxylated latex particles onto hydrophobic and hydrophilic surfaces, from aqueous dispersions of these particles containing different concentration of sodium chloride, have been investigated, *in situ*, by attenuated total internal reflection Fourier transform infrared, ATR-FTIR, spectroscopy. Adsorption of the carboxylated latex particles onto the substrates in a given sample increased exponentially with time and then leveled off to a plateau, A_{exp}. The value of A_{exp} was found to depend on the size of the carboxylated latex particles and on the electrolyte concentration in the dispersions. A_{exp} values were used to calculate the maximum coverage of the substrate by the adsorbed carboxylated latex particles ($\mathbf{1}_{max}$ - values). The $\mathbf{1}_{max}$ - values decreased with decreasing particle size and decreasing ionic strength of the medium in which a given sized carboxylated latex particle is dispersed. These results were showed the expected trend in terms of the product of the Debye length and the radius of the particles (ie., in terms of the screening parameter, $\mathbf{6}$a, Figure 3).

Plans for future research on this project. We plan to continue along with our experimental and theoretical investigations, as described above under the specific objectives for 2003-2004.

Publications Acknowledging DOE support 2003 -2004,

1. E. Hutter, K.A. Assiongbon, J.H. Fendler, D. Roy, Fourier Transform Infrared Spectroscopy Using Polarization Modulation and Polarization Selective Techniques for Internal and External Reflection Geometries: Investigation of Self-Assembled Octadecylmercaptan on a Thin Gold Film, *J. Phys. Chem. B.,* **2003**, *107(31)*, 7812-7819.
2. D. Brevnov, E. Hutter, J. H. Fendler, Digital Signal Processing for Step-Scan Phase and Electrochemical Potential Double Modulation Infrared Spectrometry, Appl. Spectrosc., in press.
3. R. Kun, J. H. Fendler, Use of Attenuated Total Internal Reflection Fourier Transform Infrared Spectroscopy to Investigate the Adsorption of and Interactions Between Charged Latex Particles, submitted to *J. Phys. Chem. B.*
4. D. Roy, J. H. Fendler, Reflection and Absorption Techniques for Optical Characterization of Chemically Assembled Nanomaterials, in press in *Adv. Mater.*

Solid-Matrix Luminescence Analysis and Coupling Solid-Matrix Luminescence with Separation Methodology

Robert J. Hurtubise, PI
Barry Smith, Matthew Marlow, Amanda Ackerman, Allison Thompson, Sara Hubbard, Graduate Students
Department of Chemistry
Department 3838
University of Wyoming
Laramie, WY 82071
hurtubis@uwyo.edu
http://uwadmnweb.uwyo.edu/chemistry

Overall research goals. The ability to understand the photophysical properties of excited fluorophors and excited phosphors and physicochemical interactions of these excited species in solid matrices is one of the primary goals of the project. In solid matrices, the photophysical properties and physicochemical interactions of the excited lumiphors are very different, in many cases, from the same excited species in solutions, especially phosphors in the excited triplet state. The unique properties of excited lumiphors in solids have been exploited extensively in chemical analysis and continue to be used in new analytical developments. Also, the excited lumiphors can be employed as "probes" in investigating the physical and chemical properties of polymers, proteins, and DNA. Another major goal is to understand the transport and equilibrium processes of solutes in liquid-liquid-liquid microextraction in microfibers. This important technique can very significantly increase the concentration of small amounts of solute and block the transport of large components such as DNA. The three-phase extraction technique can be easily coupled with solid-matrix luminescence (SML) and various separation techniques such as capillary electrophoresis (CE).

Specific objectives for 2003-2004. The specific objectives for the research are: (1) to understand the relationships between the glass transition temperatures, melting points ratios, and heat capacities of sugar glasses to the radiative and nonradiative deactivation of excited phosphors in sugar glasses; (2) to expand the fundamental principles of liquid-liquid-liquid microextraction (LLLME) with both aqueous and nonaqueous acceptor phases; (3) to couple LLLME with SML and CE.

Significant Achievements

Sugar Glasses. Solid-matrix phosphorescence (SMP) intensities and lifetimes for heterocyclic aromatic amines were acquired as a function of temperature for these phosphors in glucose glasses prepared from crystalline glucose and a glucose melt, both with and without a heavy-atom salt [1]. Several important results and conclusions were obtained from the data. For example, there were dramatic differences in the changes in the solid-matrix phosphorescence (SMP) lifetimes of the phosphors in the two types of glasses as the temperature was lowered. This permitted conclusions to be made about intersystem crossing for the phosphors in the two types of glasses. Remarkably, for one of the phosphors, in both types of glasses with NaI present, the SMP intensity was the same at 93 K as it was at room temperature. In addition, evidence was presented that indicated the low frequency vibrations and β-relaxation phenomena in the sugars were partially responsible for the nonradiative decay of the phosphors.

Hydrophilic and Partially Hydrophobic Papers. (a) A detailed study compared the important parameters that were responsible for the SMP moisture quenching of phosphors adsorbed on Whatman No.1 (hydrophilic) and Whatman 1PS (partially hydrophobic) papers. The SMP lifetimes (about 1 s) of phenanthrene and benzo[e]pyrene on both papers were independent of the amount of adsorbed moisture, but the SMP lifetime (about 5 s) of perdeuterated phenanthrene was dependent on the moisture content for both papers. Thus, diffusional quenching did not occur for phosphors with SMP lifetimes in the 1 s range, but did occur for the phosphor in the 5 s range. A major portion of SMP intensity decrease by moisture adsorption was caused by matrix quenching in which the cellulose matrix participated in the quenching process. The quenching models developed are important for SMP, but also for fundamental studies on how moisture adsorbs in cellulose [2]. (b) Unique methods were developed for treating Whatman No.1 paper with dichloromethylsilane and with poly(hydrogenmethylsiloxane) to extract polycyclic aromatic hydrocarbons (PAH) from water and directly detect the PAH on the paper via SMP. The detection limit was 29 fmole/mL for benzo[e]pyrene [3].

Separation and Detection of Tetrol I-1 in DNA Solutions. A new approach was developed for the separation and detection of tetrol I-1 in the presence of DNA using capillary electrophoresis and laser induced fluorescence [4]. The methodology developed can be used to detect several polycyclic aromatic hydrocarbon metabolites in the presence of DNA.

Characterization of Tetrol I-1 and PAH-DNA Adducts by SML. (a) Detailed SMF data were obtained for benzo[a]pyrene (B[a]P)-DNA adducts, and preliminary SMF data were acquired for dibenzo[a,l]pyrene-DNA adducts. Unique SMF quenching methods were developed for the characterization of tetrol I-1 and B[a]P-DNA adducts using $TlNO_3$ and NaI salts. Each salt provided a unique way to investigate the samples. Comparison of the quenching data for the B[a]P-DNA adducts and tetrol I-1 revealed significant differences in how the adducts and tetrol I-1 interact with the solid matrix. Several SMF quenching models were developed which were quite different for the two quenching salts. The methodology developed would have applicability to samples of DNA modified with phosphors at several different levels [5]. (b) In a comprehensive investigation, novel SMP photophysical methods were developed for the detection and characterization of B[a]P-DNA adducts and tetrol I-1 with the external heavy-atom effect using $TlNO_3$ and NaI salts to enhance the SMP. Fundamental equations and calculated photophysical parameters were used to interpret the data and characterize the samples. For example, from the SMP lifetime data, the pre-exponential factors and fractional contributions to the SMP decay curves showed that the fractional populations of tetrol I-1 and B[a]P-DNA adducts were essentially independent of the amount of $TlNO_3$ adsorbed.

The approaches developed can be used to detect and characterize any DNA samples modified at a level that gives a reasonably strong SMP signal [6].

Plans for future research in this project. The research for the coming year will follow two main avenues, namely, sugar glasses and liquid-liquid-liquid microextraction (LLLMC). Our goals for the sugar glasses are: *(1) Acquire the ratios of melting temperature to glass transition temperatures for several sugar glasses*. These ratios are related to various properties of the sugars such as vibrational mobilities and free volume of the sugar glasses. The ratios will be correlated with SMF and SMP spectra, lifetime and intensity data for several lumiphors in the sugar glasses. Basic knowledge about how the properties of the sugar glasses affect SMF and SMP will be obtained. *(2) Obtain heat capacity data for the sugar glasses over a wide temperature range*. These data will be used to develop a fundamental model for the nonradiative deactivation of the excited triplet state of phosphors in amorphous sugar glasses. Our goals for LLLME are: *(1) Acquire data for two-phase and three-phase microextraction system*. We showed recently that a two-phase microextraction system is more efficient in extracting large molecular-weight hydroxyl aromatic metabolites than a three-phase microextraction system. The fundamental processes that are important for the transport of the solute from the donor phase to the acceptor phase will be investigated. *(2) Obtain Mass Balance Data and Partition Coefficients*. The mass balance data and partition coefficients will be related to fundamental theoretical equilibrium equations that describe the distribution of the solute in the three phases.

Publications Acknowledging DOE Support – 2002-2004

[1] Mendonsa, S. D.; Hurtubise, R. J. “A Comparative Study of the Solid-Matrix Phosphorescence of Heterocyclic Aromatic Amines in Glucose Glasses as a Function of Temperature,” J. Luminescence **2002**, 97, 19-33.
[2] Ackerman, A. H.; Hurtubise, R. J. “Moisture Quenching of Solid-Matrix Phosphorescence on Hydrophilic and Partially Hydrophobic Filter Papers.” Appl. Spectrosc. **2002**, 56, 1368-1375.
[3] Ackerman, A. H.; Hurtubise, R. J. “Methods for Coating Filter Paper for Solid-Phase Microextraction with Luminescence Detection and Characterization of the Coated Filter Paper by Infrared Spectrometry,” Anal Chim. Acta **2002**, 474, 77-89.
[4] Marlow, M; Hurtubise, R. J. “Separation and Detection of a Benzo[a]pyrene Metabolite with Capillary Electrophoresis in the Presence of DNA Using Laser-Induced Fluorescence,” Talanta **2002**, 57, 193-201.
[5] Smith, B. W.; Hurtubise, R. J. “Characterization of Tetrol I-1 and (±)-anti-BPDE-DNA Adducts with Solid-Matrix Fluorescence Quenching,” Appl. Spectrosc. **2003**, 57, 943-949.
[6] Smith, B. W.; Hurtubise, R. J. “New Methodology for the Characterization of (±)-anti-BPDE-DNA Adducts and Tetrol I-1 with Solid-Matrix Phosphorescence,” Anal. Chim. Acta, **2004**, 502, 149-159.

2004 DOE/BES Analysis Program
Contractors' Meeting

Abstracts
Session 6

Multinuclear Magnetic Resonance Study of Silica and Modified Silica

Gary E. Maciel, P.I.; I-Ssuer Chuang, Research Associate; Shaokuan Zheng, Postdoctoral; Jianhua Li, Graduate Student
Department of Chemistry, Colorado State University, Fort Collins, CO 80523
maciel@lamar.colostate.edu

Overall Research Goals. This project focuses on the following two important aspects of silica surface chemistry: 1) An experimental/computational examination of structural details of the silica surface in terms of a model previously suggested by our prior research and 2) a study of the reactivity of the silica surface with "simple" organometallic reagents (specifically, methyl-metal compounds). The first topic is important and timely because silica surface structure is at the heart of several important aspects of silica-based chemistry, including separations, catalysis, composite materials, soils chemistry and geochemistry. The second topic is aimed at providing a fundamental chemical foundation for the largely empirical practice of "immobilizing" a catalytic (or other) center on a silica surface.

Specific 2003 Objectives. 1) Establish molecular modeling approaches to predict hydrogen-exchange behavior of surface silanols and begin experimental verification. 2) Finalize a methodology for stepwise NMR study of metal-metal/SiO_2 systems.

Progress in 2003.

1) Structural Details of the Silica Surface. A combination of ^1H->^{29}Si NMR experiments and molecular modeling (MM, using the Cerius^2 program) is being applied to testing/verifying/quantifying features of the silica surface that are based on our previously published hypothesis that the silica surface consists of segments of the hydroxylated surfaces of the beta-crystobalite crystal structure, with the <111> surface corresponding to Q3 (single) silanols and the <100> surface corresponding to Q2 (geminal) silanols, with numerous intersections of those segments. Figure 1 shows cartoon diagrams of edge views of these surfaces and intersections, with short lines representing OH groups, long lines representing edge views of planes containing silicon atoms attached to the OH groups. Dotted lines represent hydrogen bonds. Our strategy is to employ ^1H-^2H exchange with specifically tailored molecular probes that contain labile hydrogens (alcohols, phenols or NH^+-containing species) to determine (by subsequent NMR experiments) which surface features are present and in what amounts. For example, MM modeling indicates that, of the structures shown in Fig. 1, only E is too restricted an environment to permit hydrogen exchange of its most hindered silanols with the probe molecule, Ph_3COH (Ia). Similarly, the more hindered probe, (2,6-di-t-Bu-Ph)$_3$COH (Ib), can distinguish structures D and E from all the others, while the even more bulky probe, [3,5-di-(4-t-Bu-phenyl)-phenyl]$_3$COH (Ic) can distinguish the combination of C, D and E (the "concave" surface features) from all the others. These predictions are based on the assumption that the hydrogens to be exchanged must be able to approach within 3Å of each other in order for hydrogen exchange to occur efficiently. If that assumption turns out to be incorrect (e.g., if an approach within 2.5Å is necessary), then the predictions will be shifted toward smaller probes (e.g., for a 2.5Å limit, Ia would be replaced by t-

Bu-alcohol, Ib, by Ia, Ic, by Ib). Thus, examination of the experimental NMR results on hydrogen exchange should provide valuable insight into the fundamental structural requirements of hydrogen exchange. Analogous approaches are currently being explored to discriminate the "convex" surface features (F, G, H and I) shown in Figure 1; currently, the most promising probe molecules are of the type, 2,6-di(triphenylmethyl)phenol, which is capable of hydrogen exchange of the apex silanols of surface structure I, but not with most of the other surface structures represented in Figure 1.

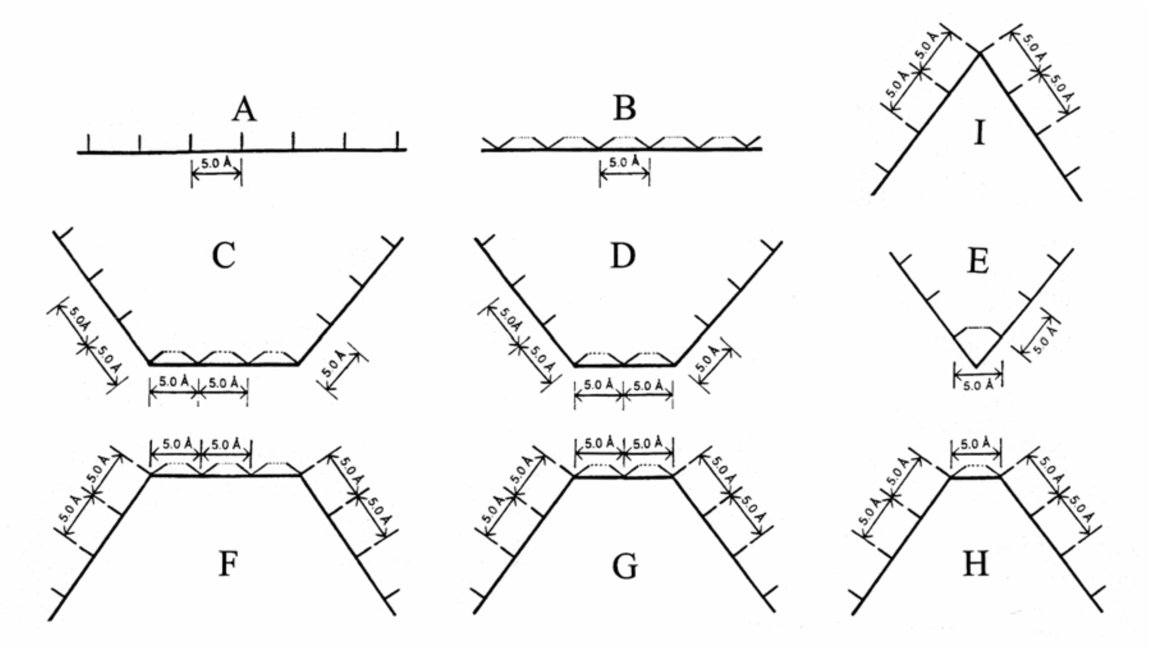


Fig. 1. Edge-on views of various beta-cristobalite based surface segments.

Figures 2a, 2b, 2c and 2d show the closest approach views of typical MM computer experiments. Fig. 2a shows the result of simulating the closest approach of probe molecule Ia to the hindered silanols of surface structure E, an approach that is not close enough (>3Å) to facilitate exchange. Analogous no-exchange predictions correspond to the probe molecule Ib with surface structure D (Fig. 2b) and probe molecule Ic on surface structure C. A positive exchange prediction comes from the simulation of closest approach for probe molecule Ic with surface structure A (single silanol <111> surface), represented in Figure 2d.

2) A Fundamental Basis for Silica Immobilization of Organometallic Species. The overall goal of this segment of the project is to establish a fundamental knowledge base for the reactions of "simple" organometallic species (i.e., metal-methyl compounds) with the silica surface. Our plan includes the study of $AlMe_3$, MeMgBr, $ZnMe_2$ and MeLi reactions on silica systems that have been dehydrated to various degrees. To date we have largely completed work on the $AlMe_3/SiO_2$ system with the silica dehydrated under vacuum at $150^{\circ}C$. The overall experimental strategy in this study is a stepwise NMR examination of the samples according to the following scheme: a) Carry out reaction of $AlMe_3$ (TMA) with SiO_2 in dry toluene (8 hr), measuring CH_4 evolution. b) Wash reaction mixture with dry toluene and remove toluene under vacuum (Sample 1 for ^{13}C, ^{29}Si and ^{27}Al NMR); b) treat toluene wash with n-propanol and measure CH_4 evolved. c) Wash powder with dry ether, then remove ether (Sample 2 for NMR); treat ether wash with n-propanol and measure CH_4 evolved. d) Add 1 equiv. H_2O in ether (based on stoichiometric estimate of Al-Me remaining), measuring CH_4 evolved; wash powder with dry ether, then remove ether (Sample 3 for NMR). e) Repeat step d) until no CH_4 evolution is detected (Samples 3', 3'', etc). f) Wash powder with acetone, water, methanol and remove solvent under vacuum (Sample 4).

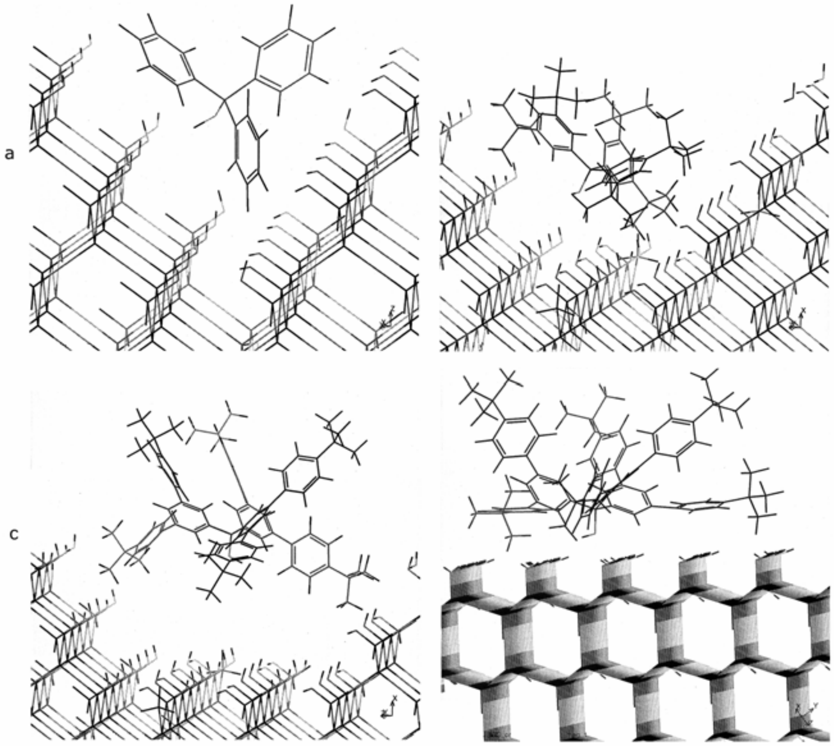


Figure 2. Representative MM predictions of closest-approach configurations for specific combinations of probe molecules and silica surface segments. See text for details.

Specific 2004 Goals/Plans. Build/capitalize on the accomplished 2003 goals (*vide supra*).

Publications from this Project in 2003.

1. C. Keeler and G. E. Maciel, "Quantitation in the Solid-State ^{13}C NMR Analysis of Soil and Organic Soil Fractions," *Anal. Chem.*, **75**, 2421-2432 (2003).
2. G. E. Maciel and I-S. Chuang, "Multinuclear NMR Studies of Silica Surfaces, 2nd Edition, H. Bergna, Ed., Am. Chem. Soc., in press.
3. M. R. Seger and G. E. Maciel, "NMR Investigation of the Behavior of an Organo-thiophosphate Pesticide, Chlorpyrifos, Sorbed on Clays," *Envir. Sci. Technol.*, subm.
4. M. R. Seger and G. E. Maciel, "NMR Investigation of the Behavior of an Organo-thiophosphate Pesticide, Methyl Parathion, Sorbed on Clays," *Env. Sci. Techn.*, subm.
5. C. Keeler, E. Kelly and G. E. Maciel, "Solid-State ^{13}C NMR Studies of Humic Materials from a Lower Montane Forest Soil," *Geoderma*, submitted.

Thermal Diffusion Shock Waves

Gerald J. Diebold, PI
Sorasak Danworaphong, student
Dept. Chemistry
Brown University
Providence, RI 02912
Gerald_Diebold@brown.edu

Overall research goals: The primary objectives of this research are to prove the existence of thermal diffusion “shock waves” and to introduce a new method of determining thermal diffusion factors. The Ludwig-Soret effect, also known as thermal diffusion, refers to the separation of chemical mixtures as a result of the imposition of a temperature gradient. The preferred method of studying the Ludwig-Soret effect is to create an optical interference pattern by crossing two phase coherent laser beams in a weakly absorbing fluid. The resulting interference pattern generates a sinusoidal temperature field with large thermal gradients.

The differential equation governing the mass density fraction c(x,t) in space and time of one species in a binary mixture subjected to a one-dimensional, sinusoidal temperature field of amplitude T_0 is given by

$$\frac{\partial c(x,t)}{\partial t} = T_o D' K \frac{\partial}{\partial x}\left\{c(x,t)[1-c(x,t)]\right\} \cos Kx \ + D\frac{\partial^2 c(x,t)}{\partial x^2} , \qquad (1)$$

where D’ is the thermal diffusion coefficient, D is the mass diffusion coefficient, and K is the grating wavenumber. Equation 1 is a nonlinear partial differential equation, where the first term on the right hand side describes the Ludwig-Soret effect, and the second, the effects of diffusion which tend to oppose thermal diffusion. Deletion of the diffusion term to give the main features of the effect yields

$$\frac{\partial c}{\partial \tau} = -\frac{\partial f}{\partial z}, \qquad \text{where} \qquad f(c,z) = -\alpha\, c(1-c) \cos z , \qquad (2)$$

where z=Kx, τ is a dimensionless time given by $\tau = DK^2 t$, α known as the thermal diffusion factor is given by $\alpha = D'T_0/D$, and f (c,z) is a “flux function”. It can be shown that $c(\beta(\tau), \tau)$ is a solution to Eq. 2 where c and β are solutions to the Hamiltonian pair of equations

$$\frac{\partial \beta}{\partial \tau} = \frac{\partial f(c,\beta)}{\partial c}, \qquad \frac{\partial c}{\partial \tau} = -\frac{\partial f(c,\beta)}{\partial \beta}. \qquad (3)$$

If the flux function is linearized to give an approximate solution for c<<1, then f becomes $f = -\alpha\, c \cos(z)$ and Eq. 3 becomes

$$\frac{\partial z}{\partial \tau} = -\alpha \cos(z), \qquad \frac{\partial c}{\partial \tau} = -\alpha\, c \sin(z) \qquad (4)$$

We find the solution to Eq. 3 to be

$$c(z,\tau) = \frac{c_0}{\cosh(\alpha\tau) + \sin(z)\sinh(\alpha\tau)} , \qquad (5)$$

where c_0 is the original density fraction before application of the temperature field. This expression governs the initial time evolution of the solution and can be applied to reduction of data in grating experiments designed for measurements of D’.

When the flux function with the nonlinearity is considered, no solution to the Hamiltonian pair is evident. However, it is possible to carry out a numerical integration which gives the curves shown in Fig. 1.

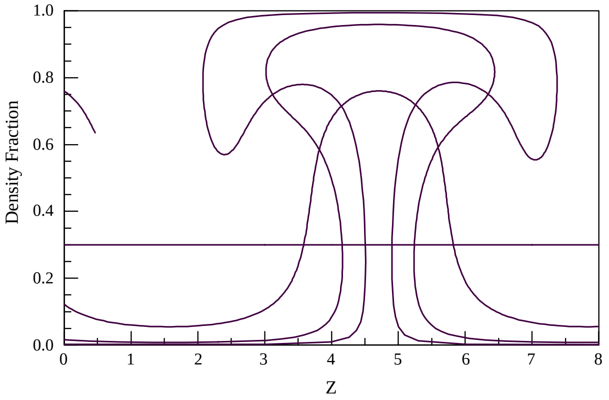


Fig. 1. Density fraction versus dimensionless coordinate z from numerical integration of the Hamiltonian pair for the nonlinear problem for several values of τ calculated with α=20. The temperature field is sinusoidal in space with the coldest region at 3π/2. The flat line at c=0.3 is the concentration profile at t=0.

In reality, when dc/dz first becomes infinite shocks are formed. The equation of motion for the shock front is then found from Eq. 3 to be

$$\frac{dz}{d\tau} = \alpha(-1 + c_l + c_r)\cos z \tag{6}$$

where c_l and c_r are the density fractions on the left and right sides of the shock for the side of the shock nearest the origin. The shock starts with a speed of zero, increases in speed, and then slows back to a speed of zero when $c_r=1$.

Specific research objectives for 2003 and 2004: For the coming year the goals of the research are to record the time development of suspensions of iron oxide particles in solvents under a microscope equipped with a video camera that views the cell where the Ludwig-Soret effect is produced. The time evolution of the suspension if determined by illuminating the cell with second laser beam and recording the absorption pattern as a function of time. It should be possible to confirm the predictions of the mathematics by fitting the experimental data to the equations of motion predicted above. Second, it is not difficult to show that for long times, when the Ludwig-Soret effect is balanced by mass diffusion that the density fraction profile is given by

$$c(z) = \frac{1}{1 + F(\alpha, c_o)e^{\alpha \sin z}} \tag{7}$$

where F is a function of α and c_0. It is thus possible to determine thermal diffusion factors in an experiment by fitting absorbance profiles to Eq. 7.

Significant achievements: To date, we have recorded absorption profiles in suspensions of iron oxide in several solvents. We have also made progress on the analytical solution as well as on numerical integration of the Hamiltonian pair.

Plans for future research on this project: The present work points out that particles can possess Soret coefficients so large that they can be manipulated with light. There thus exists the possibility of making photonic structures of nanoparticles using the Ludwig-Soret effect.

Publications Acknowledging DOE Support 2002-2003:

“The Photoacoustic Effect Generated by an Incompressible Sphere” with A. C. Beveridge and T. Hamilton, *J. Acoust. Soc. Am.* **112**, 1780 (2002)

“Internally Excited Acoustic Resonator for Photoacoustic Trace Detection” with S. Danworaphong, I. Calasso, a. Beveridge, C. Gmachl, F. Capasso, D. Sivco, and A. Cho, *Appl. Optics*, **27** 5561 (2003)

“The Photoacoustic Effect at Reflecting Interfaces”, *Rev. Sci. Instrum.*, **74**, 801 (2003)

“Evaluation of Photodynamic Therapy Agents through Transient Grating Measurements” with A. C. Beveridge, B. A. Bench, and S. M. Gorun, *J. Phys. Chem.* A 107, 5138 (2003)

“Thermal Diffusion in a Sinusoidal Temperature Field” with S. Danworaphong, and W. Craig submitted to *Phys. Rev. Lett*.

"Inelastic Neutron Scattering and Periodic DFT Studies of Hydrogen Bonded Structures"

Bruce S. Hudson, PI
Damian G. Allis, Jennifer Ciezak, Hegui Hu, Timothy Jenkins, Mark Kosmowski, Yanmei Lan, Graduate Research Assistants
Department of Chemistry, 1-014 Center for Science & Technology , Syracuse University, Syracuse, NY 13244-4100, bshudson@syr.edu, http://hudsonlab@syr.edu

Overall research goals.

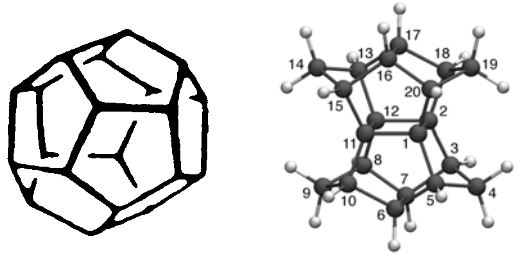
This project is directed at a fundamental understanding of hydrogen bonding, the primary reversible interaction leading to defined geometries, networks and supramolecular aggregates by organic molecules. Hydrogen bonding is still not sufficiently well understood that the geometry of such supramolecular aggregates can be predicted. In our approach existing quantum chemical methods capable of treating periodic solids are applied to hydrogen-bonded systems of known structure. The equilibrium geometry for the given space group and packing arrangement will be computed and compared to that deduced from diffraction studies. The second derivatives and normal modes of vibration are then computed and from this inelastic neutron scattering (INS) spectra are calculated using the normal mode eigenvectors to give spectral intensities. These computed spectra are compared with experimental results obtained for low-temperature polycrystalline samples. INS spectra are used because of lack of selection rules, ease of computation of spectral intensities and good coverage of the low frequency region. A premise of this work is that vibrational spectra are more sensitive than diffraction data to details of structure. The ultimate goal of these studies is to be able to define the thermodynamics of organic molecular crystals with sufficient reliability that the relative stability of two polymorphic forms can be computed. Ultimately our aim is reliable *ab initio* prediction of crystal structures.

Specific objectives for 2002-2003.

During this past year we directed our attention at the two alkanes, isomers of $C_{20}H_{20}$, two forms of a hydrogen bonded system, an ionic molecular solid and several cases of short, strong symmetric hydrogen bonds. The objective was to find out what is needed in the quantum chemical treatment of these systems in order to adequately describe the structures and spectra of these materials. Specifically, the DMol^3 periodic DFT method using an atom centered basis set was applied. Several plane-wave basis set procedures were also tested for their utility.

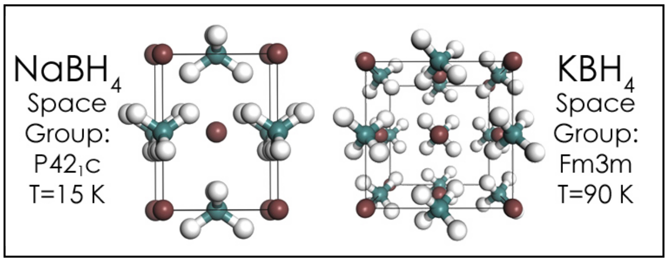
Significant Achievements

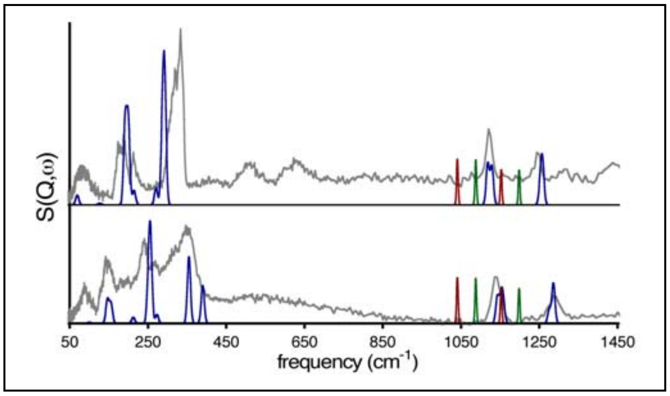
Dodecahedrane (C only) and Pagodane (C & H atoms).



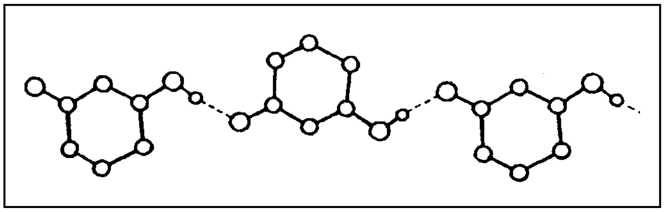
Vibrational spectra of molecules in solids are usually very similar to those observed for the isolated molecule in vapor phase. This correlation is expected to particularly valid for hydrocarbons. In some cases, however, these differences are of interest. Two isomers of $C_{20}H_{20}$, dodecahedrane and pagodane, have been studied this year. In dodecahedrane the challenge has been to compute and understand the splitting of the degenerate vibrations of the I_h molecule in the T_h symmetry of the crystal. The computing part has been successful. For pagodane the issue is that the low frequency part of the INS spectrum of the crystal differs considerably from that calculated. This has been largely reproduced in calculations.

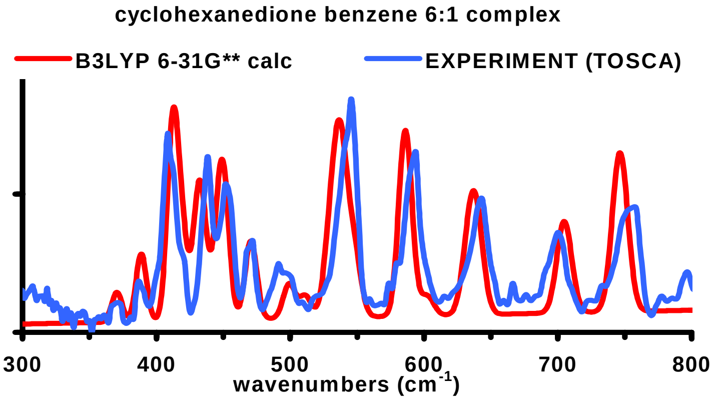
Simple solids such as Na and K BH_4 exhibit very large differences between the molecular anion vibrations as seen in the solid and those calculated for the isolated anion and observed in liquid ammonia solution. The INS spectra at the bottom right for KBH_4 (top) and $NaBH_4$ (bottom) are compared to isolated ion calculations (green and red) and those for the periodic solid (blue). The nature of the effect of the lattice on the molecular vibrations is being investigated.





1,3-cyclohexane dione (CHD) and its benzene cyclamer complex. β-Diketones such as 1,3-cyclohexane dione exist in their crystal structures in the enol form in linear hydrogen bonded arrays as shown at the right. This system is of interest because it exhibits a kind of pseudo-polymorphism in which minor substitutions result in very different crystal structures. The structure of this molecule in its crystal differs considerably from that of the isolated molecule, showing evidence of cooperative hydrogen bonding. This material forms a crystalline complex with benzene in which six CHD units in a plane surround a benzene molecule. The calculated and observed INS spectra of this complex are shown at the right. This analysis shows that hydrogen bonding can have significant effects on molecular structures and that hydrogen bonding energies are not additive due to these cooperative structural changes.





Publications Acknowledging DOE Support – 2002-3

1. Johnson, M. R.; Parlinski, K.; Natkaniec, I.; Hudson, B. S., "*Ab initio* calculations and INS measurements of phonons and molecular vibrations in a model peptide compound – urea", Chemical Physics (2003) 291, 53-60.
2. Alexander, Jacob S.; Allis, Damian G.; Hudson, Bruce S.; Ruhlandt-Senge, Karin, "An Examination of Metal-Ligand Binding Modes in Rubidium Diphenylmethanide", J. Am. Chem. Soc. (2003) 125, 15002-15003.
3. Damian G. Allis and Bruce S. Hudson, "Inelastic Neutron Scattering Spectra of $NaBH_4$ and KBH_4: Experiment and Solid State DFT Analyses", Chem. Phys. Lett., in press.
4. Damian G. Allis, Horst Prinzbach, and Bruce S. Hudson, "Inelastic Neutron Scattering Spectra of Pagodane: Experiment and DFT Calculations", Chem. Phys. Lett., submitted.

2004 DOE/BES Analysis Program
Contractors' Meeting

Abstracts
Session 7

Molecular Aspects of Transport in Thin Films of Controlled Architecture

Paul W. Bohn, PI
Carla B. Swearingen, Joseph J. Tulock, Donald M. Cannon, Jr., Postdoctoral Associates
John S. Kirk, Ishika Lokuge, Bethany Reynolds, Travis King, Graduate Assistants
Department of Chemistry and Beckman Institute
University of Illinois at Urbana-Champaign
600 S. Mathews Ave.
Urbana, IL 61801
bohn@scs.uiuc.edu
http://barney.scs.uiuc.edu/

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

Specific objectives for 2003-2004. Our specific objectives are listed here: (1) Characterize the use of nanocapillary array membranes to achieve reactive mixing with attomole-femtomole amounts of reactants; (2) Complete the quantitative characterization of mass transport rates in injection and sampling; (3) Develop protocols based on focused ion beam bombardment for the fabrication of single nanopores and small (<10) arrays of nanopores in PMMA. Significant accomplishments in these areas are described below.

Significant Achievements

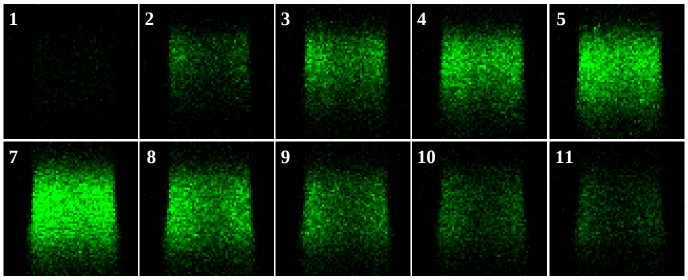


Figure 1. Confocal fluorescence microscopy showing a time sequence of images of nanofluidic mixing, in which a fluorescent dye stream is injected into an unlabeled buffer stream. Each image represents the same XZ plane under the membrane at 210 ms intervals, and the membrane is at the top of each frame.

Reactive Mixing. We seek to extend microfluidic devices to create hybrid three-dimensional microfluidic/nanofluidic architectures by exploiting the unique transport properties of nanocapillary array membranes. One significant capability which results is the ability to use diffusion as a transport mechanism to mix two solutions, when one is injected into the other through a membrane in which the nanocapillaries are laterally separated by sub-μm distances. Typically these membranes contain ~ 3×10^4 nanopores in 100×100 μm^2, *i.e.* the mean interpore separation is ~580 nm. Because fluid is transferred under electrokinetic control at appreciable velocity (v_{max} ~ 2.5 mm s^{-1}), there is significant convective mixing in the receiving stream, which aids mixing, *viz.* Fig. 1.

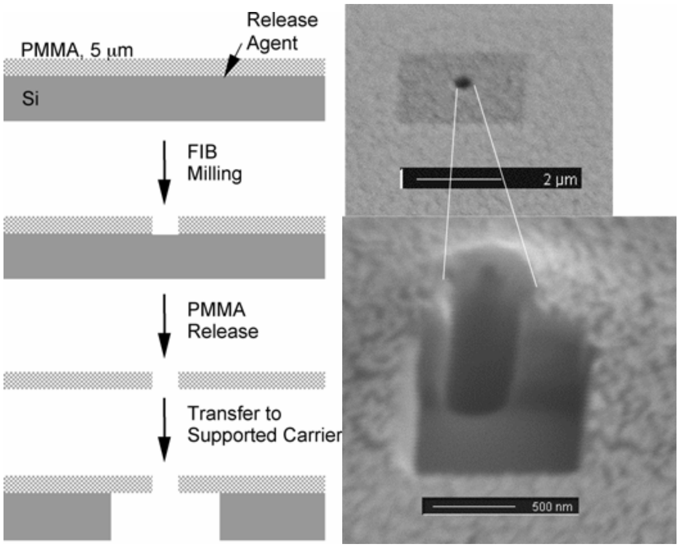


Figure 2. (*Left*) Fabrication strategy for making single nanopores in a supported PMMA membrane. In our work, the supported carrier is a glass or poly(dimethylsiloxane) microfluidic chip. (*Right*) Single nanopore in PMMA, d ~ 400 nm, prepared by FIB milling. The bottom SEM shows a pore which overlaps with an area which has been ion milled to *ca.* 500 nm depth.

Single Nanopore Fabrication/Imaging. Our approach uses focused ion beam (FIB) etching to drill cylindrical pores in PMMA. Using 5 μm films it is possible to etch completely through the film creating a pore in a supported film. The PMMA film is then lifted off the Si carrier, with the aid of a release agent, and incorporated into a crossed microfluidic channel structure to achieve a new kind of hybrid architecture. Single pore measurements are of interest, because (1) multiple pore membranes naturally have some dispersion in pore properties, and (2) the properties of individual nanopores may be characterized in detail, they are much more useful in testing theoretical predictions of potential-driven molecular transport.

Plans for future research on this project. Our efforts in the coming year will extend and explore in greater detail the results presented here. In particular our goals are:

(1) Characterize the reactive mixing for different analytes and for readouts without fluorescent tags. One fluorigenic reaction uses *in vitro* selected DNA aptamer which binds Pb(II). The two strands are capped with a fluorophore and a quencher, respectively. When Pb(II) binds to the target strand, it cleaves the fluorophore-containing portion which can then be excited and emit. *(2) Initiate single pore transport measurements.* We will characterize electrokinetic transport in single nanofluidic channels by measuring nanochannel flow and intrinsic transport rates for analytes of varying size and structure.

Publications Acknowledging DOE Support – 2003-4

(1) T.-C. Kuo, H.-K. Kim, D.M. Cannon, Jr., M.A. Shannon, J.V. Sweedler, and P.W. Bohn, "Nanocapillary Array Membranes Effect Rapid Mixing and Reaction," *Angew. Chem. Intl. Ed. Engl.*, in press.
(2) D.M. Cannon, Jr., T.-C. Kuo, J.V. Sweedler, M.A. Shannon, and P.W. Bohn, "Nanocapillary Arrays Produce Gated Analyte Injection for Separations and Analysis in Three-dimensional Microfluidic Architectures," *Analyt. Chem.* **2003**, 75, 2224-2230.
(3) T.-C. Kuo, D.M. Cannon, Jr., M.A. Shannon, J.V. Sweedler, and P.W. Bohn, "Hybrid Three-Dimensional Nanofluidic/Microfluidic Devices Using Molecular Gates," *Sens. Actuat. A* **2003**, 102/3, 223-233.
(4) T.-C. Kuo, D.M. Cannon, Jr., W. Feng, M.A. Shannon, J.V. Sweedler, and P.W. Bohn, "Gateable Nanofluidic Interconnects in Multilevel Microanalytical Systems," *Analyt. Chem.* **2003**, 75, 1861-1867.

Novel separation processes via hierarchically structured materials and ionic liquids

Sheng Dai

Chemical Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831
dais@ornl.gov

Overall research goals. Chemical separations have been central to the mission of DOE and its predecessor agencies since their inception. They are of importance in energy production and in environmental remediation. The overall objective of this project is to investigate fundamental chemistry involved in novel separation processes via rational synthesis and development of new separation media.

Specific objectives for 2002-2003. Our specific objectives are listed here: (1) Continue the synthesis of porous materials via imprinting synthesis for separation; (2) Understand the effect of the secondary environment on adsorption sites; (3) Develop new methodologies for synthesis of monolithic separation media; (4) Initiate the synthesis of anion-exchanger resins based on porous hybrid materials; (5) Develop applications of ionic liquids as liquid membranes for QCM devices. Significant accomplishments in these areas are described below.

Significant Achievements

Demonstration of Imprinting of Protons: Molecular imprinting is a versatile technique to create affinity in solid matrixes toward target chemical species through controlled selection of functional group locations. The inhomogeneity for such distribution of the functional groups is deliberately generated in the host matrixes via the imprinting synthesis. Imprinting synthesis utilizes either a covalent or a noncovalent interaction between the target molecule and functional ligands in the host matrix. We have described a technique for the successful imprinting of different structural stages of a pH indicator in a hybrid sol-gel matrix. The proton affinity of the indicator is strongly dependent on this imprinting synthesis. Therefore, we can view this imprinting synthesis as a proton-imprinting technique. Proton ions were successfully imprinted in a hybrid matrix through a protonation reaction with a covalently entrapped pH indicator. The pK_a value of the indicator is significantly changed by the imprinting synthesis. This fine-tuning of the reactivity for pH indicators via the imprinting synthesis may find application in making pH sensors with tailored pK_a values.

Imprinting Synthesis on Layered Materials: A new methodology has been developed to provide effective functionalization of the surface of ordered, crystalline, layered magadiite via an imprinting technique. This methodology has resulted in a simplified experimental procedure for functionalizing layered silicate with a good control of the distributions of functional ligands on magadiite. Our results demonstrated imprint-functionalized-magadiite has a better selectivity and a higher capacity for the metal ion templates than the non-imprinted analogues. These properties make them ideal for many separation applications that require recyclable and phases.

Development of Bifunctional Anion-Exchange Resins: Organic polymer anion-exchange resins are widely used to recover anions from various process waste streams. Among the various organic anion-exchange resins, quaternary ammonium resins are one of the most popular and effective in these applications. However, drawbacks are associated with all organic anion-exchange resins: (1) instability in harsh chemical environments, (2) limited surface areas, (3) hydrophobicity of polymer backbones, (4) thermal instability, (5) swelling and deformation in contact with solvents, and (6) difficulty to recycle. For these reasons, we have initiated the research to rationally synthesize organic-inorganic hybrid anion-exchange resins. Such anion-exchange resins have controlled mesopores and surface areas. The surface bifuctionality can be readily introduced to facilitate the stripping of absorbed anions.

Development of Nanostructured Monolithic Materials for Separation: The development of monolithic columns is one of the key advances in HPLC. We have developed a gel-casting procedure for the synthesis of monolithic silica columns with a bimodal pore structure. Monolithic columns with a large diversity of mesopore morphology were readily prepared by using various silica precursors. The total porosity and hydraulic resistance of the column were easily tailored by gel-casting of silica colloids of various sizes. Our procedure also demonstrated that gel-casting is a convenient method for the synthesis of hierarchically structured silica with designed shape. Gel-casting of various silica precursors made it possible to fine-tune the design of monolithic silica columns. Although silica-based monolithic columns can be utilized under various environments, the major obstacle to a wider use of silica-based rod columns is their limited resistance to hydrolysis, which restricts their operation to a relatively narrow pH range. This deficiency prompted us to develop carbon-based monolithic materials for separation applications. We have successfully demonstrated a methodology using silica beads as templates for generation of macropores in monolithic carbon materials.

Investigation of Molecular Diffusion in Mesopores: The translational motion of rhodamine 6g dye molecules near the surface of a mesoporous glass with a disordered pore structure and a nominal pore diameter of 130 Å is measured by the application of fluorescence correlation spectroscopy (FCS) to fluorescence burst data as dye molecules diffuse through the laser excitation volume. FCS analysis indicates that the motion of the rhodamine 6g molecules in the mesoporous glass deviates from simple Brownian motion with a single diffusion constant. Two models, including two-component diffusion and diffusion plus adsorption) are utilized to fit the correlation data. The multi-component diffusion model comprised of free diffusion (with diffusion coefficient of $4.89 \times 10^{-7} cm^2/s$) and transient adsorption/desorption (desorption time of 67ms) provides the best fit and the most plausible explanation of the correlation data.

Development of Sensing Media Based on Ionic Liquids: Ionic liquids have negligible vapor pressure. Their strong affinities for selected chemical species prompted us to consider the fabrication of vapor-sensing devices based on ionic liquids. A quartz crystal microbalance (QCM) device employing ionic liquids as the sensing materials for organic vapors has been developed and evaluated. The sensing mechanism is based on the fact that the viscosity of the ionic liquid membrane decreases rapidly due to solubilization of analytes in the ionic liquids. This change in viscosity, which varies with the chemical species of the vapors and the types of ionic liquids, results in a frequency shift of the corresponding quartz crystal. The QCM sensor demonstrated a rapid response (average response time of less than 2 s) to organic vapors with an excellent reversibility because of the fast diffusion of analytes in ionic liquids. Furthermore, the ionic liquids, with zero vapor pressure and stable chemical properties, ensure a long-term shelf life for the sensor.

Plans for future research on this project. Our efforts in the coming year will continue the above research activities. In particular, our goals are:

(1) Conduct hierarchical imprinting based on hybrid materials. We want to investigate the synergistic effect of the second coordination shell and bifuctionality on separation processes. (2)

Explore the synthesis of nanoporous monolithic carbon materials via controlled phase segregation. These materials provide unique substrates to study adsorption processes tunable with electric field. (3) Investigate new methodologies for formation of hydrophobic ionic liquids. The applications of new ionic liquids for separation will be studied. (4) Study the effect of anions on the ionic-liquid-based extraction of cationic species using neutral ligands. The hydrophobic ionic liquids with different anions will be synthesized to study solvation processes involved in separation processes.

Publications Acknowledging DOE Support – 2002-3

1. Lee, B.; Luo, H.; Yuan, C. Y.; Lin, J. S.; and Dai, S. "Synthesis and Characterization of Organic-Inorganic Hybrid Mesoporous Silica Materials With New Templates," *Chem. Comm.* **2004**, 240.
2. Mahurin, S. M.; Dai, S.; Barnes, M. D.; "Probing the Diffusion of a Dilute Dye Solution in Mesoporous Glass with Fluorescence Correlation Spectroscopy**,"** *J. Phys. Chem. B.* **2003**; *107*, 13336-13340.
3. Liang, C.; Dai, S.; Guiochon, G. "A Graphitized-Carbon Monolithic Column**,"** *Anal. Chem.* **2003**; *75*(18); 4904-4912.
4. Zhang, Z.; Saengkerdsub, S.; Dai, S., "Intersurface Ion-Imprinting Synthesis on Layered Magadiite Hosts," *Chem. Mater.* **2003**; *15*(15); 2921-2925.
5. Lee, B., Bao, L. L., Im, H. J., Dai, S., Hagaman, E. W., Lin, J. S., "Synthesis and characterization of organic-inorganic hybrid mesoporous anion-exchange resins for perrhenate (ReO_4^-) anion adsorption," *Langmuir*, **2003**, 19, 4246-4252.
6. C. D. Liang, S. Dai, and G. Guiochon, "Use of gel-casting to prepare HPLC monolithic silica columns with uniform mesopores and tunable macrochannels," *Chem. Commun.*, **2002**, 2680.
7. Liang, C. D.; Weaver, M. J.; and Dai, S. "Change of Indicator's pK_a via Molecular Imprinting," *Chem. Comm.* **2002**, 1621-1622.
8. Liang, C. D.; Yuan, C. Y.; Warmack, R. J.; Barnes, C. E.; and Dai, S. "Ionic liquids: A new class of sensing materials for detection of organic vapors based on the use of a quartz crystal microbalance," *Anal. Chem.*, **2002**, *74*, 2172-76.
9. Dai, S. and Barnes, C. E. "Mesoporous Materials," in *Encyclopedia of Supramolecular Chemistry*, Marcel Dekker, in press.
10. Dai, S. "Molecular Imprinting Using Hybrid Materials as Hosts," in *Molecularly Imprinted Materials: Science and Technology*, Marcel Dekker, in press.
11. Burleigh, M. C. and Dai, S. "Molecularly Imprinted Sorbents," in *Nanoporous Materials: Science and Engineering*, Oxford Press, in press.
12. Dai, S.; Zhang, Z. T.; Liang, C. D. "Hierarchically Imprinted Nanostructures for Separation of Metal Ions," in *Encyclopedia of Nanoscience and Nanotechnology*, Marcel Dekker, in press.

Abstract S7-3

Study of the Homogeneity of Adsorbent Surfaces (work done under current grant)

Georges Guiochon, PI
Gustaf Götmar, Fabrice Gritti, Postdoctoral Research Associates
Lance Riddle, Graduate Research Assistant
Department of Chemistry, University of Tennessee, Knoxville, TN, 37996-1600
guiochon@utk.edu

Overall Research Goals. The surface of all adsorbents is heterogeneous. These surfaces are rough at the molecular level and impurities of the bulk material making the adsorbent tend to segregate at its surface (e.g., boron or iron in silica). The bonds between polyvalent atoms at the surface are strained at the fluid-solid interface. The distribution of the electrical field above the surface, hence of the distribution of the adsorption energy (AED) of any probe are non-uniform. Attempts at relating the experimental isotherms of different probes and the characteristics of their adsorption energy distribution have lead to a complex theory with several methods to derive numerical solutions that disagree markedly and no valid tests for the lack of reference surfaces with a known adsorption energy distribution.

The goal was to measure the adsorption isotherm data of pairs of enantiomers on a chiral surface, to use the different approaches of the theory of adsorption on heterogeneous surfaces to derive the AED of the two enantiomers, and to compare the difference between the AEDs of two enantiomers and the differences between their energy of interaction with the chiral group involved measured by microcalorimetry.

Significant Achievements.

AED on Imprinted Polymers. The AED of L- and D-Phenylalanine Anilide (LPA) were derived from their isotherm data acquired on a polymer molecularly imprinted for LPA. The mobile phase was a solution of an aqueous phosphate buffer in acetonitrile. The data suggested a strong surface heterogeneity. The AEDs were calculated using two different methods. The first method is a version of the conventional approach, developed by Umpleby et al., that fits the isotherm data to the Freundlich isotherm, then derives the AED from the energy distribution associated with this isotherm model. Obviously, much arbitrary information is introduced in this calculation process and the result is not satisfactory (see Figure 1). This Figure shows plots of the affinity spectra of LPA and DPA versus the logarithm of their binding constants. The number on each curve is the heterogeneity parameter of the Freundlich isotherm that best accounts for the experimental isotherm data.

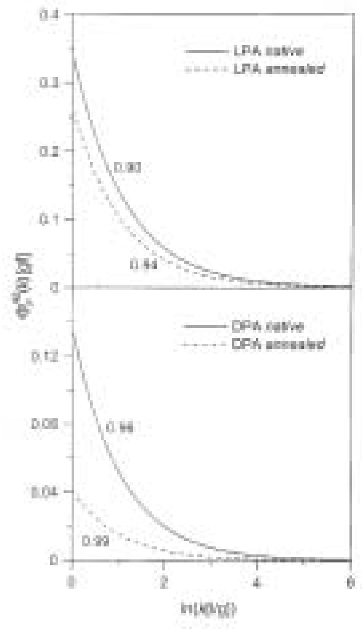


Figure 1. *Influence of thermal annealing on the AEDs derived from experimental data and calculated with the AS method.*

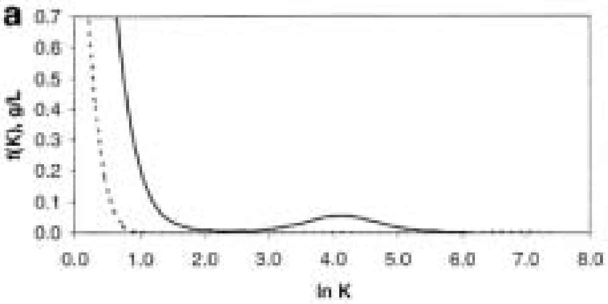


***Figure 2**. AED of LPA (solid line) and DPA (dotted line) on annealed polymer at 40 C.*

The results obtained with the second (EM) method are markedly different (Figure 2). They exhibit a bimodal distribution, in agreement with the adsorption data of LPA and DPA on the MIP fitting much better to a bilangmuir than to a Freundlich isotherm model [23]. The high energy mode is clearly characterized. Its average energy and size are in agreement with the experimental results. The low energy mode is incomplete because it was not possible to investigate a wide enough concentration range, due to the limited solubility of LPA and DPA in the mobile phase. This result demonstrates the importance and interest of the EM method. This method affords results that are clear and straightforward to interpret.

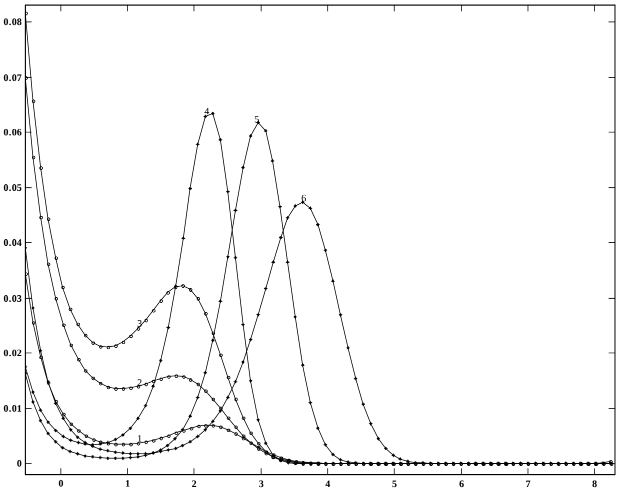


***Figure 3**. AED of propranolol on immobilized Cel7A.*

AED on an Immobilized Protein. Adsorption data of several β-blockers were measured on a CSP made by immobilizing on silica a protein, Cel7A, a cellobiohydrolase that has a long tunnel that threads and hydrolyzes cellulose molecules and contains adsorption sites enantioselective for the β-blockers. The AEDs (plots of the density of sites versus the logarithm of their binding constant) are shown in Figure 3 for propranolol. The different curves correspond to the enantiomer (dashed lines for the *R*-enantiomers, # 1 to 3, and solid lines for the *S*-enantiomers, # 4 to 6 that has the stronger binding energy), and to the pH of the eluent, (1) and (4) 5.01, (2) and (5) 5.51, and (3) and (6) 6.02. Although the exact relationship between adsorption energy and binding constant is difficult to derive, the difference between the adsorption energies of two modes is simply related to the difference between the logarithms of the corresponding binding constants. The results obtained show that the difference between the adsorption energies of the enantioselective modes of the two enantiomers is in excellent agreement with the value obtained by calorimetry and reported by a different group at this pH.

Our work demonstrates the validity of the theory of adsorption on heterogeneous surfaces and of the EM method of derivation of the AED from adsorption isotherms. It provides useful specifications for the range and accuracy required for these experimental measurements. It is now used systematically in our group in the investigation of retention mechanisms in RPLC.

Separation of Highly Complex Mixtures by Two-dimension Liquid Chromatography (proposal for grant renewal)

Overall Research Goals. Current combinations of separation and identification methods of analysis are too slow and not sensitive enough to solve a few very difficult but very important separation problems, e.g.:

- copolymers, including block and random copolymers, possibly terminated;
- pesticides, pollutants, or other contaminants in food products;
- proteomic (e.g., protein digests) metabolomic, petroleomic samples.

Far more powerful methods are needed. It is proposed to develop them by combining two or more different chromatographic methods with mass spectrometry. We investigate two possible combinations:

- *comprehensive bidimensional chromatography* (LC×LC) that consists in carrying out the systematic separation of the fractions eluting from a first column (slow but highly efficient) on a second column, very fast if less efficient.

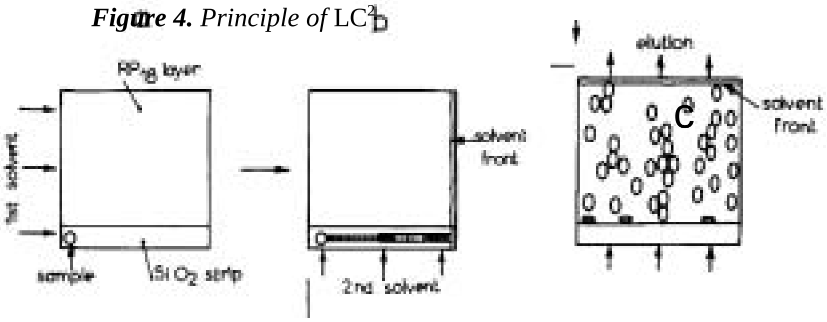
- and *true bidimensional chromatography* (LC^2) that consists in packing a thin, rectangular column with two different materials and in carrying out a development step along one dimension, through one material, and an elution step along the other one, through the other material.

In either case, two different, orthogonal retention mechanisms are used, so that compounds interfering on one phase system are separated on the other. The separation power afforded by either method is potentially several orders of magnitude higher than that obtained now on the best HPLC columns, with peak capacities of 10^4 to 10^5 in LC^2, 2×10^3 to 10^4 in LC×LC, both achieved in less than twice the time needed to generate a 200-peak-capacity separation in conventional isocratic HPLC. However, the former method is more complex to implement and generates intense data streams still difficult to generate and handle.

Specific Objectives for 2004. These objectives are: (1) Investigate the retention mechanisms available in chromatography for the separation of peptides; (2) Determine to which degree they are correlated; (3) Select pairs of mechanism that are nearly independent (i.e., orthogonal); (4) Design and prepare columns compatible for a LC×LC implementation; (5) Apply the principle to the separation of protein digests; and (6) Couple the LC×LC system to mass spectrometry for identification of the compounds separated.

In the same time, work will begin on the design and construction of a LC^2 unit (see principle in Figure 4).

Figure 4. *Principle of* LC^2



Studies of Solvation Processes in Supercritical Fluids

Frank V. Bright, PI
Siddharth Pandey, Postdoctoral Research Associate
Gary A. Baker, Sheila N. Daniel, Maureen A. Kane, Chase A. Munson, Wendy E. Gardinier, Philip M. Page, and Taylor A. McCarty, Graduate Research Assistants
Department of Chemistry
University at Buffalo, The State University of New at Buffalo
Natural Sciences Complex
Buffalo, NY 14260-3000
chefvb@acsu.buffalo.edu
http://www.chem.buffalo.edu/Bright.html

Overall research goals. Reactions and separations present challenges when they are carried out in liquids. A liquid may exhibit a high boiling point and be hard to remove from the products, it may be expensive to purchase, or difficult to dispose without incurring substantial costs and/or adversely affecting the environment or personnel. Moreover, slow mass transfer in liquids limits many reactions and separations. These problems are exacerbated because the Montreal Protocol, Kyoto Agreement and EPA limit and/or propose outright bans on certain liquid solvents. As a result, there is substantial motivation to replace traditional liquids solvents with environmentally friendly alternatives. Our work aims to develop a molecular-level view of solute solvation and dynamics in supercritical fluids and room temperature ionic liquids – two classes of replacement solvents.

Specific objectives for 2002-2003. Our specific objectives are to: (1) Determine the dynamics of polymers in liquids, molten polymers, and pure and cosolvent-modified CO_2; (2) Quantify solute-fluid interactions at interfaces; and (3) Quantify transient solvation kinetics in room-temperature ionic liquids. Recent accomplishments in these areas are described below.

Significant Achievements

Polymer dynamics. To investigate the behavior of CO_2 expanded liquids on dissolved polymers we have investigated the tail-tail cyclization and unfolding kinetics of poly(dimethylsiloxane) end-labeled with pyrene (Py-PDMS-Py). In liquid toluene (a good solvent) as a function of added CO_2 (0 - 204 bar), the Py-PDMS-Py excimer emission is entirely intramolecular. Addition of CO_2 to toluene (up to ~90 bar) results in a systematic decrease in the mean free distance between the PDMS termini. This change in the distance is consistent with an excluded volume argument, in line with Monte Carlo simulations and small-angle neutron scattering experiments. Above ~ 90 bar $CO_{2,}$ the mean free distance between the termini begins to increase. This arises from an increase in the solvent quality with increasing CO_2 density.

Many materials are derived from polymeric junctions/networks. We have constructed a PDMS-based three-armed junction that contains a single dansyl reporter group to study polymeric junctions. Initial experiments in good, theta, and poor liquid solvents and pure methyl-terminated PDMS show that a decrease in solvent quality produces a collapse of the junction's PDMS arms around the dansyl reporter group, inhibition of the dansyl residue's ability to form its twisted intramolecular charge transfer state, and impedance of the dansyl residue's ability to reorient. There is evidence for chain length dependent interpenetration of the PDMS "solvent" molecules into the junction and modulation of the local microenvironment surrounding the dansyl residue.

When Py-PDMS-Py is dissolved in pure supercritical CO_2 ($scCO_2$) there are at least two forms of Py-PDMS-Py (constrained and unconstrained) in the ground state prior to photoexcitation. The constrained species arises from intramolecular hydrogen bonding between the opposing peptide segments within the Py-PDMS-Py terminal region that were introduced during Py-to-PDMS labeling step. This species precludes normal excimer formation. The unconstrained species leads to classic excimer formation. The constrained species dominates at lower CO_2 densities (86 ± 2 % contribution at a reduced density of 1.40); however, its dominance wanes as the CO_2 density increases (14 ± 2 % contribution at a reduced density of 1.95). The mean-free distance between termini also depends on the CO_2 density. At low CO_2 densities, the Py residues on the unconstrained Py-PDMS-Py molecules are closer together on average than they were at higher CO_2 densities. However, in scCO_2, the unconstrained Py-PDMS-Py termini are never as far apart, on average, as they are in liquid toluene. Our results are also consistent with the presence of upper and lower critical solution pressures/densities for dilute PDMS dissolved in scCO_2.

Outcomes for chemical reactions are often different in scCO_2. Given this, we have explored the ring closing metathesis (RCM) of a 16-membered mock diene (6-(1-pyrenyl)hexyl-11-(1-pyrenyl)undecanoate, [1-Py$(CH_2)_{10}COO(CH_2)_6$1-Py]) in scCO_2. In scCO_2, we found that the 1-Py$(CH_2)_{10}COO(CH_2)_6$1-Py excimer-to-monomer intensity ratio (*E*/*M*) correlates directly with (1) the observed RCM yield for Leitner and Fürstner's original 16-membered diene and (2) the solvent refractive index function. The steady-state and time-resolved fluorescence of 1-Py$(CH_2)_{10}COO(CH_2)_6$1-Py in scCO_2 showed two excimers. The typical dynamically-formed excimer,emitting at 470-480 nm (*E1*), forms within 2 ns of optical excitation; however, it is ***not*** the dominant species at low CO_2 densities. *E1* is equivalent to the species that goes on to form the RCM product in Leitner and Fürstner's original reaction. The second excimer (*E2*) emits in the 410-440 nm region. *E2* is associated with intermolecular pre-associated forms of the pyrene residues within a collection of 1-Py$(CH_2)_{10}COO(CH_2)_6$1-Py molecules, and this species dominates at low CO_2 densities. *E2* is equivalent to the species that goes on to form the oligomeric product in the original Leitner and Fürstner reaction. As the CO_2 density increases, the *E1* excimer contribution increases relative to the *E2* excimer contribution. The fluorescence and reaction outcome results have been used to explain Leitner and Fürstner's previous density-dependent RCM yields.

Solute-fluid-surface interactions. We have prepared a series of model silica-based interfaces that have been "labeled" with a solvatochromic probe molecule (dansyl) at surface loadings that vary by a factor of 10^5. The fluorophore serves simultaneously as the solute and an environment sensitive probe. Unlike in solution, adsorbed molecules can be surrounded by other adsorbates, they can be distributed within an ensemble of sites with differing physicochemical properties, or they can be located in sites that are inaccessible to solvent molecules. All of these scenarios are observed for dansylated controlled pore glasses in contact with organic liquids and scCO_2.

Room temperature ionic liquids. An attractive aspect of using room temperature ionic liquids as solvents is the potential for removing reagents/products with an environmentally benign solvent like CO_2. In this context, we have determined the local microenvironment that surrounds a series of fluorescent solutes dissolved in a 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) as a function of temperature and added CO_2 (T = 308 K; P = 0-150 bar). In dry [bmim][PF_6] at 293 K, the cybotactic region exhibits a dielectric constant and refractive index of 11.4 ± 1.0 and 1.523 ± 0.025, respectively. Interestingly, even though CO_2 is highly soluble in [bmim][PF_6] (CO_2 mole fraction = 0.6 at 313 K and 68 bar), addition of up to 150 bar CO_2 to [bmim][PF_6] at 308 K caused the solute's cybotactic region dipolarity to decrease by less than 15 %.

Solvatochromic measurements have been used to determine the $E_T(30)$ values and Kamlet-Taft solvent parameters [bmim][PF_6] as a function of temperature (10 - 70 °C) and water content. The results show that dry [bmim][PF_6] exhibits a hydrogen bond donor strength on the order of short chain alcohols with a linear temperature dependence. Dry and wet [bmim][PF_6] exhibit hydrogen bond acceptor abilities, that are weak functions of temperature, intermediate between that of water and acetonitrile. The π^* parameter for wet and dry [bmim][PF_6] is higher than short chain alcohols, but lower than water or DMSO at ambient conditions, and it exhibits a strong linear temperature dependence.

We have reported the picosecond time-resolved fluorescence of 6-propionyl-2-(*N,N*-dimethylamino)naphthalene (PRODAN) dissolved in [bmim][PF_6] at 298 K as a function of solubilized water in the [bmim][PF_6] phase. The observed solvent relaxation dynamics can be described by three components with apparent relaxation times that occur over a large time regime (< 15 ps to > 10 ns). The average relaxation dynamics become faster as the water concentration in the [bmim][PF_6] phase increases. Libration and vibration, ion ballistic motion, ion local basin exploration, and ion basin hoping, ion diffusion, and/or the ultrafast relaxation from water (or other small molecules/impurities) are suggested as possible reasons for the yet unquantified sub-15 ps dynamics. The sub-ns dynamics are consistent with [PF_6] anion relaxation. This process is water dependent, slowing as the amount of solubilized water in the [bmim][PF_6] phase increases. We speculate that this slowing arises from the formation of 1:2 H-bonded [PF_6]-HOH-[PF_6] complexes. The ns dynamics are consistent with the cation, decreasing slightly with an increase in the amount of solubilized water.

Plans for future research on this project. (1) Studies on oligomer/polymer tail and junction point accessibility, dynamics, and mobility in pure and cosolvent-modified scCO_2. (2) Solute-fluid interactions at interfaces in contact with pure and cosolvent-modified scCO_2. (3) Solvent properties of room temperature ionic liquids as a function of dissolved cosolvents and pure CO_2.

Publications Acknowledging DOE Support – 2002-3

[1] S. Pandey, M.A. Kane, G.A. Baker, F.V. Bright, A. Fürstner, G. Seidel and W. Leitner, “The Photophysics of 6-(1-Pyrenyl)hexyl-11(1-pyrenyl)undecanoate Dissolved in Neat Liquids and Supercritical Carbon Dioxide: Impact on Olefin Metathesis,” *J. Phys. Chem. B* **2002** *106*, 1820-1832.
[2] S.N. Baker, G.A. Baker and F.V. Bright, “Temperature-Dependent Microscopic Solvent Properties of ‘Dry’ and ‘Wet’ 1-Butyl-3-methylimidazolium Hexafluorophosphate: Correlation with $E_T(30)$ and Kamlet-Taft Polarity Scales,” *Green Chemistry* **2002** *4*, 169-169.
[3] C.M. Cardona, T. Wilkes, W. Ong, A.E. Kaifer, T. Donovan-McCarley, S. Pandey, G.A. Baker, M.A. Kane, S.N. Baker and F.V. Bright, “Dendrimers Functionalized with a Single Pyrene Label: Synthesis, Photophysics and Fluorescence Quenching,” *J. Phys. Chem. B* **2002** *106*, 8649-8656.
[4] S.N. Baker, G.A. Baker, C.A. Munson, F. Chen, E.J. Bukowski, A.N. Cartwright, and F.V. Bright, “Effects of Solubilized Water on the Relaxation Dynamics Surrounding 6-propionyl-2-(N,N-dimethylamino)naphthalene Dissolved in 1-Butyl-3-methylimidazolium Hexafluorophosphate at 298 K,” *Ind. Engr. Chem.* **2003** *42*, 6457-6463.
[5] F.V. Bright and C.A. Munson, “Time-Resolved Fluorescence Spectroscopy for Illuminating Complex Systems,” *Anal. Chim. Acta* **2003** *500*, 71-104.
[6] C.A. Munson, G.A. Baker, S.N. Baker and F.V. Bright, “Effects of Sub-Zero Temperatures on Fluorescent Probes Sequestered within Aerosol-OT Reverse Micelles,” *Langmuir*, **2004** in press.

2004 DOE/BES Analysis Program
Contractors' Meeting

Registration List

2004 DOE/BES Analysis Program Contractors' Meeting

Last Name	First Name	Organization	Address	City	State	Zip Code	Phone	Fax	E-Mail	Abstract
Barnes	Michael	Oak Ridge National Laboratory	P.O. Box 2008, MS-6142	Oak Ridge	TN	37831	865-574-4923	865-574-8363	barnesmd1@ornl.gov	S5-1
Bohn	Paul	University of Illinois at Urbana-Champaign	Chemistry Dept., Box 62-5 Roger Adams Lab 600 S. Mathews Avenue	Urbana	IL	61801	217-333-0676	217-244-8068	bohn@scs.uiuc.edu	S7-1
Borguet	Eric	University of Pittsburgh	Department of Chemistry	Pittsburgh	PA	15260	412-621-6024	412-621-8611	borguet@pitt.edu	S3-3
Bowers	Michael	University of California - Santa Barbara	Department of Chemistry & Biochemistry	Santa Barbara	CA	93106-9510	805-893-2893	805-893-8703	bowers@chem.ucsb.edu	P2
Bright	Frank	University of Buffalo, The State University of New York	511 Natural Sciences Complex	Buffalo	NY	14260-3000	716-645-6800 Ext. 2162	716-645-6963	chefvb@acsu.buffalo.edu	S7-4
Buchanan	Michelle	Oak Ridge National Laboratory	P.O. Box 2008, MS-6129	Oak Ridge	TN	37831-6129	865-574-4986	865-574-4902	buchananmv@ornl.gov	
Bushaw	Bruce	Pacific Northwest National Laboratory	P.O. Box 999, MSIN K3-58	Richland	WA	99352	509-375-2209		bruce.bushaw@pnl.gov	S5-2
Crooks	Richard	Texas A&M University	Department of Chemistry P.O. Box 30012	College Station	TX	77842-3012	979-845-5629	979-845-1399	crooks@tamu.edu	S3-1
Dai	Sheng	Oak Ridge National Laboratory	1 Bethel Valley Road	Oak Ridge	TN	37831	865-576-7307		dais@ornl.gov	
Delmore	James	Idaho National Engineering and Environmental Laboratory	Box 1625	Idaho Falls	ID	83415-2208	208-526-2820	208-526-8541	jed2@inel.gov	S4-6
Dickinson	Tom	Washington State University	Department of Physics	Pullman	WA	99164	509-335-4914	509-335-7816	jtd@wsu.edu	S1-2
Diebold	Gerald	Brown University	Department Chemistry, Box H	Providence	RI	02912	401-863-3586	401-863-2594	Gerald_Diebold@Brown.edu	S6-2
Duckworth	Douglas	Oak Ridge National Laboratory	P.O. Box 2008, MS-6131	Oak Ridge	TN	37831	865-576-6296	865-574-6906	duckworthdc@ornl.gov	S4-4
Eyring	Edward	University of Utah	315 S 1400 East	Salt Lake City	UT	84112-0850	801-581-8658	801-587-9919	eyring@chem.utah.edu	S5-4
Farnsworth	Paul	Brigham Young University	Department of Chemistry and Biochemistry	Provo	UT	84058	801-422-6502	801-422-0153	paul_farnsworth@byu.edu	S2-4
Fendler	Janos	Clarkson University	Center for Advanced Materials Processing - Box 5814	Potsdam	NY	13699-5814	315-268-7113	315-268-4416	fendler@clarkson.edu	S5-5
Futrell	Jean	Pacific Northwest National Laboratory	P.O. Box 999	Richland	WA	99352	509-372-4140	509-375-2698	jean.futrell@pnl.gov	S2-1
Gamez	Gerardo	Indiana University-Bloomington	Department of Chemistry 800 E. Kirkwood Avenue	Bloomington	IN	47405	812-855-7905	812-855-0958	ggamez@indiana.edu	S4-7
Goeringer	Douglas	Oak Ridge National Laboratory	P.O. Box 2008, MS-6131	Oak Ridge	TN	37831	865-574-3469	865-576-8559	goeringerde@ornl.gov	S4-2
Gornushkin	Igor	University of Florida	Department of Chemistry P.O. Box 117200	Gainesville	FL	32611	352-392-0792	352-392-4651	igorg@ufl.edu	

2004 DOE/BES Analysis Program Contractors' Meeting

Last Name	First Name	Organization	Address	City	State	Zip Code	Phone	Fax	E-Mail	Abstract
Guiochon	Georges	University of Tennessee	Department of Chemistry	Knoxville	TN	37996-1600	865-974-0733	865-974-2667	guiochon@novell.chem.utk.edu	S7-3
Harrison	Willard	University of Florida	Department of Chemistry	Gainesville	FL	32611	352-392-7009	352-392-4651	harrison@chem.ufl.edu	S1-5
Houk	Sam	Ames Laboratory	B27 Spedding Hall	Ames	IA	50011	515-294-9462	515-294-5233	rshouk@iastate.edu	S4-3
Hudson	Bruce	Syracuse University	1-014 Center for Science and Technology	Syracuse	NY	13244-4100	315-443-5805	315-443-4070	bshudson@syr.edu	S6-3
Hupp	Joseph	Northwestern University	Department of Chemistry 2145 Sheridan Road	Evanston	IL	60208	847-491-3504	847-491-7713	j-hupp@northwestern.edu	
Hurtubise	Robert	University of Wyoming	Department of Chemistry	Laramie	WY	82071	307-766-6241	307-766-2807	hurtubis@uwyo.edu	S5-6
Laskin	Julia	Pacific Northwest National Laboratory	P.O. Box 999, K8-88	Richland	WA	99352	509-376-4443	509-376-3650	Julia.Laskin@pnl.gov	S2-1
Maciel	Gary	Colorado State University	Department of Chemistry	Ft. Collins	CO	80523	970-491-6480	970-491-1801	maciel@lamar.colostate.edu	S6-1
McLuckey	Scott	Purdue University	560 Oval Drive	West Lafayette	IN	47907-2084	765-494-5270	765-494-0239	mcluckey@purdue.edu	S4-1
Miller	John	U.S. Department of Energy	Basic Energy Sciences 19901 Germantown Road	Germantown	MD	20874	310-903-5806		john.miller@science.doe.gov	
Millman	William	U.S. Department of Energy	Basic Energy Sciences 19901 Germantown Road	Germantown	MD	20874	301-903-5805	301-903-4110	villiam.millman@science.doe.gov	
Montaser	Akbar	George Washington University	Department of Chemistry	Washington	DC	20052	202-994-6480	202-994-2298	montaser@gwu.edu	S2-6
Noll	Robert	Purdue University	560 Oval Drive	West Lafayette	IN	47907	765-494-5265	765-494-9421	rnoll@purdue.edu	S2-5
Omenetto	Nicolo'	University of Florida	Department of Chemistry P.O. Box 117200	Gainesville	FL	32611	352-392-9853	352-392-5362	omenetto@chem.ufl.edu	S1-3
Pemberton	Jeanne	University of Arizona	Department of Chemistry	Tucson	AZ	85721	520-621-8245	520-621-8248	pembertn@u.arizonia.edu	S5-3
Pitts	Leslie	DOE/NNSA/NA-22 Office of Nonproliferation Research and Eng.	1000 Independence Avenue S.W.	Washington	DC	20585	202-586-7994	202-586-0485	les.pitts@hq.doe.gov	
Porter	Marc	Iowa State University	42 Spedding Hall	Ames	IA	50011-3020	515-294-6433	515-294-3254	mporter@porter1.ameslab.gov	S3-2
Russell	David	Texas A&M University	3255 TAMU, Department of Chemistry	College Station	TX	77843-3255	979-845-3345	979-845-9485	russell@mail.chem.tamu.edu	S2-2
Russo	Richard	Lawrence Berkeley National Laboratory	1 Cyclotron Road MS 70-108B	Berkeley	CA	94720	510-486-4258	510-486-7303	rerusso@lbl.gov	S1-1
Schaaff	T. Gregory	Oak Ridge National Laboratory	P.O. Box 2008, MS-6131	Oak Ridge	TN	37831	865-574-4878	865-576-8559	schaaffg@ornl.gov	S2-3
Shaw	Robert	Oak Ridge National Laboratory	P.O. Box 2008, MS-6142	Oak Ridge	TN	37831	865-574-4920	865-574-8363	shawrw@ornl.gov	
Smith	Ben	University of Florida	Box 117200 Chemistry	Gainesville	FL	32611	352-392-0256	352-846-2298	bwsmith@ufl.edu	S1-3

2004 DOE/BES Analysis Program Contractors' Meeting

Last Name	First Name	Organization	Address	City	State	Zip Code	Phone	Fax	E-Mail	Abstract
Svanberg	Sune	Lund Institute of Technology	Department of Physics, P.O. Box 118	Lund	Sweden	SE-2001 00	+46-46-2227650	+46-46-2224250	sune.svanberg@fysik.lth.se	P1
Talamini	Karen	U.S. Department of Energy	Basic Energy Sciences 19901 Germantown Road	Germantown	MD	20874	301-903-4563	301-903-0271	karen.talamini@science.doe.gov	
Vertes	Akos	George Washington University	725 21st Street, N.W. Department of Chemistry	Washington	DC	20052	202-994-2717	202-994-5873	vertes@gwu.edu	S1-4
Whitten	William	Oak Ridge National Laboratory	P.O. Box 2008, MS-6142	Oak Ridge	TN	37831	865-574-4921	865-574-8363	whittenwb@ornl.gov	
Zelenyuk	Alla	Pacific Northwest National Laboratory	P.O. Box 999	Richland	WA	99352	509-376-7696		alla.zelenyuk@pnl.gov	S1-6