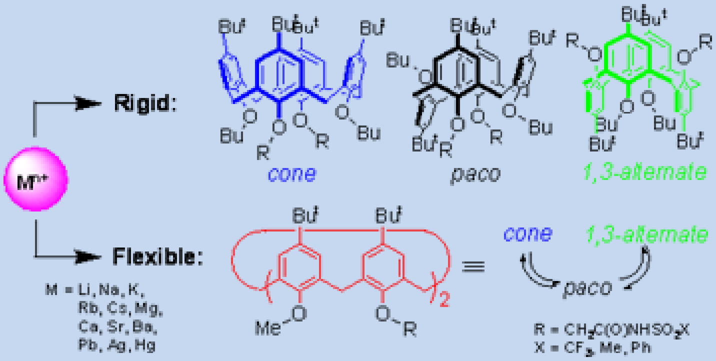


Program and Abstracts

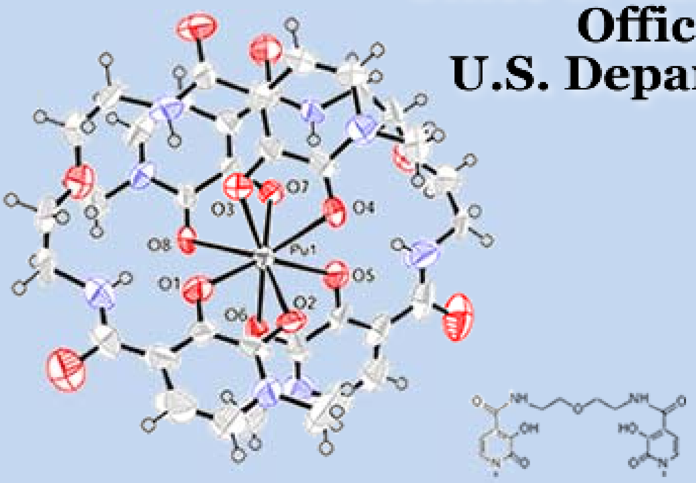
Separations Program
Heavy Element Chemistry Program

Contractors' Meeting

Doubletree Hotel
Rockville, Maryland

April 27-30, 2005

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



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Cover graphics:

Rigid and flexible calixarene-based ligands for selective metal ion separations (see abstract by BARTSCH et al.)

Molecular structure of Pu(IV)-hyrdroxypyridonatye complex, a model for actinide decorporation agents (see abstract by GORDEN et al.)

This document describes activities performed under contract number DE-AC05-00OR22750 between the U.S. Department of Energy and Oak Ridge Associated Universities.

FOREWORD

This abstract booklet provides a record of the sixth U.S. Department of Energy (DOE) contractors' meeting in separations sciences and the third in heavy element chemistry. The Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences and its predecessors have sponsored research in heavy element chemistry and separations sciences for some sixty years. Although these are distinct disciplines, they have much in common for many reasons, in particular because novel separations research is needed to produce pure heavy-element samples and because heavy element chemistry provides the basis for many separations processes. In addition, separation processes are major industrial sources of energy consumption and waste generation. This is the second joint meeting of these programs.

The objective of this meeting is to provide a fruitful environment in which researchers with common interests will present and exchange information about their activities, will build collaborations among research groups with mutually reinforcing strengths, will identify needs of the research community, and will focus on opportunities for future research directions. The agenda has keynote talks, oral presentations, and posters, organized so that papers in related disciplines – such as ligand design, theory and bonding, and interfacial science – are loosely clustered together. With ample time for discussion and interactions, we emphasize that this is an informal meeting for exchange of information and building of collaborations; it is not a review of researchers' achievements or a forum to choose future directions.

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

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

We thank Diane Marceau of the Chemical Sciences, Geosciences and Biosciences Division, and Sophia Kitts and Kellye Sliger of the Oak Ridge Institute for Science and Education for the technical and logistical features of this meeting.

William S. Millman

Gregory J. Fiechtner

Lester R. Morss

Norman Edelstein

Meeting Overview

Time	Wednesday, April 27	Thursday, April 28	Friday, April 29	Saturday, April 30
7 a.m.		Continental Breakfast *Regency Foyer*	Continental Breakfast *Regency Foyer*	Continental Breakfast *Regency Foyer*
8 a.m.		(8:30) Welcome and Intro's: Walt Stevens, John Miller (8:45) Keynote: Bruce Bursten	Keynote: Mike Ramsey Oral Session 4: Theory and Bonding *Plaza*	Oral session 6 Polymers, Solutions, Thermodynamics *Plaza*
9 a.m.				
10 a.m.		(9:45 – 10:10) Coffee Break	(10:30 – 11:00) Coffee Break	Discussion: Highlights and Opportunities for New Directions
11 a.m.		Oral Session 1 Ligand Design *Plaza*	Oral Session 4 cont'd.	
noon		Lunch *Plaza*	Lunch *Plaza*	Lunch *Atrium* (Meeting adjourned)
1 p.m.		Oral Session 2 Coordination Chemistry *Plaza*	Oral Session 5 Surfaces and Interfaces *Plaza*	
2 p.m.				
3 p.m.		(3:00 – 3:30) Coffee Break		
4 p.m.		Poster Session 1 *Regency/Randolph*	Poster Session 2 *Regency/Randolph*	
5 p.m.				
6 p.m.	Reg. begins *Regency Foyer* PI's Setup 1st set Posters *Regency* Cash Bar *Plaza*	Cash bar *Plaza* Wrkg. Dinner *Plaza* PI's Setup 2nd set Posters *Regency*	Dinner and evening on your own	
7 p.m.	No host Dinner *Plaza*	Oral Session 3 Synthesis *Plaza*		
8 p.m.				
9 p.m.				

DOE Heavy Element Chemistry-Separations Contractors' Meeting
Rockville (MD) Doubletree Hotel, April 27-30, 2005
Agenda

Wednesday April 27

Registration and cash bar 6:00 – 7:00 pm, followed by no-host dinner at Rockville Doubletree for those interested

Thursday April 28

8:30 *Welcome and Introductions* (Walt Stevens, John Miller)
8:45 *Keynote lecture 1:* Bruce Bursten – From Large Molecules to Small Molecules to Grand Challenges: A Personal Perspective on Molecular Electronic Structure Theory Applied to Heavy Element Chemistry

9:45 *Coffee break*

Oral session 1: Ligand design
10:10 O1-1 Bosnich – Weak Force Generated Allosteric Effects
10:30 O1-2 Alexandratos – Ion-Selective Polymer-Supported Reagents: Tuning Ionic Affinities of Primary Ligands with Auxiliary Groups
10:50 O1-3 Paine – Preorganized and Immobilized Ligands for Metal Ion Separations
11:10 O1-4 Raymond – Actinide Coordination Chemistry: from just Super to Supramolecular
11:30 O1-5 Sessler – Actinide Coordination to Expanded Porphyrins
11:50 *Discussion*

12:00 *Working lunch*

Oral session 2: Coordination chemistry
1:00 O2-1 Hupp – Supramolecular-Coordination-Chemistry-Derived Membranes Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities
1:20 O2-2 Bartsch – New Proton-Ionizable Calixarene-Based Ligands for Selective Metal Ion Separations
1:40 O2-3 Davis – Self-Assembled Ionophores
2:00 O2-4 Assefa – Syntheses, X-ray crystallography, Raman and luminescence studies of coordination polymers of actinides and group 11 dicyanides
2:20 O2-5 Meyer – CO/CO2 Activation and Nitrogen-Atom Transfer Chemistry Utilizing Low- and High-Valent Uranium Coordination Complexes
2:40 O2-6 Kiplinger – Tuning Metal-Ligand Bonding Interactions and Novel Reactivity Patterns in Organometallic Actinide Complexes
3:00 *Discussion*

3:10 *Coffee break*

3:30-5:30 *Poster session 1*
P1-1 Belfort – Chemical Interactions Between Protein Molecules and Polymer Materials
P1-2 Burns/Soderholm – Actinide Aggregation Studies
P1-3 Choppin – Actinide Research: Cyclohexyl Separation Agents and Room Temperature Ionic Liquids
P1-4 Dorhout/Selby – Syntheses, Structures, and Physical Properties of K/Cu/An(Th,U)/S Phases: $KCuAnS_3$, $K_2Cu_2AnS_4$, $K_3Cu_3Th_2S_7$, and $K_3Cu_2US_6$
P1-5 Freeman – Nanostructured Hybrid Materials for Advanced Membrane Separations
P1-6 Gorden – Plutonium Encaged: The First Structurally Characterized Pu-Hydroxypyridonate Complex
P1-7 Haire – Probing the Bonding and Electronic Nature of Actinides
P1-8 Heaven – Spectroscopic Studies of Prototype Actinide Compounds
P1-9 Miller – Flotation Chemistry of Soluble Salt Minerals
P1-10 Moody/Stoyer – Production and Chemical Properties of the Heaviest Elements
P1-11 Nitsche – Heavy Element Nuclear and Radiochemistry
P1-12 Pemberton – Vibrational Spectroscopy of Chromatographic Interfaces
P1-13 Scuseria – Non-stoichiometry and magnetic ordering in plutonium oxides: A hybrid density functional theory study
P1-14 Wirth – Spectroscopic probing of the function of membrane proteins

6:00-7:00 *Working dinner*

Oral session 3: Synthesis

7:00 O3-1 Yaghi/Sudik – Metal-Organic Frameworks and Polyhedra for Separation of Gases and Organic Molecules
7:20 O3-2 Clearfield – The Synthesis, Structures and Chemical Properties of Macrocyclic Ligands Covalently Bonded into Layered Arrays
7:40 O3-3 Bruening – Investigation of Size-Selective Separations and Mitigation of Fouling by Multilayer Polyelectrolyte Membranes
8:00 O3-4 Custelcean – Principles of Chemical Recognition and Transport in Extractive Separations: Metal- Organic Frameworks as Solid-Phase Anion Exchangers
8:20 O3-5 Albrecht-Schmitt – Synthesis, Structure, and Ion-Exchange Properties of Open-Framework Actinyl Materials
8:40 O3-6 Ibers – Actinide Transition-Metal Chalcogenides and Pnictides
9:00 *Discussion*

Friday April 29

8:00 *Keynote lecture 2:* Mike Ramsey – Molecular Transport Through Fabricated Nanoscale Channels

Oral session 4: Theory and Bonding

9:00 O4-1 B. Hay – Principles of Chemical Recognition and Transport in Extractive Separations: Molecular Modeling and Host Design
9:20 O4-2 Batista – Theoretical Studies of Thermochemistry and Excited States of Actinide Complexes
9:40 O4-3 Scuseria – All-electron relativistic methods for molecules and extended systems
10:00 O4-4 Ray – A Fully-Relativistic Density Functional Study of the Role of 5f Electrons in Chemical Bonding in Transuranium Elements
10:20 *Discussion*

10:30 *Coffee break*

11:00 O4-5 Conradson – Intrinsic Nanoscience: Nanoscale Heterogeneity and Collective Properties of Complex Materials
11:20 O4-6 Jensen – Understanding Bonding in Actinide-Soft Donor Complexes
11:40 O4-7 Gibson – Gas-Phase Actinide Ion Chemistry—Reaction Kinetics and Molecular Thermodynamics

12:00-1:00 *Working lunch*

Oral session 5: Surfaces and interfaces

1:00 O5-1 Koros – Thickness & History Dependent Effects on Crosslinked Polyimide Membrane Materials for Natural Gas Separation
1:20 O5-2 Yeung – Motion of Single DNA Molecules at a Liquid-Solid Interface as Revealed by Variable-Angle Evanescent-Field Microscopy
1:40 O5-3 Blanchard – Chemical Selectivity and Reactivity within Ultrathin Layered Polymer Structures
2:00 O5-4 Antonio – f-Ion–Polyoxometalate Interactions
2:20 O5-5 Soderholm – X-Ray Studies of Actinide-Ion Speciation
2:40 O5-6 Bohn – Molecular Aspects of Transport in Thin Films of Controlled Architecture
3:00 O5-7 Booth – Intermediate-valence Ground States in Cerocene and Selected Ytterbocenes
3:20 O5-8 Way – Investigation of Transport Mechanisms in Surface Modified Inorganic Membranes
3:40 O5-9 Dai – Chemistry of Novel Separation

4:00-6:00 *Poster session 2*
P2-1 Bursten – The Electronic Structure of Heavy Element Complexes
P2-2 Duckworth – Electrochemically-Modulated Separation of Uranium and Plutonium
P2-3 Ewing/Lian – Radiation Effects and Thermal Stability of Murataite Ceramics as Candidate Nuclear Waste Forms
P2-4 Grey – Joint NMR and Diffraction Studies of Catalyst Structure and Binding
P2-5 Harris – Spectroscopic Methods to Characterize Adsorption and Binding to Surface-Immobilized Ligands
P2-6 Houk – Chemical Analysis at Nanodomains: Inorganic Mass Spectrometry with ICP and Electrospray Ionization Sources
P2-7 Liu – The Impact of Ion-Phonon Interaction on f-Element Chemistry
P2-8 Maciel – Multinuclear Magnetic Resonance Study of Silica and Modified Silica (Derivatization of Silica by PCl_5)
P2-9 Moyer – Principles of Chemical Recognition and Transport in Extractive Separations: Selectivity in Liquid-Liquid Extraction of Anions
P2-10 Pitzer – f-shell Calculations: Er^{3+}:GaN and CUO
P2-11 Sepaniak – Advancing the Capabilities of SERS in Chemical Analysis
P2-12 Shuh – Soft X-ray Synchrotron Radiation Investigations of Actinide Materials

Dinner and evening on your own

Saturday April 30
Oral session 6: Polymers, solutions, thermodynamics
8:00 O6-1 Rogers – Alternative (Potentially Green) Separations Media: Aqueous Biphasic and Related Systems - Extending the Frontier
8:20 O6-2 Basaran – Fundamentals of Electric Field-Enhanced Multiphase Separations and Analysis
8:40 O6-3 Rao – Actinide Solution Chemistry: Chemical Thermodynamics and Structure of Actinide Complexes in Solution
9:00 O6-4 Dietz – Probing Metal-Ligand Interactions with Neoteric Solvent Systems
9:20 O6-5 Chiarizia – Organization of Solutes in Solvent Extraction
9:40 O6-6 Bright – Studies of Solvation Processes in Supercritical Fluids and Ionic Liquids
10:00 O6-7 Yonker – Fundamental Phase Partitioning for Supercritical Fluids

10:20-12:00 *Highlights and opportunities for new directions*

Table of Contents

Keynote lecture 1

Oral session 1: Ligand design

Oral session 2: Coordination chemistry

Poster session 1

Oral session 3: Synthesis

Keynote lecture 2

Oral session 4: Theory and Bonding

Oral session 5: Surfaces and interfaces

Poster session 2

Oral session 6: Polymers, solutions, thermodynamics

Keynote Lecture 1:

Bruce Bursten – From Large Molecules to Small Molecules to Grand Challenges: A Personal Perspective on Molecular Electronic Structure Theory Applied to Heavy Element Chemistry

From Large Molecules to Small Molecules to Grand Challenges: A Personal Perspective on Molecular Electronic Structure Theory Applied to Heavy Element Chemistry

Keynote Lecture
2005 DOE Heavy-Element Chemistry–Separations Contractors' Meeting

Bruce E. Bursten
Department of Chemistry
The Ohio State University
Columbus, OH 43220
bursten.1@osu.edu

The application of molecular electronic structure theory to probe the structure, bonding, and energetics of actinide and transactinide complexes has developed in concert with the experimental studies of these systems. Insofar as many of the heavy elements are difficult or impossible to explore experimentally, electronic structure theory is arguably more important for advancing heavy-element science than it is for any other part of the periodic table. Further, the application of molecular electronic structure theory to actinide and transactinide complexes offers challenges not found in other parts of the periodic table, and so provides an opportunity for advancing theoretical methods and computational techniques.

In this lecture, the author will present some of his views concerning the past, present and future of theoretical contributions to heavy-element chemistry and actinide science. The systems discussed will include large organometallic complexes that provide similarities and contrasts to analogous organotransition-metal complexes and small actinide-containing molecules formed experimentally by laser ablation and matrix isolation, both of which have been studied extensively by the author and his group. Finally, he will offer some thoughts on the future of molecular electronic structure as applied to heavy-element complexes, including some of the grand (and not-so-grand but still very interesting!) challenges that this field might ultimately be able to address.

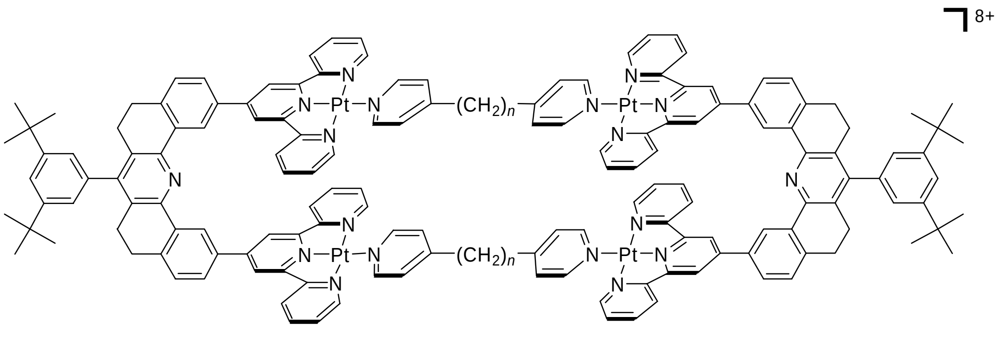
Oral Session 1:

Ligand Design

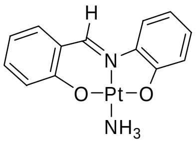
Weak Force Generated Allosteric Effects

B. Bosnich
James D Crowley
Department of Chemistry, The University of Chicago.
bos5@uchicago.edu

Biological systems use allosterism to regulate their activity. Positive allosterism arises when, for example, a receptor bearing two identical sites has the second stability constant for guest association larger than that of the first. Allosterism is caused by mechanical coupling between the sites, so that after the first association, conformational changes occur which "prime" the other site for association. Initial attempts to achieve allosterism in synthetic systems involved the synthesis of binucleating ligands which bind metals in two complexation sites; binding in the first-site causes the second site to dispose its donor atoms correctly for complexation of the second metal. Many examples of metal coordination-induced allosterism are known. Recently, the somewhat more subtle effects of hydrogen bonding-induced allosterism have been deployed in a few cases but, as far as we are aware, no examples have been described in which weak π-stacking interactions were used for allosterism. We describe such examples here.



1 (n = 0) **2** (n = 2) $(SbF_6^-)_8$



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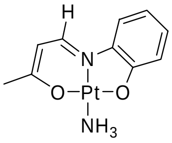

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The two rectangular receptors, **1** and **2** have identical clefts formed by the terpy-Pt-units. These clefts can incarcerate the guests, **3** and **4**, giving 1:2 host-guest adducts. The statistically normalized association constants are given in the Table. Within experimental error, the two constants for the **1-(3)$_2$** adduct, as well as those for the **2-(3)$_2$** adduct are all the same. No allosterism is observed for these systems. Adducts, **1-(4)$_2$** and **2-(4)$_2$**, however, show substantial allosterism, 3.58 and 4.58 respectively. ^{1}H NOESY spectra indicate that, for the adduct, **1-(3)$_2$**, the guest does not form weak Pt-Pt bonds but that the **1-(4)$_2$** adduct does, suggesting that the receptor, **1**, provides a better fit for the guest **4** than for the guest **3**. The "better fit" of the smaller guest, **4**, is likely to promote greater mechanical coupling between the binding sites because the receptor can conformationally adjust fully to the incarceration of the first guest, which, in turn, will adjust the other site favorably for binding. When the guest is larger, as for **3**, the guest cannot fully insert into the molecular clefts and, consequently, the binding affinity is likely to be less sensitive to conformation coupling between the two sites.

Table: Microscopic Stability Constants (M^{-1}) for Host-Guest Formation

Adduct	K_1	K_2	K_2/K_1
1-(3)$_2$	4,100M^{-1} ± 200	4,200M^{-1} ± 200	1.02
2-(3)$_2$	3,800M^{-1} ± 300	4,400M^{-1} ± 100	1.15
1-(4)$_2$	1,450M^{-1} ± 200	5,200M^{-1} ± 400	3.58
2-(4)$_2$	1,250M^{-1} ± 200	5,600M^{-1} ± 400	4.58

These results are important because they represent the first synthetic example where weak forces involving π-π interactions and, possibly, Pt-Pt interactions, are deployed for positive allosterism in homotopic receptors.

References of work supported by this project.

1. James D. Crowley, Andrew J. Goshe and B. Bosnich, "Molecular Recognition. Electrostatic Effects in Supramolecular Self-assembly." *Chem. Comm.,* **2003,** 392-393.
2. Andrew J. Goshe, Ian M. Steele and B. Bosnich, "Supramolecular Recognition. Terpyridal Palladium and Platinum Molecular Clefts and their Association with Planar Platinum Complexes." *J. Am. Chem. Soc.* **2003,** *125*, 444-451.
3. J.D. Crowley, A.J. Goshe and B. Bosnich, "Molecular Recognition. Self-assembly of Molecular Trigonal Prisms and their Host-guest Complexes." *Chem. Commun.* **2003,** 2824-2825.
4. A.L. Gavrilova and B. Bosnich, "Principles of Mononuclear and Binuclear Design." *Chem. Rev.* **2004,** *104*, 349-383
5. J.D. Crowley, A.J. Goshe, I.M. Steele and B. Bosnich, "Supramolecular Recognition. Protonmotive Driven Switches or Motors?" *Chem. Eur. J.* **2004,** *10*, 1944-1955.
6. A.J. Goshe and B. Bosnich, "Supramolecular Chemistry. Solution and Solid State Stacking of Square Planar Metal Complexes." *Inorg. Chim. Acta.* **2004**, *357*,4544-4551.
7. J. D. Crowley and B. Bosnich, "Molecular Recognition. Use of Metal-containing Molecular Clefts for Supramolecular Self-assembly and for Host-Guest Formation." *Eur. J. Inorg. Chem.* **2005**, accepted.
8. J.D. Crowley, I.M. Steele and B. Bosnich, "Supramolecular Recognition Forces: An Examination of Weak Metal-Metal Interactions in Host-Guest Formation." *Inorg. Chem.* **2005**, accepted.

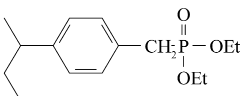
Ion-Selective Polymer-Supported Reagents: Tuning Ionic Affinities of Primary Ligands with Auxiliary Groups

Spiro D. Alexandratos
Xiaoping Zhu
Department of Chemistry
Hunter College of the City University of New York
alexsd@hunter.cuny.edu

Overall research goals: The objective of this research is to develop a fundamental understanding of designing ion-selective polymers. A significant amount of research has been done immobilizing coordinating[1,2] and anion exchange[3] ligands onto polymer supports, as well as sorbing complexants within macroporous supports.[4] Bifunctionality is one design variable that has been found to be particularly important in the preparation of ion-selective polymers with rapid complexation kinetics and the mechanism for achieving this has been studied.[5] The method by which bifunctionality can be used to tune the ionic selectivity of a given ligand is now the focus of our research.[6]

Significant achievements in 2003-2005: Ion-complexing ligands are most often immobilized onto crosslinked poly(vinylbenzyl chloride) [polyVBC] beads through nucleophilic substitution reactions. It is important that such reactions yield the expected ligands with no side-reactions resulting in unidentified groups. In the reactions we were to run, the commonly used solvent N,N-dimethylformamide (DMF) was preferred because of its compatibility with both the polymer and the reactants. Research during this period was able to determine that DMF is an inappropriate solvent for numerous nucleophilic reactions because of a hitherto unnoticed side reaction wherein the DMF aminates the polyVBC to form ion-complexing ligands. Other solvents, especially N-methylpyrollidone were recommended for reactions on polyVBC.[7]

A series of coordinating polymers were then synthesized by immobilizing polyols (ethylene glycol, glycerol, tris(hydroxymethyl)ethane, pentaerythritol, and pentaerythritol triethoxylate) onto crosslinked polyVBC (1 - 6), then monosubstituting with diethylphosphate ligands.[8] Ionic affinities were determined with a series of divalent transition metal ions: Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}. For each polymer, the variable controlling the affinity, as measured by the distribution coefficient, D, was found to be the polarizability of the transition metal ion, as measured by the Misono softness parameter, σ. For $D \geq 0$, $D = S\sigma + \sigma_{min}$, where S is the selectivity and σ_{min} is the minimum softness of a divalent transition metal ion which must be exceeded for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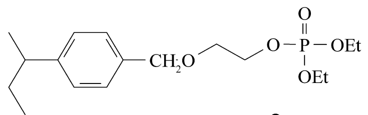
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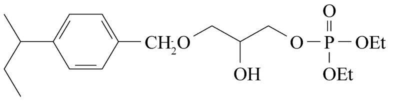
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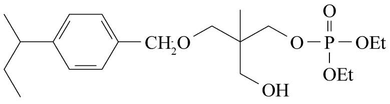
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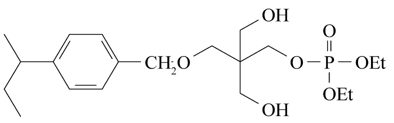
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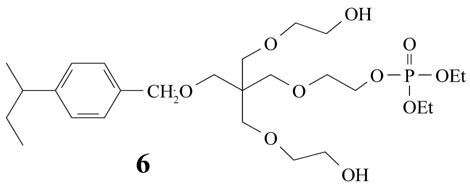
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coordination to occur. The values of S are 3810 (pentaerythritol), 1480 (pentaerythritol triethoxylate), 1340 (glycerol), 474 (tris(hydroxymethyl)ethane), and 21 (glycol); increasing S indicates greater selectivity. It is proposed that, though coordination occurs through the phosphate ligand, selectivity varies as a function of the polyol: the -OH groups act as auxiliary groups in modifying the polarizability of the phosphate ligands (the primary ligand) through hydrogen bonding and, as a result, varying the selectivity of the primary ligand. Interaction between the -OH and phosphate moieties is evident in FTIR spectra of the polymers with the absorbance of a band within the range 874-895 cm^{-1}.

Specific objectives for 2005-2006: The ability of auxiliary groups to affect the ionic selectivity of a given ligand will be investigated with sulfonate and carboxylate groups as the primary ligands and amines as the auxiliary groups. Concurrent with this research will be the study of Hg(II) - selectivity by simple amine resins.[9,10]

References of work supported by this project (2003 - 2005)

1. S.D. Alexandratos, C.L. Stine (2004) Ionic Recognition by Polymer-Supported Crown Ethers, *Reactive and Functional Polymers*, **60**, 3-16.
2. S.D. Alexandratos, C.L. Stine, R.A. Sachleben, B.A. Moyer (Dec. 2004) Immobilization of Lithium-Selective 14-Crown-4 on Crosslinked Polymer Supports, *Polymer*, submitted.
3. S.D. Alexandratos (2004) Polymer-Supported Reagents for Anionic Recognition, In "Fundamentals and Applications of Anion Separations" B.A. Moyer and R.P. Singh, Eds., Kluwer Academic: NY. pp. 169-177.
4. S.D. Alexandratos, S.D. Smith (2004) Metal Ion Complexation Kinetics of High-Stability Solvent-Impregnated Resins, *Solvent Extraction & Ion Exchange*, **22**, 713-720.
5. S.D. Alexandratos, S.D. Smith (2004) Intra-Ligand Cooperation in Metal Ion Binding by Immobilized Ligands: Effect of Bifunctionality, *Journal of Applied Polymer Science*, **91**, 463-468.
6. S.D. Alexandratos (Feb. 2005) New Polymer-Supported Ion-Complexing Agents: Design, Preparation and Metal Ion Affinities, Trans. Inst. Chem. Eng. Part B. Process Safety & Environmental Protection, submitted.
7. S.D. Alexandratos, X. Zhu (2003) Amination of Poly(vinylbenzyl chloride) with N,N-Dimethylformamide, *Macromolecules*, **36**, 3436-3439.
8. S.D. Alexandratos, X. Zhu (Jan. 2005) Bifunctional Coordinating Polymers: Auxiliary Groups as a Means of Modifying Ionic Affinities, *Macromolecules*, submitted.
9. X. Zhu, S.D. Alexandratos (Dec. 2004) Polystyrene-supported Amines: Affinity for Mercury(II) as a Function of the Pendant Groups, *Industrial & Engineering Chemistry Research*, submitted.
10. X. Zhu, S. D. Alexandratos (Feb. 2005) The Affinity and Selectivity of Immobilized N-methyl-D-glucamine for Mercury(II) Ions, *Macromolecular Chemistry and Physics*, in preparation.

Other references

L. Dambies, R. Salinaro, S.D. Alexandratos (2004) Immobilized N-Methyl-D-Glucamine as an Arsenate-Selective Resin, *Environmental Science and Technology*, 38, 6139-6146.

S.D. Alexandratos, L.D. Dambies, R. Salinaro (filed Sept. 7, 2004) Arsenic Removal *International Patent Application* No. PCT/US2004/028977.

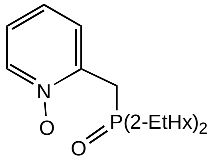
Preorganized and Immobilized Ligands for Metal Ion Separations

Robert T. Paine, Principal Investigator
Sylvie Pailloux, Sung-Joon Kim, Jean-Michael Camus, Postdoctorals
Sahrah Parveen, Graduate Student
Department of Chemistry, University of New Mexico, Albuquerque, NM 87131
rtpaine@unm.edu

Mary P. Neu, Los Alamos National Laboratory
Kenneth L. Nash, Washington State University
Benjamin P. Hay (Pacific Northwest National Laboratory)

Overall Research Goals: The objective of this project is the exploration of geometric and electronic factors that control the binding of f-block element ions to multifunctional receptor molecules. Coordination responses revealed in the studies are used to redesign new receptor molecules with properties appropriate to practical separations objectives in the DOE complex.

Significant Achievements in 2003-2005: In the preceding period we designed and synthesized a new family of organic ligands,[1] 2-(dialkylphosphinomethyl) pyridine N,P-dioxide **1** and 2,6-bis-(dialkylphosphinomethyl) pyridine N,P,P',trioxide **2**. The coordination chemistry of these ligands was explored with lanthanide(III), UO_2^{2+}, Th(IV) and Pu(IV) ions and it was discovered that the ligands present bidentate or tridentate coordination fields toward these ions. Furthermore, in collaboration with K. Nash (WSU), a detailed analysis of the extraction performance of **1** and **2** with R=2-ethylhexyl in toluene and n-dodecane solvents showed that these ligands are excellent liquid-liquid extractants for Am(III) and Eu(III) in strongly acidic (HNO_3) aqueous solutions.[2] Typical distribution ratio v.s. [HNO_3] plots are shown in Figure 1.



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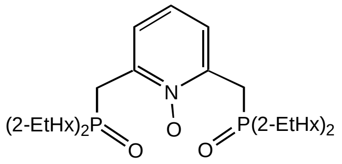

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The unique chelation and extraction properties revealed by ligands **1** and **2** have encouraged a second stage of ligand design and molecular synthesis on pyridyl phosphine oxide ligands and related platforms. The primary objectives in the 2003-2005 timeframe have been to 1) test additional steric/electronic modifications of **1** and **2**; 2) explore the synthesis of "softened" analogs of **1** and **2** and develop routes for attachment of **1-** and **2-**[1,3] type fragments to solid supports. The progress in the development of new phosphino methylpyridine N-oxides with new chelating platform arrangements has been very good. In particular, ligands **3-8** have been discovered and studies of the chelation chemistry with Ln(III) ions are in progress.

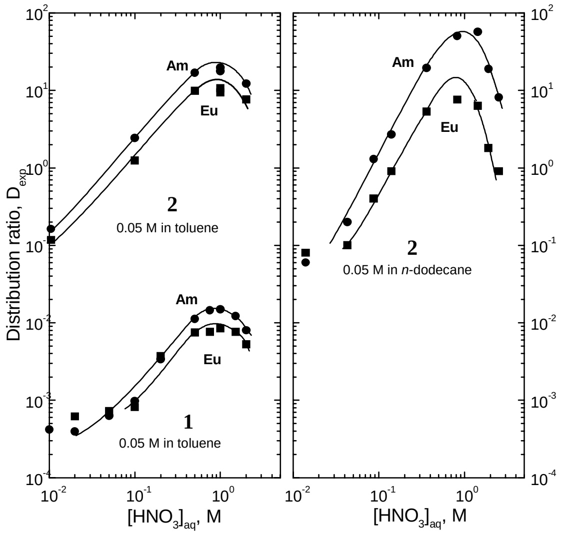
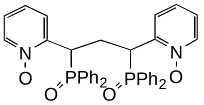


Figure 1. Dependence of the Am and Eu distribution ratios on HNO_3 concentration into toluene and dodecane solutions of **1** and **2**.



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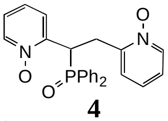

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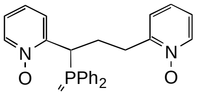

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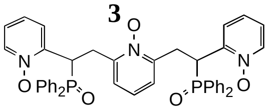

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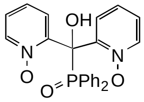

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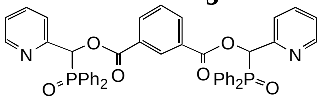

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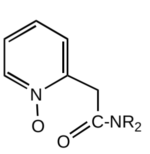
Several “softened” ligand targets have also been achieved. For example the thiophosphoryl analogs of **1** and **2** have been prepared and studies of the coordination chemistry with Pu(III) will start this year at LANL through collaboration with M. Neu. We have also set out to prepare amide analogs of **1** and **2** which should present softened chelation fields. For example, syntheses for **9** and **10** have been accomplished and coordination chemistry is in progress.

Specific Objectives for 2005-2006: The ligand development efforts described above will be continued and coordination chemistry will be more heavily emphasized in order to reveal novel coordination conditions. Additional extraction analyses will also be undertaken in order to determine the efficacy of the ligands in extractions.



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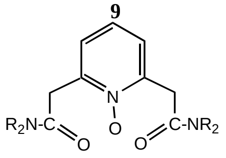

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References to Work Supported by this Project

1. X. Gan, R.T. Paine, E.N. Duesler and H. Nöth “Synthesis and Coordination Chemistry of Arene Soluble 4-Alkyl-2,6-bis[(diphenylphosphino)methyl] pyridine N,P,P´-trioxide Ligands” *J. Chem. Soc.* (Dalton) 153-159 (2003).
2. X. Gan, E.N. Duesler and R.T. Paine “Synthesis of Trifunctional Ligands Containing Thiophosphoryl, Pyridine and Pyridine N-oxide Donor Groups”, *J. Chem. Soc.*(Dalton), 4704-4708 (2003).
3. X. Gan, I. Binyamin, B.M. Rapko, J. Fox, E.N. Duesler and R.T. Paine “Layered Framework Structures Constructed from 2-(Pyridyl N-oxide) methylphosphonic Acid Ligands and Er (III). *Inorg. Chem*. **43**, 2443-2448 (2004).
4. X. Gan, B.M. Rapko, E.N. Duesler and R.T. Paine “Synthesis and Lanthanide Coordination Chemistry of 2,6-Bis[(dicyclohexylphosphino)methyl]pyridine N,P,P-Trioxide” *Polyhedron* **24**, 469-474 (2005).
5. I. Binyamin, B.M. Rapko and R.T. Paine “Synthesis of Propionamide Pyridine and Pyridine N-oxide Ligands” *Synthesis* submitted.

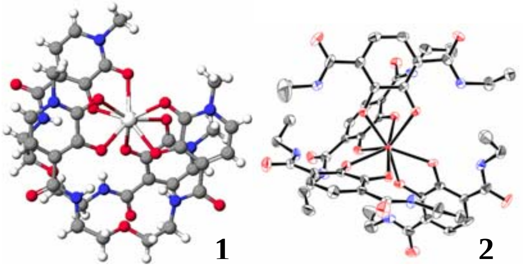
Other References Cited in Text:

1. X.Gan, E.N. Duesler and R.T. Paine, “Synthesis and Coordination Properties of New Bis(Phosphonomethyl) Pyridine N,P,P´ Trioxides,” *Inorg. Chem., 40*, 4420-4427 (2001).
2. K.L. Nash, C. Lavallette, M. Borkowski, R.T. Paine and X. Gan, “Features of the Thermodynamics of Two-Phase Distribution Reactions of Americium (III) and Europium (III) Nitrates into Solutions of 2,6-bis[(di-2-ethylhexylphosphino)methyl]pyridine-N,P,P-trioxide” *Inorg. Chem. 41*, 5849-5858 (2002).

Actinide Coordination Chemistry: from just Super to Supramolecular

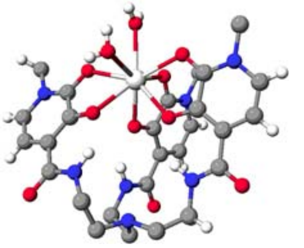
Kenneth N. Raymond, *Principal Investigator*
Jide Xu, *Staff Scientist,* Anne E. V. Gorden, John D. Gorden, *Postdoctoral Researchers*
Valérie Pierre, Géza Szigethy, Bryan E. F. Tiedemann, Eric Werner, *Graduate Students*
Seaborg Institute for Transactinium Science, Chemical Sciences Division, Lawrence Berkeley National Laboratory *and* Department of Chemistry, University of California, Berkeley CA
raymond@socrates.berkeley.edu *www.cchem.berkeley.edu/knrgrp/home.html*
Collaborators: Patricia W. Durbin, Linfeng Rao, David Shuh, *Principal Investigators*, Seaborg Institute for Transactinium Science, Chemical and Life Sciences Divisions, LBNL
Glenn E. Fryxell, Benjamin Hay, *Principal Investigators*, PNNL
Gordon D. Jarvinen, Norman C. Schroeder, Barbara F. Smith, *Principal Investigators* LANL

Overall Research Goals: Metal ion specific complexing agents play key roles in many areas of technology (e.g. industrial chelating agents, MRI enhancement agents, radiopharmaceuticals). Specific recognition of actinide ions is also an important goal but relatively little developed. Our approach to complexing Pu(IV) has been based on similarities in the chemical and biological properties of Fe(III) and Pu(IV).[1] The focus now is on the structural and thermodynamic characterization of the complexes of these ligands with actinides and lanthanides. More stereospecific ligands are being developed for oxo actinide cations. In another area, the formation of large molecular aggregates from smaller subunits, supramolecular chemistry, is an active field, with future applications that may include separation science and catalysis. However, there was no actinide supramolecular cluster reported in the literature. Our goal is to explore and develop actinide supramolecular chemistry.



Molecular structures of Ce(IV)-(5LIO-(Me-3,2-HOPO))$_2$(**1**) and Th(IV)-(ETAM)$_4$ (**2**) designed as models for Pu(IV) complexes of the sequestering agents with Pu(IV).

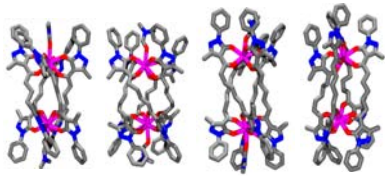
Significant Achievements in 2003 - 2005: This work is part of a program to study fundamental actinide coordination chemistry, with applications to waste remediation, actinide decorporation, and the development of ligands to selectively coordinate or extract actinides.[1] Complexes prepared with hydroxypyridonate (HOPO)[2] and terephthalamide (TAM)[5] ligands using Th(IV) as a model for Pu(IV) have provided information about the preferred coordination geometries of these systems. HOPO ligands have been investigated in both *in vivo*[3] and *in vitro*[4] to determine their potential utility in actinide decorporation. TAM and HOPO ligands have been developed and characterized as extraction agents for Pu(IV), both as ligands for use in liquid-liquid extractions[8] and incorporated into water soluble polymers[6] or mesoporous supports.[14]



Molecular structure of Gd(III) (TREN-Me-3,2-HOPO)(**3**), representative of potential MRI contrast agents with faster water exchange rates, high stability, and high selectivity over the physiologically important ions Ca(II), Zn(II), and Cu(II).

Studies using Gd(III) complexes as models for Am(III) resulted in a Gd(III)TREN-Me-3,2-HOPO(**3**) complex; unique in that it coordinates two water molecules in the inner sphere, endowing it with superior capabilities for use in MRI (magnetic resonance imaging). "Second Generation" contrast agents will use enhanced relaxivity through incorporation into dendrimers, proteins, or ligand modifications to enable a nine coordinate state allowing the system to coordinate three waters.[9-13] Lanthanide complexes of ortho diamide phenolate ligands are the basis for a new family of highly luminescent agents and the underlying photochemistry is being studied, with the goal of providing a rational basis for design of improved agents.

Specific Objectives of 2005-2006: We have recently reported the characterization of a series of Th(IV) hydroxypyridonate and terephthalamide complexes.[2, 5] Our current goal is to synthesize and characterize both in solution and structural studies the corresponding Pu(IV) complexes.[15] Toward this end, we will continue to investigate the solution behavior of bidentate 1,2-, and 3,2-hydroxypyridinonate and terephthalamide ligands with solution thermodynamic studies using spectrophotometric titrations and thermocalorimetry with these systems with Pu(IV) as well as studies with EXAFS (Extended X-ray Absorption Fine Structure) for comparison of the complexes in solution with the structures determined in the solid state using XRD. This work will be complemented by the design and characterization of new bis-HOPO complexes with rigid linkers for highly selective coordination of U(VI) and comparisons with Np(IV)/Np(V). In addition, we will design and synthesize new mixed HOPO-TAM ligands, and continue to evaluate these ligands as Dy(III) and Gd(III) complexes toward improved contrast agents for MRI.


Comparison of Thorium quadruple helicates with 4-acylpyrazolone ligands of different strand lengths

References of work that were supported by this project:

1. A. E. V. Gorden, J. Xu, K. N. Raymond, P. W. Durbin *Chem. Rev.* **2003**, *103*, 4207-4282.
2. J. Xu, D. W. Whisenhunt, Jr., A.C. Veeck, L. C. Uhlir, K.N. Raymond. *Inorg. Chem.* **2003**, *42*, 2665 - 2674.
3. P.W. Durbin, B. Kullgren, J. Xu, K. N. Raymond, M.-H. Hengè-Napoli, T. Bailly, R. Burgada. *Rad. Prot. Dosim*. **2003**, *105*, 503-508.
4. R. A. Guilmette, R. Hakimi, P.W. Durbin, J. Xu, K.N. Raymond, *Rad. Prot. Dosim*. **2003**, *105*, 527-534.
5. C. J. Gramer, K. N. Raymond, *Inorg. Chem.* **2004,** *43*, (20), 6397-6402.
6. C. J. Gramer, K.N. Raymond, G. Jarvinen, T. Robison, N. Schroeder, B. Smith, *Sep. Sci. Technol.*, **2004,** *39*, (2), 321-339.
7. J. Xu, A. E. V. Gorden, K. N. Raymond, *Eur. J. Org. Chem.* **2004**, (15), 3244-3253.
8. A.C. Veeck, D.J. White, D. W. Whisenhunt, Jr., J. Xu, A. E. V. Gorden, V. Romanovski, D. C. Hoffman, K.N. Raymond, *Solv. Extract. Ion Exch.*, **2004,** *22*, (6), 1037-1068.
9. J. Xu, D. G. Churchill, M. Botta; K. N. Raymond, *Inorg. Chem.*, **2004**, *43*, 5492-5494.
10. B. P. Hay, E. J. Werner, K. N. Raymond, *Bioconj. Chem.*, **2004,** *15*, 1496 – 1502.
11. V.C. Pierre, M. Melchior, D. M. J. Doble, K. N. Raymond, *Inorg. Chem*. **2004,** *43*, (26), 8520 - 8525.
12. K. N. Raymond, V.C. Pierre, *Bioconj. Chem.* **2005,** *16*¸(1), 3 - 8.
13. V.C. Pierre, M. Botta, K. N. Raymond, *J. Am. Chem. Soc.* **2005,** *127*, (2), 504 - 505.
14. Y. Lin, S. K. Fiskum, W. Yantasee, H. Wu, S. V. Mattigod, E. Vorpagel, G. E. Fryxell, K. N, Raymond, J. Xu, *Environ. Sci. Technol.*, **2005,** *39*, (5), 1332 - 1337.
15. A. E. V. Gorden, D. K. Shuh, B. E. F. Tiedemann, R.E. Wilson, J.Xu, K.N. Raymond, *Chem. Eur. J.*, **2005** (9), *in press.* [see meeting abstract and poster by A. Gorden]

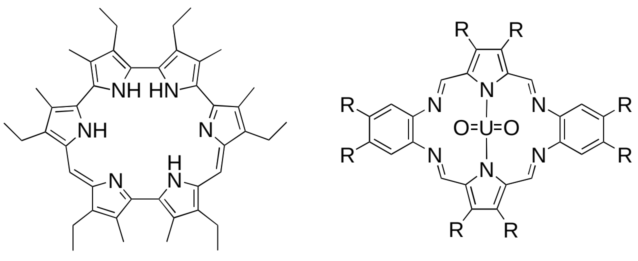
O1-5

Actinide Coordination to Expanded Porphyrins

Jonathan L. Sessler, Principal Investigator
Patricia Melfi, Amanda Hargrove, students
Department of Chemistry & Biochemistry
Institute for Cellular and Molecular Biology
The University of Texas at Austin
1 University Station A5300
Austin, TX 78712-0165 USA
sessler@mail.utexas.edu
http://www.cm.utexas.edu/sessler/

Collaborators: Drs. Mary Neu and Dave Clark, Institute for Transactinium Science and Los Alamos National Laboratory (LANL); Dr. Mark Dietz, Argonne National Laboratory (ANL); Dr. Duncan Bruce, University of Exeter; Dr. H. Neil Gray, University of Texas at Tyler

Overall research goals: The primary goal of this project is to generalize the finding that a specific expanded porphyrin, namely isoamethyrin, can coordinate the actinide cations uranyl(VI) and neptunyl(V) and trigger a colorimetric response by i) studying this system further and ii) preparing other expanded porphyrins that allow for the stabilization of complexes derived from these cations, as well as plutonyl(VI). In addition to this, an ancillary project goal is to investigate further and improve other promising systems that might allow for the so-called 'naked-eye' detection of actinide cations. A natural extension of this investigation will involve mapping out more fully in a general sense how such classic ligand "variables" as size, shape, donor number, charge, and ease of oxidation/reduction effect the actinide coordination process. A fundamental understanding of the differences in complexation characteristics (in both a kinetic and thermodynamic sense) displayed by the cations under investigation, U, Np and Pu, and also competing cations, such as the transition metals and lanthanides is necessary to achieve the long-range goal of having a useful optical sensor system that could function under various real-life conditions, including those associated with a response to a terrorist 'dirty bomb' attack. Towards this latter end, effort is being devoted to the development of methods that will allow such systems to be incorporated into so-called "smart materials", either through attachment to a solid support or through incorporation into liquid crystals.



Isoamethyrin

Alaskaphyrin

R = $O(CH_2)_9CH_3$, $O(CH_2)_{13}CH_3$

Significant achievements for 2003-2005:

Qualitative and initial quantitative studies were performed with the intent of investigating expanded porphyrins as easy-to-visualize sensors. It has been previously shown[3] that isoamethyrin undergoes an impressive color change upon actinide cation coordination. A preliminary study discussing the extent of uranyl complexation to isoamethyrin in relation to metal or ligand concentration has been published.[1] In addition, preliminary competition studies have shown that most common metals (Zn^{2+}, Mn^{2+}, Cd^{2+}, Ni^{2+}, Gd^{3+}) do not easily complex isoamethyrin with the exception of Cu^{2+}.

Towards the goal of the development of 'smart materials' the first uranyl liquid crystal has recently been reported by our group.[2] Uranyl alaskaphyrins (shown above) with varying alkyl chains produce discotic liquid crystals with columnar mesophases.

Specific Objectives for 2005-2006:

1) Explore the determinants of cation coordination selectivity, as a function of both changes in ligand type and, for a given ligand, as the cation is varied across the uranyl, neptunyl, and plutonyl series.
2) Investigate the kinetics and extent of complexation of the actinides with isoamethyrin.
3) Synthesize new actinide-coordinating expanded porphyrins.
4) Prepare more actinide-containing liquid crystals and study their properties.
5) Attachment of expanded porphyrins to solid supports and investigation of their reactivity.
6) Extend our coordination studies to the low valent actinides (U(III) and Pu(III)).

References:

1. Sessler, J. L.; Melfi, P. J.; Siedel, D.; Gorden, A. E. V.; Ford, D. K.; Palmer, P. D.; Tait, C. D. "Hexaphyrin(1.0.1.0.0.0). A new colorimetric actinide sensor" *Tetrahedron*, **2004**. *60*(49), 11089-11097.
2. Sessler, J. L.; Callaway, W. B.; Dudek, S. P.; Date, R. W.; Bruce, D. W. "Synthesis and Characterization of a Discotic Uranium-Containing Liquid Crystal," *Inorg. Chem.* **2004**. *43*(21), 6650-6653.

Other References:

3. Sessler, J. L.; Seidel, D.; Vivian, A. E.; Lynch, V.; Scott, B. L.; Keogh, D. W. "Hexaphyrin(1.0.01.0.0): An Expanded Porphyrin Ligand for the Actinide Cations Uranyl (UO_2^{2+}) and Neptunyl (NpO_2^{+})," *Angew. Chem. Int. Ed., Engl.* **2001**, *40*, 591-594.

Oral Session 2:

Coordination Chemistry

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

Joseph T. Hupp, SonBinh T. Nguyen, Randall Q. Snurr
Dr. Baoqing Ma, Jodi O'Donnell, Houston Frost, Dr. Hyungeui Lee
Depts. of Chemistry and Chemical & Biological Engineering, Northwestern University
j-hupp@northwestern.edu, stn@northwestern.edu, snurr@northwestern.edu

Overall research goals: The premise of this project is that new materials should create new opportunities, and new nanostructured materials should create those opportunities at the molecular level. Of particular interest are separations, and particularly attractive here are membrane-based separations. Our general goal is to develop, and exploit for vapor and condensed-phase separations, well defined and highly porous soft materials derived from coordination chemistry. Our materials focus is on: 1) aggregates of hollow molecules, especially molecular squares, and 2) permanently microporous metal-organic frameworks (MOFs).

Significant achievements in 2003-2005: Detailed descriptions of recent work can be found in the DOE-sponsored papers listed below. Here are some summary descriptions:

Fabrication of pinhole-free polymeric molecular-square membranes displaying sharp permeant-size cutoffs. Self-limiting copolymerization at liquid-liquid interfaces was employed to obtain pinhole-free membranes that are functional for nanofiltration, with a sharp size cutoff thatmatches the ca. 22 angstrom cavity diameter of an isolated square.

Layer-by-layer assembly of robust supported microporous films of molecular squares. Phosphonate-functionalized porphyrin squares were used as microporous building blocks for the robotic assembly of rigid thin films via zirconium/phosphonate chemistry. This chemistry allows for predictable and exceptionally precise (atomic force microscopy validated) control of porous film thicknesses. Additionally, the assembly chemistry is remarkably efficient: the films display excellent molecular sieving behavior with as few as three molecular layers.

Evaluation of analyte transport in molecular-square films via wall-jet electrochemistry. An unusual but useful electrochemical strategy for measuring rates of molecular transport through thin films was developed and validated using the materials described above.

Modeling methane storage by molecular-square and MOF materials. Using atomistic grand canonical Monte Carlo simulations we have modeled with very good success methane storage in nanoporous soft materials. We obtained quantitative agreement with experiment, where data were available (studies by Yaghi and coworkers), and we proposed new, not-yet-synthesized materials predicted to absorb 36% more methane than the best materials tested to date.

Modeling hydrocarbon separations by metal-organic-framework materials. Separation of higher hydrocarbons from natural gas (mainly methane) is important in natural gas processing. We have used molecular simulations to assess the suitability of MOFs as adsorbents for such separations. By using grand canonical Monte Carlo simulations, the influence of the MOF linkers on the adsorption of methane, n-butane, and their mixtures was determined. Detailed analysis of the energetics as well as the siting of molecules in the MOF cavities allowed us to resolve the impact of different linkers on the selectivity and to propose new, not yet synthesized materials, which should show even higher selectivities. The results suggest that MOFs are promising materials for hydrocarbon separations.

Specific objectives for 2005-2006: On the experimental side we are transitioning from predominantly molecular-square materials to predominantly metal-organic-framework materials. With both types of materials we are seeking to build robust membranes by assembling the materials within the meso- and macropores of thin alumina membranes. Related work in progress, some which may be reported at the conference, includes:

Xenon NMR based measurements. Information concerning cavity size and accessibility in molecular square materials is being obtained.

Redox-switchable membranes. Cobalt-containing molecular square membranes exhibit oxidation-state dependent metal ligation behavior that can be used to block and re-open channels.

Oriented MOFs. We have successfully synthesized a handful of new permanently microporous mixed-ligand MOFs – materials featuring one ligand type in the *x* and *y* directions and another ligand in the *z* direction. Subsequently we have succeeded in growing one of the new MOFs in oriented fashion within porous alumina membranes. We are now seeking to demonstrate experimental control over the orientation and we hope to demonstrate membrane-based hydrocarbon separations with both orientations. We anticipate that selectivities will differ for the two. Additionally we are seeking to model anisotropic transport and to use the modeling results to identify new candidate materials for efficient separations.

References of work supported by this project (2003-2005)

M. Massari, et al. (2003), "Ultrathin Micropatterned Porphyrin Films Assembled via Zirconium Phosphonate Chemistry", *Polyhedron*, **22**, 3065-3072.

P. Dinolfo, et al. (2004), "Molecular Squares, Boxes and Cubes", *Encyc. Supra. Chem.*, 909-916.

M. H. Keefe, et al. (2003), "Permeable, Microporous Polymeric Membrane Materials Constructed from Discrete Molecular Squares", *Advanced Materials.*, **15**, 1936-1939.

K.F. Czaplewski, J. Li, J. T. Hupp, and R. Q. Snurr (2003), "Vapor Permeation Studies of Membranes Made from Molecular Squares", *J. Membrane Sci*., **221**, 103-111.

M. Massari, et al. (2004), "Walljet Electrochemistry: Quantifying Molecular Transport through Metallopolymeric and Zirconium Phosphonate-Assembled Porphyrin Square Thin Films", *Langmuir*, **20**, 4422-4429.

T. Duren, et al. (2004), "Design of New Materials for CH_4 Storage", *Langmuir*, **20**, 2683-2689.

S. -S. Sun, et al. (2004), "Directed-Assembly of Transition-Metal-Coordinated Molecular Loops and Squares from Salen-Type Components…", *J. Am. Chem. Soc.*, **126**, 6314-6326.

R. Q. Snurr, J. T. Hupp, S. T. Nguyen (2004), "Prospects for Nanoporous Metal-organic Materials in Advanced Separations Processes," *AIChE J*., **50**, 1090.

T. Duren, R.Q. Snurr (2004), "Assessment of Isoreticular Metal-Organic Frameworks for Adsorption Separations: A Molecular Simulation Study of Methane/n-Butane Mixtures," *J. Phys. Chem. B* **108**, 15703-15708.

L. Sarkisov, K.F. Czaplewski, R.Q. Snurr, "The role of diffusion in applications of novel nanoporous materials and in novel uses of traditional materials", NATO Advanced Study Institute on "Fluid Transport in Nanoporous Materials," in press.

L. Sarkisov, T. Duren, R.Q. Snurr (2004), "Molecular modeling of adsorption in novel nanoporous metal-organic materials", *Mol. Phys*. **102**, 211.

J. Libera, et al. (2004) "X-ray Nanoscale Profiling of Layer-by-Layer Assembled Metal/Organo-Phosphonate Films", *Langmuir*, **20**, 8022-8029.

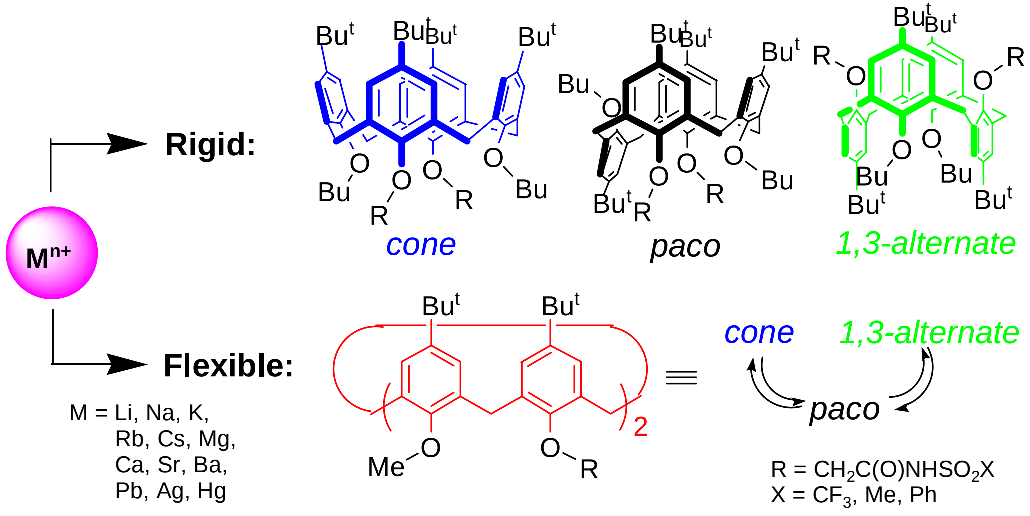
J. Libera, et al. (2005) "Comparative X-ray Standing Wave Analysis of Metal-Phosphonate Multilayer Films…," *J. Phys. Chem. B*, **109**, 1441-1450.

New Proton-Ionizable, Calixarene-Based Ligands for Selective Metal Ion Separations

Richard A. Bartsch
Texas Tech University
Richard.Bartsch@ttu.edu

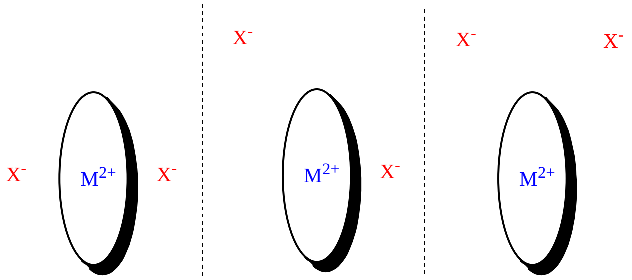
Overall research goals: The calix[4]arene framework provides an unusually versatile scaffold for the construction of new metal ion complexing agents. Attachment of one to four acidic side arms through the lower-rim phenolic oxygens can produce ligands that form electroneutral complexes with mono-, di-, tri- and tetravalent metal ion species, respectively. By avoiding the requirement for concomitant extraction of an aqueous phase anion into an organic medium with the metal ion in a separation process, such "charge matching" markedly enhances the propensity for metal ion transfer into the organic medium in a solvent extraction or liquid membrane transport process compared to non-ionizable analogues. By selection of appropriate lower-rim substituents, ligands can be prepared in conformationally mobile forms or in conformationally locked cone, partial-cone and 1,3-alternate conformations. In our work, particular attention is focused upon *N*-(X)sulfonyl carboxamide [-C(O)NHSO$_2$X] groups as the pendent acidic functionality, since the acidity can be "tuned" by variation of the electron-withdrawing properties of X.

Significant achievements in 2003-2005: A major study was undertaken to determine the effect of ligand preorganization for metal ion recognition by lower-rim functionalized calix[4]arenes. The following strategy for the design of ionophores with enhanced selectivity toward particular cations was evaluated: *synthesis of a conformationally mobile, di-ionizable calix[4]arene → determination of the referred conformation of the ligand in the complex with a targeted metal cation by NMR spectroscopy → restriction of the calixarene to this specific conformation via synthesis*. The strategy is further illustrated below.



Thus, the flexible ligand is prepared and contacted with the desired metal ion species in solution to form a complex whose conformation (cone, partial cone or 1,3-alternate) is determined by ^{1}H NMR spectroscopy. By changing from a methyl group on the lower rim of the flexible ligand to a butyl group, the rigid ligand may be produced in which there is a single conformation. The rigid ligand is then synthesized and its efficiency and/or selectivity in solvent extraction of metal ions from aqueous solution into chloroform determined. By comparison of the results, it can be determined whether the flexible ligand or rigid ligand preorganized in a single conformation is the better. We were very surprised to find that for the metal ion species examined, except Ag(I), a flexible ligand was better than a rigid ligand with a preorganized binding site.

When two of the phenolic oxygens on the lower rim of calix[4]arene are connected with a polyether chain, calixarene-crown ligands are produced. For di-ionizable calix[4]arenes with a crown-6 linkage between alternate phenolic oxygens, the calix[4]arene scaffold can be utilized to probe the effect of spatial variation of the ionizable groups in the ligand relative to the polyether cavity. In the cone ligand **1**, one ionized group is located directly above and one directly below a metal ion complexed in the polyether cavity. In the partial cone ligand **2**, one ionized group is located over the polyether ring and the other is remote. In the 1,3-alternate ligand **3**, both ionized groups are remote.



1 **2** **3**

Rigid di-ionizable calix[4]arene-crown-6 ligands of the type shown in the first figure were synthesized in the cone, partial-cone and 1,3-alternate conformations and evaluated in competitive alkaline earth metal ion extraction from aqueous solution into chloroform. The extraction efficiency and selectivity was found to decrease **1** > **3** > **2**. Very high extraction efficiency and selectivity for Ba(II) extraction was observed with the cone ligands.

Specific objectives for 2005: Investigation of metal ion separations by ionizable calix[4]arene-crown ligands will be expanded to include other divalent metal ions, as well as alkali metal cations. The effect of varying the crown cavity size will be probed.

References to work that were supported by this project:

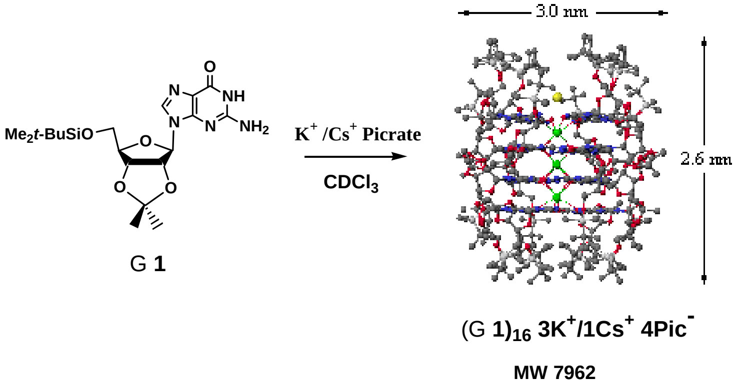
1. M. Ulewicz, W. Walkowiak, Y. Jang, J. S. Kim and R. A. Bartsch (2003), "Ion flotation of cadmium(II) and zinc(II) in the presence of proton-ionizable lariat ethers," *Analytical Chemistry,* 75, 2276-2279.
2. G. G. Talanova, V. S. Talanov, H.-S. Hwang, C. Park, K. Surowiec and R. A. Bartsch (2004), "Rigid *versus* flexible: how important is ligand 'preorganization' for metal ion recognition by lower rim-functionalize calix[4]arene?", *Organic and Biomolecular Chemistry,* **2**, 2585-2592.
3. S. Elshani, S. Chun, B. Amiri-Eliasi and R. A. Bartsch (2005), "Highly selective Ba(II) separations with acyclic, lipophilic di-[*N*-(X)sulfonyl carbamoyl] polyethers," *Chemical Communications*, 279-281.
4. H. Zhou, K. Surowiec, D. W. Purkiss and R. A. Bartsch (2005), "Proton di-ionizable *p-tert*-butylcalix[4]arene-crown-6 compounds in cone, partial-cone and 1,3-alternate conformations: synthesis and alkaline earth metal cation extraction," *Organic and Biomolecular Chemistry*, in press.

O2-3

Self-Assembled Ionophores

Prof. Jeffery T. Davis, Principal Investigator
Dr. Paul Santacroce, Postdoctoral Associate
Mark Kaucher and Jennifer Seganish, Ph.D. Students
Department of Chemistry and Biochemistry, University of Maryland, College Park
jd140@umail.umd.edu www.chem.umd.edu/faculty/organic/davis/davis.htm
Collaborators: Prof. David Reinhoudt, University of Twente, Netherlands
Professor Gang Wu, Queen's University, Kingston, Ontario, Canada

Overall research goals: Our goal is to build "self-assembled" ionophores that selectively bind cations, anions and ion pairs based on the guest's size, charge and shape. Instead of using covalent bonds, we have been using non-covalent interactions to synthesize such receptors. For example, lipophilic nucleosides such as guanosine **1** hydrogen bond to give assemblies that selectively bind various cations (**Scheme 1**). Some of these ionophores have high affinity and selectivity for ions such as Cs^+ and Ra^{+2} making them potentially valuable for separations of environmentally important cations.



Scheme 1. Lipophilic G-quadruplex (G **1**)$_{16}$·3K$^+$/Cs$^+$·4Picrate$^-$ formed by self-assembly of G **1.**

Specific objectives for 2004-2005:

1) Learn how to control structure & dynamics of nucleoside self-association and cation binding.
2) Design self-assembled ionophores that selectively bind various cations and anions.
3) Construct supramolecular structures that function as synthetic ion channels

Significant achievements: In 2003-04, we made advances in the following areas:

Cation Ionophores. We have learned much about self-assembled ionophores formed from lipophilic nucleosides. We learned that: 1) the nucleoside's structure dictates the size, shape and ion-binding selectivity of the hydrogen bonded assembly; 2) a cation is required to template and stabilize the assemblies, 3) the ionophore-cation complexes are robust in organic solvents, 4) dynamic exchange of cations, anions and ligands is a hallmark of these complexes, and 5) these lipophilic nucleosides can selectively transport cations across hydrophobic membranes.[1,2] Some of these lipophilic nucleosides were shown to be selective for extracting radium +2 cations from water into organic solvents, even in the presence of a million-fold excess of K+.[3,4]

Synthetic Ion pair Transporters. We have identified compounds that transport Cl^- across membranes.[5,6] In effect, we have extended the self-assembly approach to also include formation of synthetic anion transporters. Using a combination of structural evidence (X-ray and NMR) and functional assays we showed that some 1,3-alt calixarene amides and some acyclic phenoxyacetamides transport Cl^- anions across synthetic phospholipid membranes.

Biomimetics. There is much interest in understanding how DNA binds metal ions. Our assemblies are excellent models for DNA-metal interactions. Besides X-ray crystallography, there are few methods to locate cations in DNA. Lipophilic complexes from G **1** were used to validate new methods for direct observation of metal ions, namely ^{39}K solid state NMR.[7]

Plans for future research on this project: A significant finding in our work is that the anion cooperates with the ligand and the cation to control structure and stability in solution. Self-assembly of monomeric ligands to give ditopic receptors promises to be a fundamentally new approach for ion pair recognition. Accordingly, we need to 1) understand the factors that control ion pair recognition,[6,8,9] and 2) design ligands that self-assemble to form receptors. We would like to continue to develop a self-assembly approach toward building supramolecular receptors. Our strategy is to harness the power of non-covalent and reversible interactions to select for ligands and conditions that give optimal binding of different ions, particularly environmentally important species. In addition, we foresee using self-assembly to build functional nanostructures, such as synthetic ion channels, mini-reaction chambers and porous membranes.

References:

1. "G-Quartets 40 Years Later: From 5'-GMP to Molecular Biology and Supramolecular Chemistry." Jeffery T. Davis, *Angewandte Chemie Int. Ed.*, **2004**, 43, 668-698.
2. "Lipophilic G-Quadruplexes are Self-Assembled Ion Pair Receptors and the Anion Modulates the Kinetic Stability of these Cation-Filled Complexes." Xiaodong Shi, Katherine M. Mullaugh, James C. Fettinger, Yun Jiang, Steven A. Hofstadler and Jeffery T. Davis, *J. Am. Chem. Soc.*, **2003**, 125, 10830-10841.
3. "Selective ^{226}Ra^{2+} Ionophores Provided by Self-assembly of Guanosine and Isoguanosine Derivatives" Fijs W. B. van Leeuwen, Xiaodong Shi, Jeffery T. Davis, Willem Verboom and David N. Reinhoudt, *J. Am. Chem. Soc.* **2004**, *126*, 16575-16581.
4. "Selective Removal of ^{226}Ra^{2+} from Produced Waters of the Gas Industry." Fijs W. B. van Leeuwen, Cornelis J. H. Miermans, Hans Beijleveld, Jeffery T. Davis, Willem Verboom and David N. Reinhoudt **2005**, *Environmental Science and Technology*, submitted
5. "Chloride Transport Across Lipid Bilayers and Transmembrane Potential Induction by an Oligo-phenoxyacetamide" Vladimir Sidorov, Frank W. Kotch, Yiu-Fai Lam, Jennifer L. Kuebler and Jeffery T. Davis, *J. Am. Chem. Soc.*, **2003**, *125*, 2840-2841.
6. "Water-Mediated Assembly Provides an Ion Pair Receptor" Frank W. Kotch, Vladimir Sidorov, Katherine J. Kayser, Yiu-Fai Lam, Mark S. Kaucher, Hojun Li and Jeffery T. Davis, *J. Am. Chem. Soc.*, **2003**, *125*, 15140-15150.
7. "Direct Detection of the Potassium Cations bound to G-Quadruplex Structures by Solid-State K-39 NMR at 19.6 T" Gang Wu, Alan Wong, Zhehong Gan and Jeffery T. Davis, *J. Am. Chem. Soc.*, **2003**, *125*, 7182-7183.
8. "Kinetic Control in Non-Covalent Synthesis: Regioselective Ligand Exchange into a Hydrogen Bonded Assembly." Jeffery T. Davis, Mark S. Kaucher, Frank W. Kotch, Maura A. Iezzi, Bryna C. Clover and Katherine M. Mullaugh *Organic Letters* **2004**, 6, 4265 - 4268.
9. "Using Diffusion NMR to Characterize Guanosine Self-Association. Insights into Structure and Mechanism." Mark S. Kaucher, Yui-Fai Lam, Silvia Pierracini, Giovanni Gottarelli and Jeffery T. Davis, *Chemistry-A European Journal*, **2005**, *11*, 164-173.

Syntheses, X-ray crystallography, Raman and luminescence studies of coordination polymers of actinides and group 11 dicyanides.

Zerihun Assefa, Richard E. Sykora, Richard G. Haire
Oak Ridge National Laboratory, Chemical Sciences Division
assefaz@ornl.gov
www.ornl.gov/sci/csd

Overall research goals: The design of multidimensional supramolecular assemblies is one area of current interest for potential applications in energy transfer processes, molecular based magnets, and molecular absorption, as well as understanding their intriguing structural diversity [1-2]. Our methodology is to increase structural dimensionality by incorporation of moieties capable of generating hydrogen bonding interactions or to use anion complexes known to show metal-metal interactions with the same order of magnitudes as hydrogen bonding. We are currently exploring the solid state coordination of group 11 (Cu, Ag, Au) dicyanides with f-species and studying their photoluminescence and energy transfer properties.

Significant achievements in 2003-2005: Host-guest type energy transfer studies between the dopant actinide ions and the host zirconia matrix have been investigated in the solid state. Of special interest has been the dependence of their photo-luminescence behavior as a function of the dopant concentration. Exclusive excitation of the zirconia matrix leads to sensitized luminescence from the acceptor Cm(III) and Sm(III) ions. The presence of a strong spectral overlap region between the donor zirconia matrix and the acceptor levels facilitates the energy transfer process.

The nature of the oxidation state of cerium present during different facets of preparation of sol-gel glasses has been studied both by optical spectroscopy and XANES techniques. We found that, when cerium is introduced either as Ce^{3+} or Ce^{4+} the trivalent state normally prevails in the wet and room temperature-dried gels. Heating in air at >100 °C can generate a light yellow coloration with partial oxidation to the tetravalent state. Above 200 °C and up to ~1000 °C, cerium is oxidized to its tetravalent state [Ref. 4].

Investigations of actinide complexation with oxo- and nitrogen ligating bidentate and tridentate ligands displayed a highly efficient intramolecular energy transfer process, where $\pi-\pi^*$ excitation of the ligand provides an efficient channel for energy transfer to the 5f electronic level. Complexes of 6-methyl 2-(2-pyridyl)-benzimidazole ligand with curium(III) display efficient intramolecular energy transfers, where the sensitized orange-red emission of Cm(III) can be readily observed at low concentration.

Specific objectives for 2005-2006: Synthesis, X-ray crystallography and spectroscopic investigations of coordination polymers consisting of actinide ions and group 11 dicyanides are initiated. The initial structural, photoluminescence, and Raman work involves the trivalent f-species, americium, curium, neodymium, and praseodymium. Two different structure types for these materials have been observed, but both consist of layers of $M(CN)_2^-$ [M=Ag, Au] alternating with layers of Ln^{3+} or An^{3+} ions. One facet of this work will be to explore the driving force that determines which structure will be adopted.

The consequence of M-M interactions in directing the dimensionality and the structural motif of the coordination polymers is one area that we are currently pursuing. Each of these complexes exhibits strong photoluminescence behavior, and the Raman profile helps to elucidate the structural features. Since the M-M interactions are also the source of characteristic emission in these systems we will investigate whether the emission could be sensitized by the actinide ion through efficient energy transfer. Similar spectroscopic and solid state structural studies will also be initiated with the group 10 tetracyano complexes of Ni, Pd, and Pt. Long term projects will include attempts to synthesize cyanide bridged uranyl, neptunyl and related complexes in a reaction media consisting of minimal oxophilic competition.

References of work that were supported by this project

1) T. Yaita, H. Shiwaku, S. Suzuki, Y. Okomoto, A Shimada, Z. Assefa, R. G. Haire., "EXAFS and optical spectroscopic characterization of the structure and electronic nature of Ce-MDPhPDA complexes in methanol" *Physica B*, (2005, in press).
2) Z. Assefa, T. Yaita , R. G. Haire , S. Tachimori, "Intramolecular energy transfer in actinide complexes of 6-methyl-2-(2-pyridyl)-benzimidazole (biz): Comparison between Cm(III) and Tb(III) systems." *J. Solid State Chem.*, 178, (2005), 505-510.
3) Richard E. Sykora, Zerihun Assefa, and Richard G. Haire, Thomas E. Albrecht-Schmitt "Hydrothermal Synthesis, Structure, Raman Spectroscopy, and Self-Irradiation Studies of $^{248}Cm(IO_3)_3$" *J. Solid State Chem.*, 177, (2004), 4413 – 4419.
4) Z. Assefa, R. G. Haire, D. L. Caulder, D. K. Shuh, "Correlation of the oxidation state of cerium in sol-gel glasses as a function of thermal treatment via optical spectroscopy and XANES studies." *Spectrochimica Acta* A, 60, (2004), 1873 - 1881.
5) Z. Assefa, T. Yaita, R. G. Haire, S. Tachimori, "Photoluminescence and Raman studies of actinide complexes of 6-methyl 2-(2-pyridyl)-benzimidazole: Evidence for efficient intramolecular energy transfer" *Inorg. Chem.*, 42 (23), (2003)**,** 7375 -7377.
6) Z. Assefa, R. G. Haire, and P.E. Raison, "Photoluminescence and Vibrational Raman Studies of Lanthanide Species Doped in Zirconia Matrix: Excited-State Host-Guest Interaction between ZrO_2 and Dopant Ion." *Spectrochimica Acta, A*, 60/1-2, (2003), 87 - 93.

Other references

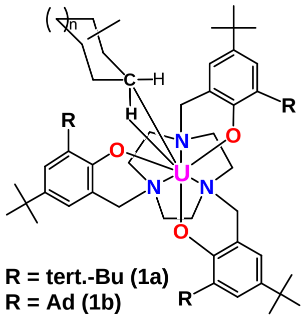
1) D. B. Leznoff, B.-Y. Xue, R. J. Batcheler, F.W.B. Einstein, B. O. Patrick, *Inorg. Chem.*, 2001, 40, 6026.
2) J. S. Miller, *Inorg. Chem*. 2000, 39, 4392.

O2-5

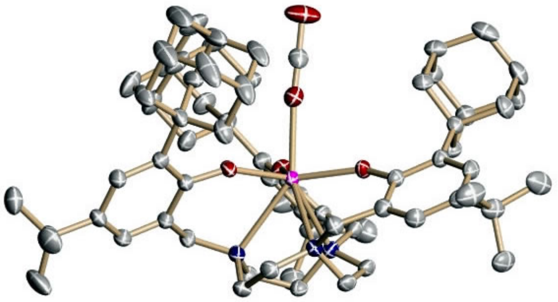
CO/CO_2 Activation and Nitrogen-Atom Transfer Chemistry Utilizing Low- and High-Valent Uranium Coordination Complexes

Karsten Meyer
Ingrid Castro-Rodríguez
University of California, San Diego
Email: kmeyer@ucsd.edu
http://www.inorganic-chemistry.net

Significant achievements in 2003 – 2005:

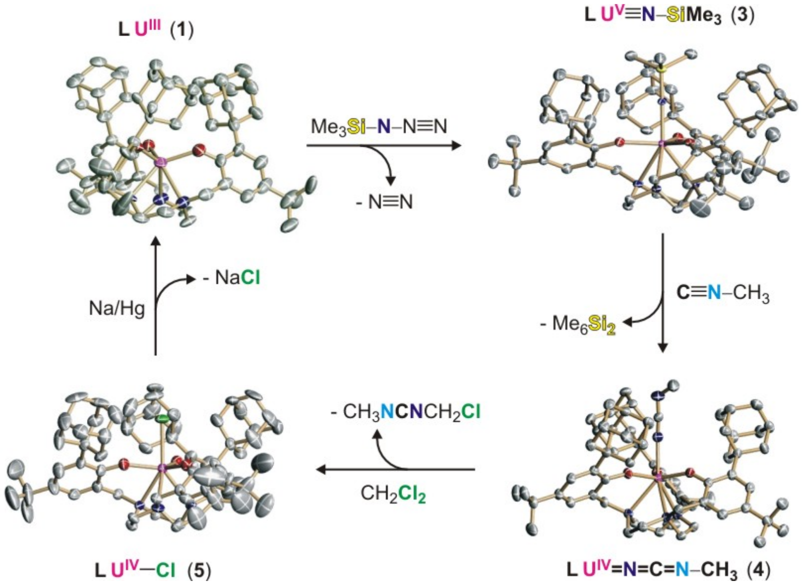


Alkane Coordination, Activation, and Functionalization. Reaction of various tris-aryloxide functionalized triazacyclononane ligands, $({}^{R}ArOH)_3$-tacn, with tris-amido uranium(III) starting material $[U(N(SiMe_3))_3]$ yields highly reactive uranium(III) species $[(({}^{R}ArO)_3tacn)U]$ (R = ^{t}Bu (**1a**), R = Ad (**1b**)).[1,2] Recrystallization of **1a** from pentane solutions containing cycloalkanes, i.e. cyclohexane affords coordination of the cycloalkane molecule in an η^2–*H,C* fashion to the electron-rich U center (see left).[3] The molecular structures of a variety of complexes with different alkanes were studied by X-ray diffraction. These species represent unique examples of metal-coordination of saturated hydrocarbons and may provide insight into catalytic C—H bond activation processes.[4]



C1 Activation Chemistry. Coordinatively unsaturated, trivalent **1a** cleanly reacts with carbon dioxide by reducing the CO_2, resulting in evolution of CO and formation of a U(IV)—O—U(IV) complex (2-electron reduction of CO_2). Complex **1a** also binds and activates CO to yield a μ-CO bridged diuranium species $[\{(({}^{t\text{-}Bu}ArO)_3tacn)U\}_2(\mu\text{-}CO)]$ (**2**). The molecular structure of **2** has been characterized crystallographically and reveals an iso-carbonyl bonding motif, which is unique in actinide chemistry. We suggest that **2** forms via a charge-separated U(IV)—$CO^{\bullet-}$ intermediate (similar to **3**, see below), which reacts with excess **1a** to yield the formally mixed-valent U(IV)—CO—U(III) species **2**.[5] Interestingly, the sterically more encumbering derivative **1b** prevents dimerization (and CO_2 cleavage) and thus, reacts with CO_2 to form the mononuclear U–CO_2 complex, namely $[(({}^{Ad}ArO)_3tacn)U(CO_2)]$ (**3**) (see Figure).[6] Complex **3** has been studied by X-ray diffraction and represents a charge-separated U(IV)—$CO_2^{\bullet-}$ species with a never before seen CO_2 coordination mode.[7] While in mononuclear complexes CO_2 is typically η^1–***CO_2*** or η^2–***OCO*** coordinated, the CO_2 ligand in **3** is coordinated to the U ion in an unprecedented linear, oxygen bound η^1–***O**CO* fashion. The metric parameters ($d_{U—O}$ = 2.351 Å, $d_{\mathbf{O}—C}$ = 1.122 Å, $d_{C—O}$ = 1.277 Å), vibrational (ν_3: $\nu_{O^{12}CO}$ = 2188 cm^{-1}, $\nu_{O^{13}CO}$ = 2128 cm^{-1}), SQUID magnetization data, and electronic absorption spectra suggest resonance structures, in which the U(III) ion is oxidized and the CO_2 ligand reduced by one electron: $U(IV){=}O{=}C^{\bullet}—O^{-}$ ↔ $U(IV)—O{\equiv}C—O^{-}$.[6] This reduction results in activation of the inert C=O double-bond and is expected to increase reactivity of the thermodynamically stable CO_2 molecule. This research (published in Science magazine) is fundamental to the discovery and production of powerful catalysts that allow for the chemical transformations of carbon dioxide into fine chemicals and fuels.

Nitrogen-Atom Transfer Chemistry. Complex **1b** reacts with TMS azide to yield two seven-coordinate uranium complexes: the U(IV) azido complex [((^{Ad}ArO)$_3$tacn)U(N$_3$)] (**4**, via Me$_3$Si radical elimination and formation of Me$_6$Si$_2$) and the U(V) imido species [((^{Ad}ArO)$_3$tacn)U(NSiMe$_3$)] (**5**, with evolution of N$_2$).[8] The sterically demanding adamantane-functionalized ligand provides a well-protected cylindrical cavity at the uranium center that hosts the axial heterocumulene ligands in a linear fashion. The high-valent U(V) imido complex **5** reacts with π-acids, such as carbon monoxide and methyl isocyanide, to form the U(IV) isocyanate complex [((^{Ad}ArO)$_3$tacn)U(NCO)] (**6**) and carbodiimide complex [((^{Ad}ArO)$_3$tacn)U(NCNMe)] (**7**) with concomitant formation of Me$_3$Si$^{\bullet}$ and Me$_6$Si$_2$, respectively.[5] Furthermore, the isocyanate and carbodiimide ligand in **6** and **7** react with CH$_3$I or CH$_2$Cl$_2$ to release the functionalized isocyanate and carbodiimide with formation of a U(IV) halide complex [((^{Ad}ArO)$_3$tacn)U(X)] (with X = Cl (**8a**); I (**8b**)), which can be regenerated to the uranium(III) starting complex **1b** via Na/Hg reduction. This series of reactions represents a synthetic cycle **1b → 5→ 7 → 8 → 1b**, in which the imido nitrogen atom is transferred from the uranium complex and incorporated into an organic substrate via C≡O and R'N≡C / U≡NR multiple-bond metathesis.[5]



Specific Objectives for 2005 – 2006: Specific objectives for the future are: I) investigation of the nature of the uranium alkane interaction via NMR, TGA/DSC, and single-crystal neutron-diffraction analysis. II) In addition, the reactivity of **1a** toward more reactive element – hydrogen bonds will be studied, e.g. silanes and boranes. III) Functionalization of the activated CO and CO$_2$ ligand in **2** and **3** will be attempted. For instance, reaction of **3** with various alkenes may lead to β-lactones. IV) Similarly, reaction of **1b** with isocyanates may lead to activated isocyanates that upon further reaction with alkenes may deliver β-lactams. V) The nitrogen atom transfer mechanism will be studied in detail, reaction conditions will be optimized, and reactivity towards other π-acids will be tested.

References of work that were supported by this project:
6) I. Castro-Rodriguez, H. Nakai, L.N. Zakharov, A. L. Rheingold, and **K. Meyer** "*A linear, O-Coordinated CO$_2$ Bound to Uranium*" *Science* **2004**, *305*, 1757—1759.
7) "*Elusive CO$_2$ binding mode snagged*" *C&E News,* **2004**, *82*, 40
Other references:
1) I. Castro-Rodriguez, K. Olsen, P. Gantzel, and **K. Meyer** *Chem. Commun.,* **2002**, 2764—2765.
2) H. Nakai, L.N. Zakharov, A. L. Rheingold, and **K. Meyer** *Inorg. Chem.* **2004**, *43*, 855—858.
3) I. Castro-Rodriguez, H. Nakai, P. Gantzel, L.N. Zakharov, A. L. Rheingold, and **K. Meyer** *JACS,* **2003**, *125*, 15734—15735.
4) "*Good evidence for stable metal-alkane coordination*" *C&E News,* **2003**, *81*, 31.
5) I. Castro-Rodriguez and **K. Meyer** *Unpublished results.*
8) I. Castro-Rodriguez, K. Olsen, P. Gantzel, and **K. Meyer** *JACS,* **2003**, *125*, 4565—4571.

Tuning Metal-Ligand Bonding Interactions and Novel Reactivity Patterns in Organometallic Actinide Complexes

Jaqueline L. Kiplinger, Principal Investigator
David E. Morris and P. Jeffrey Hay, Co-Principal Investigators
Eric J. Schelter, Jaime A. Pool, Ryan E. DaRe, and Aurora E. Clark, Postdoctorals
Kimberly C. Jantunen, Robert J. Wright, Ingrid Castro-Rodriguez, Students
Los Alamos National Laboratory, Los Alamos, NM 87545
kiplinger@lanl.gov

Collaborators: Prof. Philip P. Power (UC Davis), Prof. Paul B. Duval (U Missouri, Columbia), Dr. Wayne W. Lukens (LBNL), Dr. Jennifer C. Green (Oxford U.)

Overall research goals: This project is devoted to exploring the existence and manifestations of covalent metal-ligand bonding in complexes of uranium and other light actinides over a broad range of ligand sets and structure types through the combination of synthetic organometallic chemistry, electronic and vibrational structural characterization, and density functional theory. We also maintain an interest in the generation and investigation of actinide-ligand multiple bonds in order to probe the involvement of metal 6d/5f orbitals and f-electrons in chemical bonding and to demonstrate reaction patterns unique to f-elements.

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Significant achievements in 2003-2005:

Unusual Molecular Spectroscopic Behavior of and Assessing Covalent Interations in Organometallic Thorium and Uranium Complexes. We have completed a detailed electrochemical and spectroscopic investigation of a range of uranium and thorium metallocene complexes having a wide array of ancillary ligands ranging from simple σ-donors such as alkyls to nitrogen-based σ- and π-donors including hydrazonato and ketimido ligands.[2,4] Clear trends have emerged in both the electrochemistry and spectroscopy that are traceable to the varying degrees of stabilization of the metal f-orbitals via bonding interactions with the ligands.[6] This has enabled us to propose a new model for assessing covalent interactions between mid-valent actinides and σ- and π-donor ligands based on coupling of the charge-transfer states in these systems to the f-f states and the resultant enhancement in the intensity of the f-f transitions.[4,5] We have discovered new and rich molecular spectroscopy for the first examples of thorium(IV) and uranium(IV) bis(ketimido) complexes prepared in our labs.[2,4] These complexes are intensely colored – this is very unusual for $6d^0 5f^0$ Th(IV) complexes, which tend to be colorless. Additionally, these Th(IV) ketimide complexes exhibit visible luminescence spectra and enhancement in the Raman vibrational spectra, which is behavior that has never been observed for molecular thorium systems. The resonance enhancement in the Raman vibrational spectra of all these ketimide complexes is in resonance with either CT or ligand-localized excited states.[7] The resonance Raman behavior represents the only other example of this spectroscopic behavior since the work on uranocene reported in 1979. We have carried out density functional (DFT) calculations to investigate the bonding and spectroscopic properties of the bis(ketimido) complexes $(C_5R_5)_2M\text{-}[N{=}CPh_2]_2$ (M= Th, U, and Zr) to complement the experimental described above.

Activation of Carbon-Hydrogen and Carbon-Nitrogen Bonds in Pyridine N-Oxides using Organometallic Uranium and Thorium Complexes. Transition metal complexes possessing the terminal Schrock-type alkylidene and alkylidyne functionalities are well known, although related actinide complexes have remained elusive. Recent reports have shown that oxidatively induced α-hydrogen abstraction may be used to prepare early transition metal alkylidene complexes. The propensity of uranium to exist in the hexavalent oxidation state coupled with the known oxophilicity of tetravalent uranium, suggested to us that uranium(VI) alkylidene complexes of the type, $(C_5Me_5)_2U(=O)(=CHR)$, might be prepared by oxidatively-induced α-hydrogen abstraction chemistry between uranium(IV) bis(alkyl) complexes such as $(C_5Me_5)_2U(CH_2R)_2$ and an appropriate oxygen atom transfer agent.

Pyridine N-oxide is a prototypical oxygen atom transfer reagent that has been routinely used in the synthesis of high-valent transition metal and actinide oxo complexes. We have found that uranium(IV) and thorium(IV) bis(alkyl) complexes of the type $(C_5Me_5)_2AnR_2$ (An = U, Th; R = CH_3, CH_2Ph) instead activate the sp^2 and sp^3 hybridized C-H bonds in pyridine N-oxide and lutidine N-oxide to produce the corresponding cyclometallated complexes, $(C_5Me_5)_2An(R)[\eta^2\text{-}(O,C)\text{-}ONC_5H_4]$ and $(C_5Me_5)_2An(R)[\eta^2\text{-}(O,C)\text{-}ON\text{-}2\text{-}CH_2\text{-}5\text{-}CH_3\text{-}C_5H_3]$. Interestingly, the thorium(IV) bis(alkyl) and bis(aryl) complexes $(C_5Me_5)_2ThR_2$ (Me = CH_3, R = $CH_2C_6H_5$ or C_6H_5) have been found to mediate ring-opening and dearomatization of the pyridine ring in pyridine N-oxide under ambient conditions to afford the first thorium η^2-(O,N) oximate complexes.[8] These reactions provide rare examples of C-H and C=N activation chemistry mediated by actinide metal centers, and such transformations represent new types of reactivity available to pyridine N-oxide. Recent developments in this exciting area of chemistry will be presented.

<u>Specific objectives for 2005-2006:</u>

We will continue to examine the novel electrochemical and spectroscopic properties of the highly-colored thorium(IV) and uranium(IV) ketimide complexes. In particular, we will extend the nitrile insertion chemistry towards the preparation of fluorinated uranium(IV) and thorium(IV) ketimide complexes. This will provide a range of complexes of varying electron-density in the metal-ketimide linkage that will enable us to test more fully our recent models of covalency in the actinide-ligand bonding. We will also investigate the electrochemical and spectroscopic properties of new uranium(V) complexes. This is an exceedingly rare oxidation state for uranium and the chemistry and physical properties of complexes of this metal valence are poorly understood.

We will continue to examine the reactivity of uranium and thorium metallocene complexes with aromatic N-heterocyclic compounds (e.g quinoline, indole, picoline, and N-oxide ring systems) to probe the generality of the novel C-H and C-N activation chemistry that we have discovered.

We will employ theoretical tools such as DFT to aid in understanding the bonding, reactivity and spectroscopic properties of organoactinide complexes with nitrogen-containing ligands. We have gained some computational experience with the insertion chemistry of these ligands into actinide-carbon and transition metal-carbon bonds. As the complexes described above are synthesized, we will continue to explore how their chemistry and spectroscopy varies as a function of the ligand electronic properties and the nature of the actinide metal.

References of work that was supported by this project

1. "Theoretical Studies of Organometallic Complexes of Uranium Involving Nitrogen Ligands Using Density Functional Approaches," P. J. Hay, *Faraday Discussions*, **2003**, *124*, 29-83.
2. "Thorium(IV) and Uranium(IV) Ketimide Complexes Prepared by Nitrile Insertion into Actinide-Alkyl and -Aryl Bonds," Kimberly C. Jantunen, Carol J. Burns, Ingrid Castro-Rodriguez, Ryan E. Da Re, Jeffery T. Golden, David E. Morris, Brian L. Scott, Felicia L. Taw, and Jaqueline L. Kiplinger, *Organometallics* **2004**, *23*, 4682-4692. **Featured in *C&EN News.***
3. "Uncommon η^3-(N,C,C')-1-Azaallyl Bonding Mode for the Nacnac Ligand: A Bis(β-diketiminato) Uranium(III) Iodide Complex," Robert J. Wright, Philip P. Power, Brian L. Scott, and Jaqueline L. Kiplinger, *Organometallics* **2004**, *23*, 4801-4803.
4. "Trends in Electronic Structure and Redox Energetics for Early Actinide Pentamethylcyclopentadienyl Complexes," David E. Morris, Ryan E. Da Re, Kimberly C. Jantunen, Ingrid Castro-Rodriguez, and Jaqueline L. Kiplinger, *Organometallics* **2004**, *23*, 5142-5153. **Featured in *C&EN News.***
5. "Organometallic Actinide Chemistry: Developing a Comprehensive Picture of the Chemical Behavior of the 5f Elements," Jaqueline L. Kiplinger and Carol J. Burns, *Los Alamos National Laboratory-Actinide Research Quarterly* **2004**, LALP-04-060, pp 23-27.
6. "New Perspectives from Organometallic Chemistry: Electronic Structure and Bonding in 5f-Element Complexes," David E. Morris and Jaqueline L. Kiplinger, *Los Alamos National Laboratory-Actinide Research Quarterly* **2004**, LALP-04-060, pp 31-35.
7. "Molecular Spectroscopy of Uranium(IV) Bis(ketimido) Complexes. Rare Observation of Resonance-Enhanced Raman Scattering from Organoactinide Complexes and Evidence for Broken-Symmetry Excited States," Ryan E. Da Re, Kimberly C. Jantunen, Jeffery T. Golden, Jaqueline L. Kiplinger, and David E. Morris, *J. Am. Chem. Soc.* **2005**, *127*, 682-689. **Featured in *C&EN News.***
8. "A New Mode of Reactivity for Pyridine N-Oxide: C-H Activation with Uranium(IV) and Thorium(IV) Bis(alkyl) Complexes," Jaime A. Pool, Brian L. Scott, and Jaqueline L. Kiplinger, *J. Am. Chem. Soc.* **2005**, *127*, 1338-1339. **Featured in *C&EN News.***

Poster Session 1

Chemical Interactions Between Protein Molecules and Polymer Materials

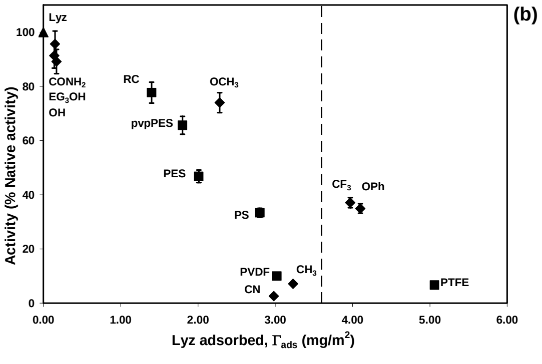
Georges Belfort (PI), Chao Zhu and Anankrishnan Sethuraman
Rensselaer Polytechnic Institute
<belfog@rpi.edu>
http://www.rpi.edu/dept/chem-eng/WWW/faculty/belfort/
Collaborators: Ravi Kane, Rensselaer Polytechnic Institute

Overall research goals: The overall research goal is to successfully address a serious bioseparations problem currently facing the biotechnology industry. The performance of synthetic polymer membranes when filtering bioprocessing fluids is severely limited by the interaction of proteins with the surface of the membranes. Synthesizing membranes with polymers that reduce such interactions have resulted in improved filtration performance. Our efforts to develop and test protein adhesion resistant membranes (i.e. surfaces that exhibit minimal adhesive energy *and* minimal amounts of protein adsorption) and to determine protein-substrate adhesion and protein conformational stability directly address this problem. In this research we have combined *biophysical methods* and *surface science approaches* to achieve the goal of producing protein adhesive resistant surfaces for filtration of bioprocessing fluids. As planned, we have measured protein adhesion and conformation during adsorption, and expanded and tested the data set of protein resistant molecules. We have also compared novel protein adhesion resistant molecules as candidates for use with synthetic membranes for bioseparations.

Significant achievements in 2003-2005: The significant overall achievements for the past two years are the following:

- Three functional groups (-$CONH_2$, -OH, -EG_3OH) have been identified as protein resistant through their effects on protein adhesion (lowest), lysozyme activity (highest), protein conformational disturbance (lowest). Their performance is predicted to be superior as compared with current commercial membranes (regenerated cellulose, poly(vinyl pyrolidinone) with poly(ether sulfone), and poly(vinylidine difluoride) used for synthetic membrane filtration (Fig. 1).
- The effect of a range of different wettable surfaces (8 homogeneous and 6 heterogeneous) on the adhesion properties and conformational stability of 7 globular proteins has been clearly elucidated. Globular proteins loose their α-helices and gain β-sheet over many hours as a result of their interaction with solid substrates and with themselves (lateral interactions).

FIG. 1 ACTIVITY OF ADSORBED LYSOZYME AT 16 MG/ML IN PBS BUFFER, PH 7.4 AND 25 °C AFTER 48 H



Lysozyme activity adsorbed onto eight SAM (◆) and six polymeric (■) substrates versus the amount of lysozyme adsorbed.

- A kinetic predictive reaction model describing the conversion of native structure to intermediate to intra- and inter-molecular β-sheet structures has been successfully tested against the data. α-helix loss is 50 times faster than β-sheet formation.

- A new structural parameter called the composite index, *n* (the product of the percent helix plus random content times relative molecular weight as a fraction of the largest protein in the set) was proposed and successfully correlated with the normalized adhesion forces. It may possibly be used as a measure of the structural stability of globular proteins.

Hence, we have completed specific aims 1-3 in our original proposal and more.

Specific objectives for 2005-2006:

The goal for the next year will be to address the Specific Aims #4 & #5 in our original proposal. They involve grafting smart (i.e. environmentally responsive (ER)) polymers onto surfaces and trying to trigger a structural change so as to dislodge adherent irreversibly bound protein (Aim #4), and modifying and testing grafted or coated microporous synthetic membranes for protein adhesion resistance (Aim #5).

References of work that were supported fully or partially by this project (2003-2004)

1. Sethuraman, A, Vedantham, G, Przybyccien T., and Belfort, G (2004) Protein unfolding at interfaces: Slow dynamics of α-helix to β-sheet transition, *Proteins: Structure, Function and Bioinformatics*, 56 (4) 669-678.
2. Sethuraman, A. Han, M., Kane, R. S. and Belfort, G (2004) Effect of Surface Wettability on the Adhesion of Proteins, *Langmuir*, 20, 7779-7788.
3. Taniguchi, M, and Belfort, G (2004) Low Protein Fouling Synthetic Membranes by UV-Assisted surface graft Modification, *J. Membrane Sci*., 231, 147-157.
4. Kilduff, J. E. Mattaraj S. and Belfort G. (2004) Flux decline during nanofiltration of naturally-occurring dissolved organic matter: effects of osmotic pressure, membrane permeability, and cake formation *J. Membrane Sci.*, 239, (1) 39-53.
5. Han, M, Sethuraman, A., Kane, R, S., and Belfort, G (2003) Nanometer-scale roughness having little effect on the amount or structure of adsorbed protein, *Langmuir*, *19*(23); 9868-9872.
6. Taniguchi, M, Kilduff, J. E., and Belfort, G (2003) Low fouling synthetic membranes by UV-assisted graft polymerization, monomer selection to mitigate fouling by natural organic matter, *J. Membrane Sci*., 222, (1-2) 59-70.
7. Taniguchi, M, Pieracci, J., P.,Samsonoff, W. A. and Belfort, G (2003) UV-assisted graft polymerization of synthetic membranes: Mechanistic studies, *Chem. Mater.,* 15(20); 3805-3812.
8. Taniguchi, M, Kilduff J, E. and Belfort, G (2003) Mechanisms of Natural Organic Fouling During Ultrafiltration, *Environ. Sci & Technol*., 37(8); 1676-1683.
9. Han, M, Kane, R, Goto, M, and Belfort, G (2003) Discriminate surface molecular recognition sites on a microporous substrate: A new approach, *Macromolecules*, 36(12); 4472-4477.
10. Vedantham, G, Carothers, S. L., Belfort, G, and Przybycien, T. (2003) Structural response of bovine growth hormone to dead ended ultrafiltration, *Separaion Sci & Techn.,* 38 (2) 251-270.
11. Frank B. P. and Belfort, G (2003) Polysaccharides and sticky membrane surfaces: critical ionic effects, *J. Membrane Sci.,* 212, 205-212.

Actinide Aggregation Studies

Peter C. Burns[1,2] , L. Soderholm[1,2] , Mark P. Jensen[1], S. Skanthakumar[1], Philip Almond[1,2]
[1]Chemistry Division, Argonne National Laboratory and [2]Department of Civil Engineering and Geological Sciences, University of Notre Dame

pburns@nd.edu; ls@anl.gov

Collaborators: Jeremy Fein, University of Notre Dame
Students: Karrie-Ann Hughes Kubatko, Tori Ziemann, Drew Gorman-Lewis, University of Notre Dame

Overall research goals: Groundwater systems contain nano- and micro-particles that, when mobile, can markedly enhance contaminant transport. This effort is focused on the development of accurate models that predict the environmental effects of metal aggregation based upon a molecular understanding of wide-ranging geochemical interactions and processes. Our goal is to provide a molecular-scale understanding of actinide (U, Np) interactions that aggregate and stabilize nano- and micro-scale particles. Our approach includes assessing aggregates formed in solution and comparing them with solid-state structures to unravel energetic and crystal components driving their stability.

Significant achievements in 2003-2005: Comparing the structural properties of tetrahedral-anion ligation in solution and in the solid state has been a focus of this effort. Crystal structures have been determined of numerous uranyl and neptunyl compounds involving phosphate, arsenate and sulfate ligation [4, 6-8]. These structures have been compared to coordination environments of the uranyl ion in perchlorate [11] and sulfate [12] solutions. Whereas perchlorate is not included in the first coordination sphere of the uranyl ion, which has only waters in its equatorial coordination plane, sulfate forms a rigid, inner-sphere monodentate complex. The U-O-S bond angle is determined to be 143° in solution, consistent with a wide variety of crystals with similar ligating ions. The neptunyl structures show a preponderance for cation-cation interactions, in contrast to those seen for the uranyl analogues. Attempts to study the aquo neptunyl ion, following the work on uranyl solutions, has been complicated by cation-cation interactions that persist in solution.

Work on uranyl and neptunyl ions in peroxide solutions have resulted in the determination of a series of novel actinyl peroxo nanoclusters [13]. These structures include spheres comprised of 24, 28, and 32 actinyl ions linked through edge-sharing peroxo units. These clusters have been demonstrated to self-assemble in solution where they persist and are stable over months.

Specific objectives for 2005-2006: Work over the next year will continue to compare solution and solid-state behavior in order to understand the important molecular interactions that control structure. Synthetic focus will continue on neptunyl compounds coordinating with tetrahedral anions and actinyl-peroxide nanoclusters.

Reference of work supported by this project:

1. Gorman-Lewis, D., Fein, J.B., Soderholm, L., Jensen, M.P., and Chiang, M.-H.: Experimental study of neptunyl adsorption onto *Bacillus subtilis. Geochimica et Cosmochimica Acta* (in press).
2. Kubatko, K.-A. and Burns, P.C.: The crystal structure of the novel uranyl tricarbonate $K_2Ca_3[(UO_2)(CO_3)_3]_2(H_2O)_6$. *Canadian Mineralogist* 42 (2004) 997-1003.
3. Skanthakumar, S., Gorman-Lewis, D., Locock, A., Chiang, M.-H., Jensen, M.P., Burns, P.C., Fein, J., Jonah, C.D., Attenkofer, K., and Soderholm, L.: Changing Np redox speciation in the synchrotron beam. *Mater. Res. Soc. Proc.* 802 (2004) 151-156.
4. Burns, P.C., Alexopoulos, C.M., Hotchkiss, P.J., Locock, A.J.: An unprecedented uranyl phosphate framework in the structure of $[(UO_2)_3(PO_4)O(OH)(H_2O)_2](H_2O)$. *Inorganic Chemistry* 43 (2004) 1816-1818.
5. Locock, A.J., Burns, P.C., Duke, M.J.M., and Flynn, T.M.: Monovalent cations in structures of the meta-autunite group. *Canadian Mineralogist* 42 (2004) 973-996.
6. Locock, A.J., Burns, P.C. and Flynn, T.M.: The role of water in the structures of synthetic hallimondite, $Pb_2[(UO_2)(AsO_4)_2](H_2O)_n$ and synthetic parsonsite, $Pb_2[(UO_2)(PO_4)_2](H_2O)n$, $n \leq 0.5$, *American Mineralogist* 90 (2005) 240-246.
7. Locock, A.L. and Burns, P.C.: Structures and synthesis of framework Rb and Cs uranyl arsenates and their relationships with their phosphate analogues. *Journal of Solid State Chemistry* 175 (2003) 372-379.
8. Locock, A.J. and Burns, P.C.: Structures and synthesis of layered and framework amine-bearing uranyl arsenates and phosphates. *Journal of Solid State Chemistry* 177 (2004) 2675-2684.
9. Locock, A.J. and Burns, P.C.: Revised Tl(I)-O bond valence parameters and the structures of thallous dichromate and thallous uranyl phosphate hydrate. *Zeitschrift fur Kristallographie* 219 (2004) 1-8.
10. Locock, A.J., Skanthakumar, S., Burns, P.C., and Soderholm, L.: Syntheses, structures, magnetic properties, and x-ray absorption spectra of carnotite-type uranyl chromium(V) oxides: $A[(UO_2)_2Cr_2O_7](H_2O)_n$ ($A = K_2$, Rb_2, Cs_2, Mg; $n = 0, 4$). *Chemistry of Materials* 16 (2004) 1384-1390.
11. Neuefeind, J., Soderholm, L., and Skanthakumar, S.: Experimental electron densities of aqueous uranyl (VI) solutions. *J. Phys. Chem A* 108 (2004) 2733-2739.
12. Neuefeind, J., Skanthakumar, S., and Soderholm, L.: The structure of the UO_2SO_4 ion pair in aqueous solution. *Inorg. Chem.* 43 (2004) 2422-2426.
13. Burns, P.C., Hughes Kubatko, K.-A., Sigmon, G., Fryer, B.J., Gagnon, J.E., Antonio, M.R. and Soderholm, L.: Actinyl peroxide nanospheres. *Angewandte Chemie International Edition* 44 (2005) 2135-2139.

Actinide Research: Cyclohexyl Separation Agents and Room Temperature Ionic Liquids

Gregory Choppin
Daphne Taylor
Murali Mallekav
Department of Chemistry and Biochemistry
Florida State University
Tallahassee, FL 32306
choppin@chem.fsu.edu

Collaborator: Andy Felmy, Senior Staff Scientist, Environmental Molecular Sciences Laboratory

Overall research goals: This research program studies actinide complexes to obtain a better understanding of the factors for design of better separating agents. Lanthanide complexes are studied to use techniques which the radioactivity of transuranium cations hamper.

Research on Cyclohexyl Separation agents

Taci (1,3,5-Triamino-2,4,6-trihydroxycyclohexane) had been shown in our earlier studies to form a sandwich-type structure with Ln (III) cations. Thci (1,3,5-Trideoxy-1,3,5-tris[(2-hydroxybenzyl)amino]-cis-inositol) has now been synthesized and studied. The protonation constants of Thci were found to be similar to those of Taci. The stability constants of Thci with ^{147} Pm (III), ^{152,154} Eu (III), and ^{90} Y (III) determined by solvent extraction measurements, differed from Taci with the formation of both 1:1 and 1:2 complexes, whereas Taci formed only a 3:2 species. Laser fluorescence measurements of the $^7F_o – {}^5D_o$ spectra of the Eu (III) complexed by Thci also indicated two species. The frequencies of the $^7F_o – {}^5D_o$ peaks for the complexes Eu (Thci)$^{3+}$ and Eu (Thci)$_2^{3+}$ were at 17,230 cm^{-1} and 17,250 cm^{-1} respectively. From luminescence lifetime measurements, the calculated number of inner sphere water molecules in the Eu (Thci)$^{3+}$ and Eu (Thci)$_2^{3+}$ complexes were 12.5 $\pm$ 0.5 and 5.5 $\pm$ 0.5 respectively. These values are larger than those observed in other 1:1and 1:2 Eu (III) complexes with triply bonding ligands, as the total coordination number in such systems is usually nine. Similar studies are being done with Am (III), Cm (III), $NpO_2{}^+$, and $UO_2{}^{2+}$. We are now synthesizing the ligand, Taci - Rebek in which Taci is attached to the opposite ends of a triple ring aromatic system with an amine nitrogen in the middle ring. This ligand could provide very strong complexation binding of actinide ions to multiple donor sites.

Research on Room Temperature Ionic liquids

Room temperature ionic liquids (RTILs) based on imidazolium cation and different anions have been synthesized by microwave heating and characterized. The miscibility of extractants such as HDEHP, TBP and HTTA with these ionic liquids was examined and interpreted based on physicochemical parameters such as hydrogen bond-donor and acceptor abilities of the RTILs. To understand the underlying mechanisms of extraction with reagents such as TBP, CMPO or mixtures of these dissolved in the RTILs, 1-octyl-3-methyl imidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-octyl-3-methyl-imidazolium bis(trifluoromethyl sulfonyl) amide, solvent extraction of uranyl ion from 1M nitric acid medium was studied. The UV-visible, infrared and raman spectra of the extracted organic phases were recorded to elucidate the bonding between the metal and the organic ligands. In addition, matrix assisted laser desorption/ionization (MALDI), electrospray ionization (ESI) mass spectra were taken for the organic phases containing the uranyl species to determine the molecular structure in the solutions. Both cation exchange and solvation mechanisms are were found to be operative in these systems depending on the ionic liquid of the system.

Specific objectives for 2005-2006:
To complete these studies.

References of work that were supported by this project

D.P. Taylor and G.R. Choppin. "Lanthanide complexation with 1,3,5-triamino 2,4,6-trihydroxycyclohexane", Inorg. Chim. Acta, 358, 459-466 (2005).

G.R. Choppin and A. Kronenberg. "Present Status and Future of Academic Radiochemistry", ACS Symposium Series No. 868, 12-21 (2004)

G.R. Choppin. "Actinide chemistry: from weapons to remediation to stewardship", Radiochim. Acta 92, 519-523 (2004).

G.R. Choppin. "Actinide speciation in the environment", Radiochim. Acta 91, 645-649 (2003).

C.E. VanPelt, W.J. Crooks, III, and G.R. Choppin. "Stability constant determination and characterization of the complexation of trivalent lanthanides with polyoxometalates", Inorg. Chim. Acta, 346, 215-222 (2003).

J.-M. Monsallier and G.R. Choppin. "Influence of humic acid size of actinide complexation", Radiochim Acta 91, 135-139 (2003).

G.R. Choppin and G. Fugate. "Applications of the Judd-Ofelt theory of lanthanide-chelidamic acid complexation", Molecular Physics, 101, No.7, 935-939 (2003).

G.R. Choppin and M.Y. Redko. "Comparison of structural effects on Eu(III) complexes and cyclohexyl and benzene polycarboxylic acids", J. Solid State Chem., 171, 44-50 (2003).

G.R. Choppin and D.E. Wall. "Interaction of actinide ions with $\{NaP_5W_{30}O_{110}\}^{14-}$ and $\{P_2W_{18}O_{62}]^{6-}$", J. of Radioanalytical and Nuclear Chemistry, 255, No.1, 47-52 (2003).

Syntheses, Structures, and Physical Properties of K/Cu/An(Th,U)/S Phases: $KCuAnS_3$, $K_2Cu_2AnS_4$, $K_3Cu_3Th_2S_7$, and $K_3Cu_2US_6$

Peter K. Dorhout, Principal Investigator
Benny C. Chan and Hugh D. Selby*, Postdoctorals
Department of Chemistry, Colorado State University
C205 Chemistry, Fort Collins CO 80523
Email: pkd@lamar.colostate.edu; Internet: http://www.chem.colostate.edu/pkd/
*Los Alamos National Laboratory (C-INC), MS J514, Los Alamos NM 87545

Collaborators: Dr. Kent Abney and Dr. Ryan Hess, Los Alamos National Laboratory (NMT-2), MS E511, Los Alamos NM 87545

Overall research goals: The purpose of this project is to systematically explore the reactivity and fundamental coordination chemistry of the actinides in complex quaternary mixtures using low-melting alkali-chalcogenide fluxes as the reaction medium. Quaternary actinide systems offer tantalizing synthetic targets due to their typical wealth of physical properties, such as heavy fermion behavior and unusual magnetic coupling schemes. However, such phases are rarely systematized in the context of the thermodynamics of their composition space, making the “tuning” of a given property or the preparation of related phases largely serendipitous. We have recently begun to map the pseudo-ternary Gibbs phase diagram of the K/Cu/An/S systems. We hope to reveal new phases in these otherwise well studied systems, elucidate their electronic and magnetic properties, and map the relationships between individual points on the phase diagram in order to develop predictive trends.

Significant achievements in 2003-2005: Synthetic exploration of K/Cu/An/S (50% S, 500 deg. C. isotherm) quaternary phase space has yielded six new compounds: $KCuThS_3$, $K_2Cu_2ThS_4$, $K_3Cu_3Th_2S_7$, $KCuUS_3$, $K_2Cu_2US_4$, and $K_3Cu_2US_6$ (figure 1). The Th containing phases are semiconductors with optical band gaps of 2.95, 2.17, and 2.49 eV, respectively, while the U containing phases are very small band gap semiconductors or metallic. The compounds are all layered materials, with each layer composed AnS_6 octahedra bridged by CuS_4 tetrahedra of varying dimension. The layers are separated by well-ordered K^+ ions. The relatively wide range of optical band gaps in the Th phases is attributed to the extent of the CuS_4 motifs. As the dimension of the CuS_4 chains increases, band gaps decrease in the series. The extent of the CuS_4 motif also appears to influence the magnetic behavior of the U based phases. In the U based phases, the increasing CuS_4 dimension “dilutes” the paramagnetic centers, weakening their interactions. Only $KCuUS_3$ has a measurable antiferromagnetic transition (61K); $K_2Cu_2US_4$ and $K_3Cu_2US_6$ exhibit Curie-Weiss behavior throughout the measured temperature range. All materials were characterized by single crystal X-ray diffraction, microprobe chemical analysis, and diffuse reflectance spectroscopy (NIR-UV). Susceptibility data for the U based phases was measured using a SQUID magnetometer.

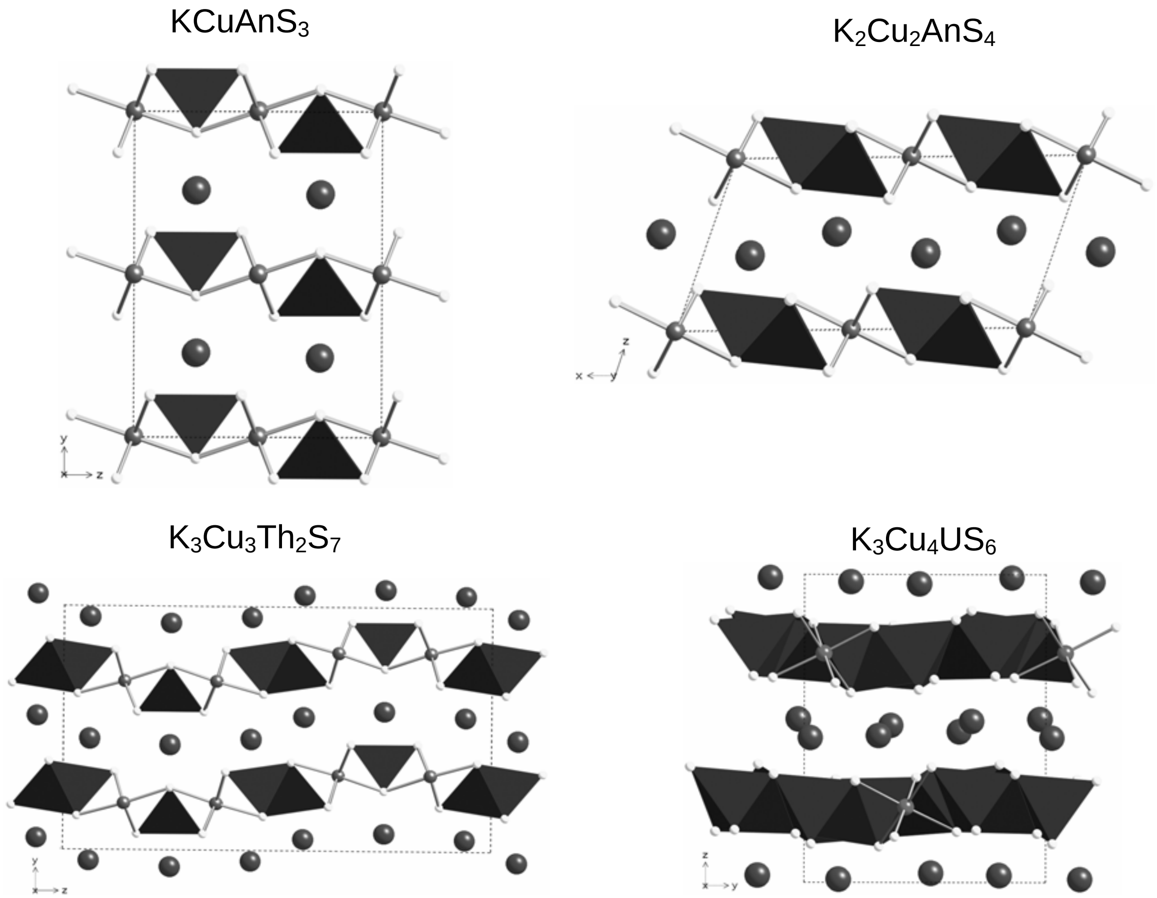

$KCuAnS_3$ $K_2Cu_2AnS_4$ $K_3Cu_3Th_2S_7$ $K_3Cu_4US_6$

Figure 1. Edge-on view of the layered structures of the title compounds. An (U,Th) = small octahedrally coordinated spheres, K = large interlayer spheres, S = An-Cu bridging spheres, Cu = tetrahedra.

<u>Specific objectives for 2005-2006:</u>

1. Complete the phase diagrams for K/Cu/Th/S and K/Cu/U/S.
2. Start exploration of the K/Cu/Pu/S and K/Cu/Np/S systems.
3. Explore the analogous very low temperature systems using K_2S_5 (m.p. < 220 deg. C.) as the flux.

<u>Selected references funded by the project:</u>

Selby, H. D., Chan, B. C., and Dorhout, P. K. "Three New Phases in the K/Cu/Th/S System: $KCuThS_3$, $K_2Cu_2ThS_4$, and $K_3Cu_3Th_2S_7$" *Submitted Inorg. Chem.* **2005**.

Chan, B. C., Hess, R. F., Feng, P. L., Abney, K. D., and Dorhout, P. K. "Synthesis and Characterization of Two Quaternary Thorium Chalcophosphates: $Cs_4Th_2P_6S_{18}$ and $Rb_7Th_2P_6Se_{21}$" *Inorg. Chem.* **2005** *44*, 2106-2113.

Chan, B. C., Hulvey, Z., Abney, K. D., and Dorhout, P. K. "Synthesis and Characterization of AU_2Se_6 (A = K, Cs)" *Inorg. Chem.* **2004** *43*, 2453-2455.

Nanostructured Hybrid Materials for Advanced Membrane Separations

Benny D. Freeman
Scott Matteucci, Scott Kelman, Haiqing Lin
The University of Texas at Austin
freeman@che.utexas.edu
http://membrane.ces.utexas.edu

Professor Toshio Masuda, Kyoto University, Japan
Dr. Anita J. Hill, CSIRO, Clayton, Victoria, Australia

Overall research goals: This research program focuses on the development of nanostructured membranes for gas separation applications. These novel membranes are based on hybrid materials of polymers and finely dispersed nonporous, nano-scale inorganic fillers.

Significant achievements in 2003-2005: We have continued out studies of using nanoparticles to alter the transport and separation properties of polymeric membrane materials. We have recently discovered metal oxide nanoparticles (ca. 2.5 nm diameter) that can enhance permeability of gases in polymers by more than one order of magnitude with only modest decreases in selectivity. We have found, in some cases, that the nanoparticles actually chemically react with the polymer matrices. This reaction can be harnessed to allow preparation of polymer-particle composites at unprecedented particle loadings, up to 95 wt. %, without the introduction of selectivity-destroying pinhole defects. We have also discovered quite recently the possibility of using nanoparticles to increase permeability, by as much as an order of magnitude, in rubbery polymers with only modest losses in selectivity. To the best of our knowledge, this phenomenon has never been reported before. We are working to understand the fundamental science governing the structure of such composite materials using tools such as PALS, AFM, SEM, TEM, XPS, and NMR.

In cooperation with Professor Toshio Masuda's group at Kyoto University, we prepared and characterized poly(1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene), PTMSDPA, a rigid polyacetylene, for use in our studies of hydrocarbon/hydrocarbon separations. This polymer is of great interest as a platform material for nanocomposite membranes. It has been reported to be highly permeable to O_2 and N_2. However, its permeation properties for higher hydrocarbons, such as butane, a marker for higher hydrocarbon contaminants in natural gas, has never been tested before our studies. Interestingly, it can be readily desilylated, yielding poly(diphenylacetylene), PDPA, which is insoluble in all known solvents and cannot be prepared at significant molecular weights by any other routes. PDPA is attractive because it is expected to have outstanding chemical resistance to natural gas contaminants. We have now made nanocomposites of PTMSDPA using very fine metal oxide nanoparticles, and we have discovered that the particles can react with PTMSDPA, simultaneously rendering it insoluble (i.e., improving its chemical resistance markedly) and improving its permeabililty. We are testing the selectivity properties of this nanocomposite now.

Specific objectives for 2005-2006: We will continue to focus on the fundamentals of transport in nanocomposite systems to determine the influence of nanoparticle concentration, size, surface chemistry, and overall chemical composition on separation performance.

References of work that were supported by this project

1. Lin, H., and B.D. Freeman, (2005), Membrane Materials to Remove CO_2 from Gas Mixtures, *J. Molecular Structure*, ASAP.

2. Prabhakar, R.S., Raharjo, R., Toy, L.G., Lin, H., and Freeman, B.D., (2005), Self-Consistent Model of Concentration and Temperature Dependence of Permeability in Rubbery Polymers, *Industrial & Engineering Chemistry Research*, ACS ASAP.

3. Lin, H., and B.D. Freeman, (2004), Gas Solubility, Diffusivity, and Permeability in Poly(ethylene oxide), *J. Membrane Sci.*, **239**, 105-117.

4. Lin, H., B.D. Freeman, L. Toy, V. Bondar, R. Gupta, S. Gupta, A. Hill, (2004), Reverse-selective polymeric membranes for hydrogen purification, Polymer Preprints (American Chemical Society, Division of Polymer Chemistry), **45(2),** 22-23.

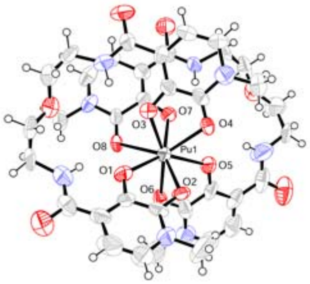
5. Merkel, T.C., Z. He, I. Pinnau, B.D. Freeman, P. Meakin, A.J. Hill, (2003), Sorption and Transport in Poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole-co-tetrafluoroethylene) Containing Nanoscale Fumed Silica, *Macromolecules*, **36(22)**, 8406-8414.

6. Merkel, T.C., Z. He, I. Pinnau, B.D. Freeman, P. Meakin, and A.J. Hill, (2003), Effect of Nanoparticles on Gas Sorption and Transport in Poly(1-trimethylsilyl-1-propyne)," *Macromolecules*, **36(18),** 6844-6855.

Plutonium Encaged: The First Structurally Characterized Pu-Hydroxypyridonate Complex

Anne E. V. Gorden, *LBNL Seaborg Center Postdoctoral Research Fellow*
Kenneth Raymond, *Principal Investigator*
Seaborg Institute for Transactinium Science, Chemical Sciences Division, Lawrence Berkeley National Laboratory *and* Department of Chemistry, University of California – Berkeley
agorden@berkeley.edu
http://www.cchem.berkeley.edu/knrgrp/acta.html
Collaborators:
Patricia W. Durbin, David Shuh, *Principal Investigators*
Géza Szigethy, Bryan E. F. Tiedemann, Richard Wilson *Graduate Students*
Jide Xu, *Staff Scientist*
Seaborg Institute for Transactinium Science, Lawrence Berkeley National Laboratory (LBNL)

Overall research goals: Ligands using hydroxypyridonate (HOPO), catecholamide (CAM), and terephthalamide (TAM) chelating subunits like those found in microbial Fe(III) chelators (siderophores) have been tested in mice as actinide decorporation agents. These biological evaluations have guided the evolution of actinide selective chelation agents based on the factors found to effect ligand efficacy such as denticity, flexibility, and solubility.[1] The limits of this method of evaluation are clear, and a detailed evaluation of the structure and bonding of actinide coordinating ligands is necessary for the rational design of new selective ligand systems.



Molecular structure of the Pu(IV) complex, Pu(IV)[Bis (5-LIO-Me-3,2-HOPO)]$_2$ [4]

Significant achievements in 2003-2005:

Procedures have been developed to determine the solid-state molecular structure of Pu complexes by small molecule X-ray diffraction (XRD) using the Advanced Light Source (ALS) synchrotron as the radiation source. Using these methods, the Pu(IV)-[5LIO(Me-3,2-HOPO)]$_2$ complex is the first of the Pu- hydroxypyridonate complexes to be characterized by single crystal X-ray diffraction. This complex crystallizes with the asymmetric unit cell containing two unique eight-coordinate plutonium complexes of opposing helicity and one perchlorate anion.[4]

Specific objectives for 2005-2006:

This provides a benchmark for additional structural studies with actinides and is hoped to be the first in a series of characterizations of actinide hydroxypyridonate complexes. Work is in progress to prepare Pu-complexes for comparison with Th complexes prepared as models for Pu systems.[2,3] Future studies include the solution behavior for complex formation in solution and extended X-ray absorption fine structure (EXAFS) of this and related complexes.

References

1. A. E. V. Gorden, J. Xu, K. N. Raymond, P. W. Durbin *Chem. Rev.* **2003**, *103*, 4207-4282.
2. J. Xu, D. W. Whisenhunt, Jr., A.C. Veeck, L. C. Uhlir, K.N. Raymond. *Inorg. Chem.*, **2003**, *42*, 2665 - 2674.
3. C. J. Gramer, K. N. Raymond, *Inorg. Chem.* **2004,** *43*, (20), 6397-6402.
4. A. E. V. Gorden, D. K. Shuh, B. E. F. Tiedemann, R.E. Wilson, J.Xu, K.N. Raymond, *Chem. Eur. J.*, **2005** (9), *in press.*

P1-7

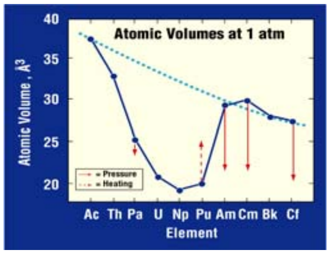
Probing the Bonding and Electronic Nature of Actinides

R. G. Haire
Oak Ridge National Laboratory
hairerg@ornl.gov
http://www.ornl.gov/sci/csd

Postdoctoral Fellow: R. E. Sykora
Collaborators: S. Heathman, T. Le Bihan, A. Lindbaum, G. Lander (ITU, Germany); G. Stewart (Univ. of Florida); M. Fluss and C. Brandon (LLNL); and P. Faure (CEA, France);

Overall research goals: Our primary objective is to perform fundamental research of f-elements with a focus on their electronic configurations, energy levels and bonding, which defines and provides an understanding of their chemistry/physics. To accomplish this objective, systematic correlations of multiple experimental studies are employed. Collaborations are stressed and are very important in achieving our objectives. The overall goal of the program is to advance f-element science and generate information applicable to multiple missions regarding them.

Significant achievements in 2003-2005: One facet of our research efforts addresses high-pressure diffraction studies of the elements and their alloys. Over this time frame, high-pressure diffraction studies have been performed on protactinium, curium, californium and americium metals (pressure and temperature varied with americium). Our results have shown that pressure can force the both the initial delocalization, or the increased participation, of 5f-electrons in the metallic bonding. This effect is reflected in the figure, which displays the atomic volumes high-pressure forms would have at atmospheric pressure (or 298 K for plutonium) as compared to those of their "normal" forms at atmospheric pressure and 298 K. In other efforts, we prepared selected alloys of neptunium and selected transition metals, and americium and plutonium, to identify potential electronic effects that may be present in these systems. We have initiated low-temperature calorimetry studies on some of these selected alloys, and shall employ the plutonium-americium alloys in multiple upcoming studies. Both of the latter pursuits involve collaborations.



Specific objectives for 2005-2006: Specific objectives for the 2005-2006 time frame in the metal-alloy arena include performing high-pressure/high-temperature diffraction studies on Am-Pu alloys, doing additional work on californium under pressure, and extending our investigations of protactinium metal to much higher pressures. In the latter effort we shall look for formation of new structure types and bonding changes that may be applicable to actinide metals in general. We also plan on examining selected actinide pnictides (compounds) under pressure using diffraction methods. We shall also investigate actinide materials that have a potential for acting superconductors or that may behave as non-Fermi liquids. Syntheses of single crystals of selected actinide materials for experimental projects and making special alloys for other collaborative investigations will round out our major thrusts dealing with metals and alloys.

Partial Reference List of work supported by this project for 2003-2005:

1. R. G. Haire, (2005, in press), "Einsteinium", Chapter 12 in *Chemistry of the Actinide and Transactinide Elements*, Katz, J. J., Morss, L. R., Fuger, J., Edelstein, N. M., eds. Kluwer, London.
2. R. G. Haire, (2005, in press), "Californium", Chapter 11 in *Chemistry of the Actinide and*

Transactinide Elements, Katz, J. J., Morss, L. R., Fuger, J., Edelstein, N. M., ed., Kluwer, London.

3. Gibson, J. K., Haire, R. G., Marcalo, J., Santos, M., Pires de Matos, A., and Leal, J. P., (2005, in press)"Determination of the Ionization Energy of NpO_2 and Comparative Ionization Energies of Actinide Oxides", J. *Nucl. Mater.*
4. Gibson, J. K., Haire, R. G., Santos, M., Marcalo, J. and Pires de Matos, A., (2005, in press), "Oxidation Studies of Dipositive Actinide Ions, An^{2+} (An = Th, U, Np, Pu, Am) in the Gas Phase. Synthesis and Characterization of the Isolated Uranyl, Neptunyl and Plutonyl Ions: UO_2^{2+} (g), NpO_2^{2+} (g) and $PuO_2{}^{2+}$(g)", *J. Phys. Chem.*
5. Yaita, T., Shiwaku, H., Suzuki, S., Okamoto, Y., Shimada, A., Assefa, Z. and Haire, R. G., (2005, in press),"EXAFS and Optical Spectroscopic Characterization of the Structure and Electronic Nature of Ce-MDPhPDA Complexes in Methanol", *Physica B.*
6. Assefa, A., Yaita, T., Haire, R. G., and Tachimori, S., (2005, in press), "Intramolecular Energy Transfer in Actinide Complexes of 6-methyl-2-(2-pyridyl)-benzimidazole (biz): Comparison between Cm(III) and Tb(III) Systems", *J. Solid State Chem.*
7. Sykora, R. E., Raison, P. and Haire, R. G., (2005, in press), "Self-irradiation Induced Structural Changes in the Transplutonium Pyrochlores $An_2Zr_2O_7$ (An = Am and Cf)", *J. Solid State Chem.*
8. Gibson, J. K. and Haire, R. G., (2004), "Ternary Gas-Phase Plutonium Oxide Cluster Ions, $Pu_xM_YO_Z{}^+$: Exploring the Oxidation Behavior of Pu", *J. Alloys Compd.*, **363**, 112-121.
9. Sykora, R.E., Assefa, Z., Haire, R. G., and Albrecht-Schmitt, T. E., (2004), "Hydrothermal Synthesis, Structure, Raman Spectroscopy, and Self-Irradiation Studies of $^{248}Cm(IO_3)_3$", *J. Solid State Chem.,* **177**, 4413.
10. Gibson, J. K. and Haire, R. G., (2004), "Activation of Pentamethylcyclopentadiene by Bk^+, Cf^+ and Es^+ Ions in the Gas Phase: A Probe of the Electronic Structures of Heavy Actinides", *Organometallics,* **24**, 119.
11. Haire, R. G., Heathman, S., Le Bihan, T., Lindbaum, A. and Iridi, M., (2004), "Investigations of Actinide Metals and Compounds under Pressure Provide Important Insights into Bonding and Chemistry", MRS Symposium Series, Vol. **802**, 15-24.
12. Haire, R. G., Heathman, S. Iridi, M., Le Bihan, T., Lindbaum, A. Rebizant, (2003), "Pressure-Induced Changes in Protactinium Provide Important Insights into Actinide Metal Bonding Concepts", J. Phys. Rev.B., **67**, 134101.
13. Lindbaum, A. Heathman, S. Le Bihan, T., Haire, R. G. Idiri, M, Lander, G. H, "High-Pressure Crystal Structures of Actinide Elements to 100 GPa, (2003), J. Phys.:Condensed Matter, 15, S-2297-302.
14. Haire, R. G., (2003), "Investigations of Protactinium and Americium Metals Provide Important Insights into Actinide Bonding Concepts", Actinide Research Quarterly, LANL, 4th Quarter, 23-29.
15. Assefa, Z., Yaita, T., Haire, R. G., Tachimori, S., (2003), "Photoluminescience and Raman Studies of Actinide Complexes of 6-methyl 2-(2-pyridyl)-benzimidazole: Evidence for Eficient Energy Transfer", Inorg. Chem., **42**(23), 7375-77.
16. Gibson, J. K. and Haire, R. G. (2003)," Einsteinium Chemistry in the Gas Phase: Exploring the Divalent Character of Heavy Actinides, (2003), Radiochimica Acta, 91,441-448.
17. Sewtz, M., Backe, H., Dretzke, A., Kube, G., Lauth, W., Schwamb, P., Eberhardt, I.,Gruning, M., Thorle,P., Trautmann, N. Kunz, P., Lassen, J., Passler, G., Dong, C. Z., Fritzsche, F., Haire, R. G. (2003), "First Observation of Atomic Levels for the Element Fermium *(Z=100),* Phys. Rev. Lett, 90, 163002, pp. 1-4.
18. Jackson, G. P., Haire, Richard G., and Duckworth, Douglas C., (2003), "A New Pulsed Glow Discharge Source with Enhanced Ion Extraction for Small Non-Conductive Samples and Atmospheric Sampling", J. Anal. Atomic Spectroscopy 18,665-669.

Spectroscopic Studies of Prototype Actinide Compounds

Michael C. Heaven, *Principal Investigator*
Jiande Han and Jin Jin, *Postdoctoral Researchers*
Vasiliy Goncharov and Chris Lue, *Graduate Student*
Department of Chemistry, Emory University, Atlanta, GA 30322
Collaborators: Bjorn Roos (Department of Theoretical Chemistry, Lund, Sweden) and Laura Gagliardi (Dipartimento di Chimica Fisica, Palermo, Italy)
Heaven@euch4e.chem.emory.edu

Overall research goals:

High-level theoretical models of the electronic structures and properties of actinide compounds are currently being developed by several research groups. This is a challenging problem due to the need for explicit treatment of relativistic effects, and the circumstance that many of these molecules exist in states where the *f* and/or *d* orbitals are partially filled. The latest generation of theoretical models must be tested and evaluated through comparisons with experimental results. Gas phase data are most suitable for this purpose, but there have been very few gas phase studies of actinide compounds. In the present project we are carrying out gas phase spectroscopic studies of simple Uranium and Thorium compounds (oxides and halides). To complement the experimental effort we are also investigating the potential for using relativistic *ab initio* calculations and empirically adjusted Ligand Field Theory (LFT) models to predict and interpret the electronic energy level patterns.

Significant achievements in 2003-2005

Multi-photon ionization (MPI) techniques were used to examine the electronic spectrum and ionization potential of ThO. Three new electronically excited states were found and previously unobserved levels of the A'(0^+) and N(1) states were characterized. A ligand field theory model was used to propose configurational assignments for twenty excited states. The IP for ThO determined from MPI measurements was 53260(10) cm^{-1} (6.6035(8) eV). This is 0.5 eV higher than the value obtained using electron impact techniques. The revised IP is greater than that of atomic Th, which shows that neutral ThO is more tightly bound than ThO^+. This behavior is consistent with semi-empirical models of the bonding in actinide oxides. Rydberg series for atomic Th were also characterized during these studies. These data provided an improved IP for Th of 50868.84 ± 0.06 cm^{-1}.

ThO was used to test and develop methods for studying actinide ions using pulsed field ionization – zero electron kinetic energy (PFI-ZEKE) spectroscopy. Rotationally resolved data were obtained for the v=0,1 and 2 vibrational levels of $ThO^+(X^2\Sigma^+)$, providing the first spectroscopic constants for this ion. The vibrational interval ($\Delta G_{1/2}=950\pm1$ cm^{-1}) and rotational constant ($B_0=0.341\pm0.002$ cm^{-1}) for the ion are greater than those of the neutral molecule. This is an intriguing result given that the ion is *less* tightly bound.

Two-photon ionization techniques were used to examine the electronic spectroscopy of UO_2 and the IPs of UO and UO_2. Twenty-two vibronic bands of UO_2 were observed.

These included transitions that originated from the $X^3\Phi(2u)$ ground state and a low-lying excited state, $^3\Phi(3u)$ (T_0=360 cm^{-1}). The existence of a low-lying electronically excited state confirms predictions that the lowest energy electronic configuration is $U(5f\phi_u 7s\sigma_g)O_2$.

High-level *ab initio* calculations were carried out to facilitate the interpretation of the UO_2 spectrum. Transition frequencies and oscillator strengths were calculated for transitions originating from the two lowest energy states. The results from these calculations were use to propose assignments for thirteen observed states.

In previous studies of matrix isolated UO_2 it had been suggested that the low-lying electronic states are re-ordered by the guest-host interaction in solid Ar, yielding $U(5f^2)O$ $^3H_{4g}$ as the ground state. Dispersed fluorescence spectra were recorded for UO_2 isolated in a solid Ar matrix. Comparisons of these spectra with the gas phase data and electronic structure calculations indicated that the ground and low-lying electronic states of UO_2 are derived from the $U(5f\,7s)$ configuration. The level of agreement between the observed and predicted electronic energies provided further validation of relativistic calculations for unperturbed UO_2.

Specific objectives for 05-06

PFI-ZEKE studies of ThO will be used to explore the low-lying excited states of ThO^+. We will focus on the excited state manifolds derived from the $Th^{3+}(6d)O^{2-}$ and $Th^{3+}(5f)O^{2-}$ configurations. *Ab initio* and LFT calculations will be performed in support of these measurements. Similarly, PFI-ZEKE will be used to characterize UO^+. We anticipate that many low-lying states will be observed due to the fact that the lowest energy configuration of the ion should be $5f^3$. Studies of UO_2^{2+} will follow.

Matrix isolation studies will be conducted in parallel with the gas phase experiments. Fluorescence excitation and IR absorption spectroscopy will be used to characterize the simplest Th and U halides. These data will lay the groundwork for future gas phase measurements.

References of work that were supported by this project

[1] L. Gagliardi, M. C. Heaven, J. W. Krogh, and B. O. Roos, "*The electronic spectrum of the UO_2 molecule*", J. Am. Chem. Soc. 127, 86 (2005).

[2] C. J. Lue, J. Jin, M. J. Ortiz, J. C. Rienstra-Kiracofe, and M. C. Heaven, *"Electronic spectroscopy of UO_2 isolated in a solid Ar matrix"* J. Am. Chem. Soc. 126, 1812 (2004).

[3] J. Han, V. Goncharov, L. A. Kaledin, A. V. Komissarov, and M. C. Heaven, *"Electronic spectroscopy and ionization potential of UO_2 in the gas phase"* J. Chem. Phys. 120, 5155 (2004).

[4] J. Han, L. A. Kaledin, V. Goncharov, A. V. Komissarov, and M. C. Heaven, *"Accurate ionization potentials for UO and UO_2: A rigorous test of relativistic quantum chemistry calculations"* J. Am. Chem. Soc. 125, 7176 (2003).

[5] V. Goncharov, J. Han, L. A. Kaledin and M. C. Heaven, *"Ionization energy measurements and electronic spectra for ThO"* J. Chem. Phys. Accepted, March 2005

Flotation Chemistry of Soluble Salt Minerals

Jan D. Miller
Zhorro Nikolov, Orhan Ozdemir
University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT
E-mail: jdmiller@mines.utah.edu
http://www.mines.utah.edu/metallurgy/Faculty.html

Overall research goals

Particulate separations by flotation are of considerable significance in many areas of technology ranging from pharmaceutics and microelectronics, to mining and construction materials industries. The primary goal of this research program is to provide a basis for improved flotation separation efficiency in nonsulfide mineral systems by establishing the fundamental features of collector (surfactant) adsorption reactions associated with the hydrophobic surface state and developing appropriate surface chemistry control strategies. The nonsulfide flotation chemistry research program involves a number of projects including interfacial water structure analysis, surfactants, surface micelles and macromolecular surface structures, particle-bubble interaction, and flotation chemistry applications. One project discussed in this presentation is the flotation chemistry of soluble salt minerals (alkali halides, alkali oxyanion, and carbonates). The significance of this flotation separation technology is revealed from consideration of the potash and trona industries. In these flotation systems collector solubility and adsorption efficiency are important issues because the separation of salt particles is accomplished from saturated solutions (brines). The problems of collector adsorption and interfacial water structure in soluble salt flotation systems have become particularly important in the U.S. in view of the depletion of high grade potash reserves and of the need for cost effective production of soda ash from trona resources.

Significant achievements in 2003-2005

Fundamental studies of interfacial chemistry suggest that the interfacial water structure and hydration states of soluble salt surfaces together with the precipitation tendency of the corresponding collector salts are of considerable importance in explaining their flotation behavior. In particular, the high concentration of ions in these soluble salt brines and their hydration appears to modify the bulk and interfacial structure of water and this effect is shown to be an important feature in the flotation chemistry of soluble salt minerals including alkali halide, alkali oxyanion and carbonate salts. The soluble salts can be classified as either structure makers, intermolecular hydrogen bonding between water molecules is facilitated, or as structure breakers, intermolecular hydrogen bonding between water molecules is disrupted. Traditionally the viscosity of the solutions is used as a macroscopic parameter of water structure making/breaking. Salts, which increase the viscosity of aqueous solutions, are considered structure makers and those, which decrease it, are considered structure breakers. We have shown that salts, which are considered structure makers by their viscosity parameters, cannot be floated with either the cationic DAH collector or the anionic SDS collector, while flotation is very effective for salts, which are structure breakers. Contact angles measured between a drop of brine and the soluble salt crystal surface, where possible, can also be considered as a macro parameter characterizing the water structure making/breaking character of the salt surface. For structure making salts the brine completely wets the salt surface and no contact angle can be measured. For structure breaking salts, the brine does not completely wet the salt surface and a finite contact angle is measured. In order to explain the flotation behavior of a range of industrially important carbonate salts at the molecular level we have employed FTIR spectroscopy to study the water structure in aqueous solutions of the salts ranging from very dilute solutions to saturated solutions. The analysis of the water OD stretching band and its comparison with the viscosity data for the respective solutions showed that changes in the OD band parameters agree with viscosity characteristics of the solutions. According to the OD band and viscosity analysis, K_2CO_3 and Na_2CO_3 have a very strong water structure making effect, while $NaHCO_3$ and NH_4HCO_3 show a weak water structure making effect. The strong water structure making character of K_2CO_3 and Na_2CO_3 agrees with the poor flotation efficiency of these salts and suggests that the poor flotation of the natural mineral trona ($Na_2CO_3 \bullet NaHCO_3 \bullet H_2O$) is due to the dominant structure making effect of Na_2CO_3 compared to that of $NaHCO_3$.

Specific objectives for 2005-2006

In the proposed research for this project we plan further studies of water structure in carbonate solutions with sum frequency spectroscopy (SFS) and surface tension measurements to study the solution/air interfaces of carbonate salt solutions with salt concentrations of up to saturation. The SF spectra of the interfacial water OH stretching band will be recorded in the range 3000 – 3800 cm^{-1} for aqueous solutions of Na_2CO_3, $NaHCO_3$, Trona, K_2CO_3, and $(NH_4)_2CO_3$. The interfacial water structure will be deduced from the spectral data and will be correlated with the results from surface tension measurements and the OD band vibrational spectroscopy of the same solutions. Results from preliminary experiments using SFS revealed an interesting difference in the interfacial water structure for $NaHCO_3$ and Na_2CO_3 solution/air interfaces. Na_2CO_3, which acts as a water structure maker in the bulk, showed that it is also a strong promoter of the water structure at the solution/air interface, while $NaHCO_3$ does not exhibit noticeable influence on interfacial water structure.

References of work that were supported by this project*

1. Z. S. Nickolov and J. D. Miller, "FTIR Studies of Water Structure in Soluble Salt Flotation Systems," 76th Colloid and Surface Science Symposium, Ann Arbor, Michigan, 23-26 June 2003. *J. Coll. Int. Sci.*, (2005), in preparation.
2. O. Ozcan, M. S. Celik, Z. S. Nickolov, and J. D. Miller, "The Effect of Thermal Stability on the Flotation Response of Sodium Carbonate Salts," *Minerals Engineering*, 16, 353 (2003).
3. Z. S. Nickolov, O. Ozcan, and J. D. Miller, "FTIR Analysis of Water Structure and Its Significance in the Flotation of Sodium Carbonate and Sodium Bicarbonate Salts," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 224 (1-3), 231 (2003).
4. Z. S. Nickolov, O. Ozdemir, and J. D. Miller, "Vibrational Spectroscopic Studies of Water Structure and its Significance in the Flotation of Carbonate Salts", SME Annual Meeting, February 28 - March 3, 2005, Salt Lake City, Utah, USA

*Publications from other projects in the Nonsulfide Flotation Chemistry Program are given in the annual report.

Production and Chemical Properties of the Heaviest Elements

K.J. Moody, J.B. Patin, J.M. Kenneally, D.A. Shaughnessy, M.A. Stoyer, N.J. Stoyer*, J.F. Wild, P.A. Wilk, J.H. Landrum, and R.W. Lougheed
*Presenting
Lawrence Livermore National Laboratory
moody3@llnl.gov
http://www-cms.llnl.gov/e114/

Collaborators:
Yu.Ts. Oganessian, V.K. Utyonkov, Yu.V. Lobanov, F.Sh. Abdullin, A.N. Polyakov, I.V. Shirokovsky, Yu.S. Tsyganov, G.G. Gulbekian, S.L. Bogomolov, A.N. Mazentsev, S. Iliev, V.G. Subbotin, A.M. Sukhov, A.A. Voinov, G.V. Buklanov, K. Subotic, V.I. Zagrebaev, M.G. Itkis, S.N. Dmitriev, S.V. Shishkin, A.V. Yeremin, V.I. Chepygin, E.A. Sokol, G.K. Vostokin, N.V. Aksenov and M. Hussonnois
Joint Institute for Nuclear Research, Dubna, Russia

K. Czerwinski and E. Wolfrom
University of Nevada, Las Vegas

H. Nitsche, R. Sudowe, and S.L. Nelson
University of California, Berkeley

Overall Research Goals: The heavy element group at Lawrence Livermore National Laboratory has a long-standing collaboration with the Joint Institute for Nuclear Research in Dubna, Russia[1,2]. Some of the most exciting work has taken place in the last seven years with the discovery of four new elements – 113, 114, 115, and 116[3,4,5,6]. One of the goals of this collaboration is to investigate the boundaries of the periodic table and discover the next "magic number" of protons, which is postulated to occur at Z=114, 120 or even 126[7]. In addition, we are searching for the "Island of Stability" where nuclides are predicted to have lifetimes much longer than those currently observed in the heavy elements. We are currently investigating the "shores" of this neutron-rich region and have already discovered isotopes of element 114 that are longer lived than their neighboring nuclei. This research is accomplished through accelerator-based experiments in Dubna by bombarding actinide targets with ^{48}Ca ion beams.

We are also developing plutonium ceramic targets for the MASHA (Mass Analyzer for Super Heavy Atoms) mass separator currently under construction in Russia. This work is in collaboration with the University of Nevada, Las Vegas. MASHA is a next generation mass separator, which is expected to have a mass resolution of 0.25 amu. The target will be a high temperature plutonium ceramic bombarded with ^{48}Ca ions to produce element 114 isotopes and subsequently heated to 2000°C so that reaction products will diffuse out of the porous target into an ion source, where they will be ionized and subsequently sent through the separator for mass identification. This separator will provide evidence for our discovery of element 114.

In collaboration with the University of California, Berkeley, we are investigating the chemical properties of the heaviest elements. We are currently researching separation methods for element 105 in support of our discovery of element 115 (see below.) Experiments designed to determine the chemical properties of element 114 are also being planned. Theorists predict that element 114 could behave as a noble gas, or it could potentially form soluble chloride complexes. We are designing an automated chemistry apparatus, which will enable us to perform aqueous chemistry on a rapid "atom-at-a-time" scale. Once this apparatus is constructed, we will conduct survey experiments on element 114 homologs at the 88-Inch Cyclotron at LBNL, and then proceed with element 114 experiments in Dubna. These experiments are challenging, but if we are successful, it will be the first chemistry performed on element 114.

Significant achievements in 2003-2005: In early 2004 the Livermore-Dubna collaboration succeeded in producing the first atoms of elements 113 and 115 ever reported[8]. Element 115 was produced in the bombardment of ^{243}Am target with ^{48}Ca ions and decayed via the emission of five successive alpha particles followed by spontaneous fission of element 105. Element 113 was produced as the decay daughter of 115, which means that two new elements were discovered during the experiment. The terminal nucleus in the decay chain was ^{268}Db, which was observed to undergo spontaneous fission with a half-life of approximately 16 hours.

Because of this exceptionally long half-life, we were able to perform chemical separations of the reaction products produced via the ^{243}Am + ^{48}Ca reaction in order to isolate the element 105 end-member of the 115 decay chain[9]. During the course of the experiment, a total of 15 spontaneous fission events were recorded with a half-life of approximately 32 hours. When the errors are considered, the two values for the half-life derived from the production and chemistry experiments overlap. This provides additional evidence for our reported discovery of elements 113 and 115.

References

1. Yu.Ts. Oganessian *et al*. (2004), Heavy Element Research at Dubna, *Nuclear Physics A*, **734**, 109-123.
2. M.G. Itkis *et al*. (2003), Fusion-Fission of Heavy and Superheavy Nuclei, *Physics of Atomic Nuclei*, **66**, 1118-1124.
3. Yu.Ts. Oganessian *et al*. (2004), Measurements of Cross Sections and Decay Properties of the Isotopes of Elements 112, 114, and 116 Produced in the Fusion Reactions ^{233}U, ^{238}U, ^{242}Pu, and ^{248}Cm + ^{48}Ca, *Physical Review C*, **70**, Art. No. 064609.
4. Yu.Ts. Oganessian *et al*. (2004), Synthesis of Superheavy Nuclei in ^{48}Ca Induced Reactions, *Progress of Theoretical Physics*, **Suppl. 154**, 406-416.
5. Yu.Ts. Oganessian *et al*. (2004), Measurements of Cross Sections for the Fusion-Evaporation Reactions ^{244}Pu(^{48}Ca,xn)$^{292-x}$114 and ^{245}Cm(^{48}Ca,xn)$^{293-x}$116, *Physical Review C,* **69**, Art. No. 054607.
6. K.J. Moody (2004), Superheavy Element Isotopes – Decay Properties, *Nuclear Physics A*, **734**, 188-191.
7. M.A. Stoyer (2005), Superheavy Elements, *2005 Yearbook of Science and Technology*, McGraw-Hill Publishers, 348-352.
8. Yu.Ts. Oganessian *et al*. (2004), Experiments on the Synthesis of Element 115 in the Reaction ^{243}Am(^{48}Ca,xn)$^{291-x}$115, *Physical Review C*, **69**, Art. No. 021601.
9. S.N. Dmitriev *et al*. (2005), Chemical Identification of Dubnium as a Decay Product of Element 115 Produced in the Reaction ^{48}Ca+^{243}Am, *Mendeleev Communications*, **15**, 1-4.

Heavy Element Nuclear and Radiochemistry

Heino Nitsche, Kenneth E. Gregorich, Darleane C. Hoffman
R. Sudowe, Staff Sci.; C. Düllmann, C. M. Folden, Postdocs; M., Calvert, S. E. Herbison, S. Nelson, R. E. Wilson, P. Zielinski, Graduate Students
University of California, Berkeley, Department of Chemistry and Lawrence Berkeley National Laboratory, Nuclear Science Division
hnitsche@lbl.gov
http://heavyelements.lbl.gov

Overall research goals: The most fundamental goal in chemistry is the determination of the chemical properties of the elements. Information on the chemical properties of the heaviest elements can be used to assess the importance of relativistic effects on theoretical calculations and our understanding of their chemical properties. Knowledge gained for the heaviest elements can be applied to understanding chemical properties throughout the periodic table. We will maintain a flexible first-rate program which can respond quickly to new research opportunities in heavy element studies, and perform a broader range of experiments requiring a) high-intensity beams, b) highly efficient or highly specific separations, and/or c) requiring the most extreme detection sensitivity. These fields of expertise will also be essential in the development of apparatus and experiments for the proposed RIA facility. The versatile and reliable LBNL 88-Inch Cyclotron with its world-leading ECR ion source development combined with the highly efficient and selective Berkeley Gas-filled Separator (BGS) is ideally suited for studies of heavy element chemical properties. The LBNL Heavy Element/Nuclear Radiochemistry program will take full advantage of these new experimental opportunities for elucidating the nuclear and radiochemistry of the heaviest elements. These exotic, frontier studies attract many undergraduate and graduate students to nuclear and radiochemistry. This research provides excellent education and training for future contributions and careers in a variety of applied areas, as well as in frontier research.

Significant achievements in 2003-2005:

- Showed, using SISAK in combination with the BGS that the 4-second isotope ^{257}Rf extracts from sulfuric acid into 0.05 M trioctyl amine, and behaves in this extraction system similar to its homologues Hf and Zr. This confirms further that Rf is indeed a Group 4 element

- Studied the decay properties of ^{253}No, the α-decay daughter of ^{257}Rf, to determine the effect of electron-α-particle summing in the detector. This knowledge is very important for the analysis and interpretation of other transactinide element experiments with SISAK.

- Continued studies on the extraction of Zr and Hf with dicyclohexano-18-crown-6 and dibenzo-18-crown-6. Determined extraction kinetics and established that both extractants posses fast enough kinetics to be suitable for a Rf study.

- Continued studies of the chemical behavior of novel gas-phase organometallic transactinide compounds. Carried out detailed experiments on the gas phase behavior of Hf and Zr hexafluoroacetylacetone (hfa) complexes including reaction yield improvements and aerosol formation.

- Joined European collaborators in a further experimental attempt at GSI to investigate the chemical properties of element 112 produced in the ^{238}U(^{48}Ca,3n)^{283}112 reaction. We could not confirm the results reported from Dubna indicating exciting possibility of studies of chemical properties of element 112 and other superheavy elements.

- The Berkeley Off-line Radioisotope Generator (BORG) project was continued. Conceptual drawings were prepared, suitable materials and control instruments were studied. A detailed equipment and parts list and a preliminary budget was prepared.

  <u>Specific objectives for 2005-2006:</u>

- Continue the program to study the chemical properties of Rf (Z = 104) by using the SISAK chemical separation system coupled to the BGS. Include initial work on dubnium (Z=105), hassium (Z=108) and possibly on seaborgium (Z=106) using the SISAK system. This would make SISAK the only liquid-phase system able to study such a heavy element.
- Continue work for improving the SISAK extraction system to allow for simultaneous detection of organic and aqueous phases
- Develop target technology and EH&S engineering and administrative procedures for the use of ^{244}Pu targets with the BGS to provide access to isotopes of elements from Rf through Hs (elements 104-108) with half-lives long enough for chemical studies (78, 33, 7,15, and 14s, respectively).
- Construct a new detection system for short–lived α-decaying transactinides in on-line studies at the BGS. This detector will first be used in an experiment on the formation of Rf-hfa complexes using pre-separated ^{257}Rf ($T_{½}$=4.3 s).
- Construct the Berkeley Off-line Radioisotope Generator (BORG)

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

J. V. Kratz, A. Nahler, U. Rieth, A. Kronenberg, B. Kuczewski, E. Strub, W. Bruchle, M. Schadel, B. Schausten, A. Turler, H. W. Gaggeler, D. T. Jost, K. E. Gregorich, H. Nitsche, C. Laue, R. Sudowe, and P. A. Wilk (2003), An EC-branch in decay of 27-s ^{263}Db: Evidence for the new isotope ^{263}Rf, *Radiochim. Acta* **91**, 59. LBNL-51398.

T. N. Ginter, K. E. Gregorich, W. Loveland, D. M. Lee, U. W. Kirbach, R. Sudowe, C. M. Folden, J. B. Patin, N. Seward, P. A. Wilk (2003), P. M. Zielinski, K. Aleklett, R. Eichler, H. Nitsche, and D. C. Hoffman, Confirmation of production of element 110 by the ^{208}Pb(^{64}Ni,n) reaction, *Phys. Rev. C-Nucl. Phys.* **6802**, 9901. LBNL-51696.

A. Turler, C. E. Düllmann, H. W. Gaggeler, U. W. Kirbach, A. B. Yakushev, M. Schadel, W. Bruchle, R. Dressler, K. Eberhardt, B. Eichler, R. Eichler, T. N. Ginter, F. Glaus, K. E. Gregorich, D. C. Hoffman, E. Jager, D. T. Jost, D. M. Lee, H. Nitsche, J. B. Patin, N. Pershina, D. Piguet, Z. Qin, B. Schausten, E. Schimpf, and et al. (2003), On the decay properties of ^{269}Hs and indications for the new nuclide ^{270}Hs, *Eur. Phys. J. A* **17**, 505. LBNL-49779.

K. E. Gregorich, T. N. Ginter, W. Loveland, D. Peterson, J. B. Patin, C. M. Folden, D. C. Hoffman, D. M. Lee, H. Nitsche, J. P. Omtvedt, L. A. Omtvedt, L. Stavsetra, R. Sudowe, P. A. Wilk, P. M. Zielinski, and K. Aleklett (2003), Cross section limits for the ^{208}Pb(^{86}Kr,n)^{293}118 reaction, *Eur. Phys. J. A* **18**, 633. LBNL-51215.

C. M. Folden III, K. E. Gregorich, Ch. E. Düllmann, H. Mahmud, G. K. Pang, J. M. Schwantes, R. Sudowe, P. M. Zielinski, H. Nitsche, and D. C. Hoffmann (2004), Development of an odd-Z-projectile reaction for heavy element synthesis: ^{208}Pb(^{64}Ni,n)^{271}Ds and ^{208}Pb(^{65}Cu,n)^{272}111, *Phys. Rev. Lett.* **93**, 21702. LBNL-56169

Vibrational Spectroscopy of Chromatographic Interfaces

Jeanne E. Pemberton
Christopher Orendorff, Zhaohui Liao, Piotr Macech, Yuan Huang; (Grad) Alison Ange (Undergrad)
Department of Chemistry, University of Arizona, Tucson, AZ 85721
Email: pembertn@u.arizona.edu Web Site: http://www.chem.arizona.edu/faculty/

Collaborator: Dr. Lane C. Sander, National Institute of Standards and Technology

Overall research goals: This effort seeks to develop vibrational spectroscopic methods to characterize the interfacial details of separations processes at the molecular level. Specific goals are: 1) a molecular-level understanding of retention processes in reversed-phase liquid chromatography (RPLC), 2) the study of interfacial chemistry in ion chromatography with a particular emphasis on systems used for the separation of lanthanides, actinides and other metal ions from complex acidic matrices, and 3) emersion spectroscopy methods for molecular-level details of interfacial solvation in chromatography.

Significant achievements in 2003-2005: Systematic structural studies of various octadecylsilane (C_{18}) stationary phases (SPs) using Raman spectroscopy.[1,2] to explore effects of ionic strength, pH, and pressure on the rotational/conformational order of the alkylsilane chains. An increase in order of C_{18} phases was observed with increasing ionic strength (see Figure 1) indicating "salting out" of the alkylsilane.[3] For certain ionizable solutes, pH also affects C_{18} order. Pressure effects on C_{18} phases found to be a function of alkylsilane surface coverage, nature of the alkylsilane surface modifier and solvent.[4]

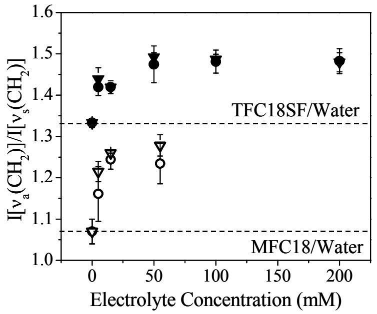


Figure 1. Raman spectral order indicator as a function of [NaCl] for polymeric (TFC18SF) and monomeric (MFC18) SPs.

Spectroscopic and chromatographic studies performed under identical conditions indicate a correlation between SP structural changes and solute retention (see Table 1.) The alkylsilane SP becomes more disordered as solute retention increases. Deviations from this behavior have been observed for certain solutes indicating special interfacial interactions like hydrogen bonding with accessible surface silanols.[5]

Table 1. Chromatographic Capacity Factors and Raman Order Indicator Values for Solutes on a Monomeric C_{18} SP.

Solute	100% MeOH		75%:25% MeOH:H_2O		50%:50% MeOH:H_2O	
	k'	$I[\nu_a(CH_2)]/I[\nu_s(CH_2)]$	k'	$I[\nu_a(CH_2)]/I[\nu_s(CH_2)]$	k'	$I[\nu_a(CH_2)]/I[\nu_s(CH_2)]$
Aniline	0.045	1.06	0.217	1.07	0.721	1.03
Anisole	0.127	1.33	0.624	1.06	3.076	1.05
Toluene	0.174	1.35	1.056	1.24	6.453	1.18

Raman spectral studies of high-density docosylsilane (C_{22}) SPs that exhibit solute shape selectivity have been completed. The temperature dependence of these materials in air indicates a change in order for *part* of the C_{22} chain that has characteristics of a first-order change (i.e., can be fit with the Clapeyron relationship, see Figure 2.)[6] Spectral studies in the presence of common polar and nonpolar mobile phase solvents indicate varying degrees of partial SP chain solvation at the distal end.[7]

A new method for the fabrication of alkylsilane RPLC SPs has been developed that eliminates the need for rigorous drying of the silica substrate or any of the reagents.[8] This method utilizes a monolayer of displaceable n-alcohol (C_2OH to $C_{16}OH$) adsorbates to control access to reactive silanol sites by C_{18} precursor molecules. The low probability of simultaneous loss of adjacent n-alcohol adsorbates minimizes binding of solution C_{18} oligomers leading to monomer-by-monomer growth of the C_{18} layer. This proposed reaction mechanism is strongly supported by the dependence of C_{18} surface coverage on n-alcohol adsorption enthalpy for a given reaction time.[9] These SPs exhibit excellent chromatographic behavior and exhibit shape selectivity comparable to C_{18} SPs requiring considerably more elaborate procedures to achieve comparable surface coverages.

Raman spectroscopy of SPs used for ion chromatography provide evidence for both electrostatic and hydrophobic contributions to retention, even for simple ions.[10] Such “mixed mode” retention is expected to contribute to the behavior observed for SPs used to separate lanthanide and actinide ions in strongly acidic media. Initial studies of the retention of select ions in this category have begun with model SPs.

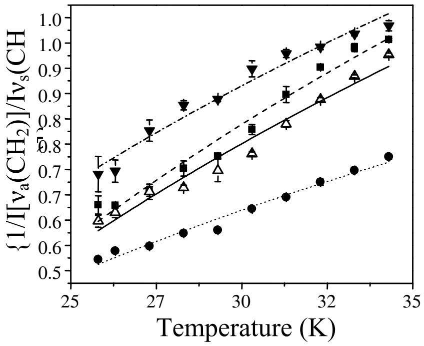


Figure 2. Inverse Raman spectral order indicator as a function of temperature in air for C_{22} SPs. Surface coverage by C_{22} increases from ~3.6 to 7.0 μmol/m^2 for data sets from top to bottom. Symbols represent experimental data, line are best logarithmic fits for Clapeyron relationship for first-order phase change.

A silica-based substrate for emersion studies of interfacial mobile phase solvent structure at alkylsilane SPs was developed.[11] This is a layered structure based on an ultrathin layer (<10 nm) of silica spin-coated from a dilute sol-gel onto a Au substrate modified with a Au_2O_3 layer that serves adhesive and wetting-control functions. Substrates are post-modified with alkylsilanes to model RPLC SPs with conventional procedures.

Specific objectives for 2005-2006: 1) Raman spectral study of a series of “self-assembled monolayer” SPs prepared from different ratios of C_1 and C_{18} in different mobile phase solvents and with solutes (in collaboration with Dr. Lane C. Sander of NIST); 2) Raman spectral investigation of ion chromatographic SPs that model TEVA and UTEVA resins with model lanthanide and actinide ions; 3) emersion vibrational spectroscopy on methanol/water, acetonitrile/water, methanol/water/THF, and acetonitrile/water/THF on model C_{18} SPs.

References of work supported by this project

1. C.J. Orendorff, M.W. Ducey, J.E. Pemberton, L.C. Sander (2004), Structure-Function Relationships in High-Density C_{18} Stationary Phases by Raman Spectroscopy. 3. Effects of Highly Ordering Solvents, *Anal. Chem.*, **75**, 3360-3368.
2. C.J. Orendorff, M.W. Ducey, J.E. Pemberton, L.C. Sander (2003), Structure-Function Relationships in High-Density C_{18} Stationary Phases by Raman Spectroscopy. 4. Effects of Model Aromatic Solutes and Bases, *Anal. Chem.*, **75**, 3369-3375.
3. C.J. Orendorff, J.E. Pemberton, (2005), Electrolyte and pH Effects on the Conformational Order of C_{18} Stationary Phases by Raman Spectroscopy, *Anal. Bioanal. Chem.*, in press.
4. Z. Liao, C.J. Orendorff, J.E. Pemberton, (2005), Effects of Pressure on the Alkyl Chain Order of C_{18} Stationary Phases in Solvents by Raman Spectroscopy, *J. Chromatogr. A*, submitted.
5. C.J. Orendorff, L.C. Sander, J.E. Pemberton, (2005), Solute, Solvent, and Stationary Phase Interactions of RPLC Systems Determined by Raman Spectroscopy, *Anal. Chem.*, submitted.
6. Z. Liao, C.J. Orendorff, L.C. Sander, J.E. Pemberton, (2005), Structure-Function Relationships in High-Density C_{22} Bonded Stationary Phases by Raman Spectroscopy and Comparison to C_{18} Bonded Stationary Phases, *Anal. Chem.*, submitted.
7. Z. Liao, C.J. Orendorff, L.C. Sander, J.E. Pemberton, (2005), Structure-Function Relationships in High-Density C_{22} Bonded Stationary Phases by Raman Spectroscopy and Comparison to C_{18} Bonded Stationary Phases 2. Effects of Common Polar and Nonpolar Solvents, *Anal. Chem.*, submitted.
8. C.J. Orendorff, J.E. Pemberton, (2005), Alkylsilane-Based Stationary Phases via a Displaceable Surface Adsorbate Approach: Synthesis, Characterization, and Chromatographic Performance, *Anal. Chem.*, submitted.
9. Z. Liao, A. Ange, J.E. Pemberton, Alkylsilane-Based Stationary Phases via a Displaceable Surface Adsorbate Approach: Adsorption Enthalpy Dependence for n-Alcohol Adsorbates, in preparation.
10. C.J. Orendorff, J.E. Pemberton, (2005), Understanding Selectivity and Structural Properties of Anion and Cation Exchange Stationary Phases by Raman Spectroscopy, *Anal. Chem.*, submitted.
11. P. Macech, J.E. Pemberton, Ultrathin Silica Layers Supported on Gold Surfaces Modified with Gold Oxide Layers, in preparation.

Non-stoichiometry and magnetic ordering in plutonium oxides: A hybrid density functional theory study

Gustavo E. Scuseria
Ionut D. Prodan
Chemistry Department, Rice University, Houston, TX 77005, USA
guscus@rice.edu
http://python.rice.edu/~guscus/

Collaborator:
Richard L. Martin, Los Alamos National Laboratory, Los Alamos, NM 87545 USA

Overall research goals:

We are developing a predictive theoretical capability for the *f*-elements that is comparable to that found for organics and transition metal compounds, and we are applying these theoretical tools to periodic systems containing actinides. We particularly seek the ability to accurately reproduce, at the same level of theory, various classes of properties such as the bulk parameters, magnetic ordering, and optical activity of a given compound.
The validation of our theoretical tools would endorse the study of systems that are difficult to characterize experimentally, such as defective actinide dioxide lattices.

Significant achievements in 2003-2005:

A new generation of hybrid density functionals (DFs), which include a portion of "exact" (Hartree-Fock type) exchange interaction, is quite promising for modeling strongly-correlated materials. These DFs provide electron localization without requiring an *a priori* knowledge of material dependent parameters or which orbitals to localize. Our previous DOE-sponsored work has shown that hybrid DFs correctly yield an antiferromagnetic ground state for UO_2 [1], with the insulating gap, lattice constant, and density of states (DOS) in good agreement with experiment.

In the present work [2], as for UO_2, we utilize the PBE0 hybrid DF [3], which is implemented in our periodic boundary condition computational code. The PBE0 predictions for PuO_2 and Pu_2O_3 are compared with those of traditional DFs in the Table. The PBE0 lattice constants are in excellent agreement with experiment. Both oxides are predicted to be small band gap insulators, and our calculations find the antiferromagnetic solution to be slightly favored in both compounds.

The non-stoichiometric $PuO_{2.25}$ is found to have lattice constant and bulk modulus essentially identical to those of PuO_2 (5.398 Å and 219 GPa, respectively). This is an important finding, as the invariance of the lattice constant is firmly established experimentally.
The spin distribution in $PuO_{2.25}$ is perhaps the most surprising result of the present work. The interstitial oxygen resembles an O^- species, coupled antiferromagnetically to the surrounding Pu spin. This scenario is compatible with both experience and Zachariesen's rules (a singly-charged interstitial ion would not require an increase in lattice constant).

Table. Calculated and experimental properties of Pu oxides. The density functionals employed are the local spin density approximation (LSDA), the Perdew-Burke-Ernzerhof (PBE) realization of generalized gradient approximation, and the hybrid version of the latter (PBE0). Entries are for the ferromagnetic (F) and antiferromagnetic (AF) solutions, respectively. E_F - E_{AF} represents the difference in total energy between these solutions.

Compound	Method	Band gap (eV)		Lattice constant *a* (Å)		Bulk modulus (GPa)		$E_F - E_{AF}$ (meV)
		F	AF	F	AF	F	AF	
PuO_2	LSDA	0	0	5.278	5.285	229	222	-310
	PBE	0	0	5.399	5.412	189	182	-259
	PBE0	2.4	3.4	5.387	5.385	221	221	+14
	Experiment	> 1.8		5.398		178		≥ 0
Pu_2O_3	LSDA	0	0	3.690	3.680	181	175	-185
	PBE	0	0	3.790	3.791	146	136	-291
	PBE0	2.5	3.5	3.823	3.824	176	181	+9
	Experiment	> 0		3.838		---		> 0

Specific objectives for 2005-2006:

The development of new exchange and correlation density functionals has represented a major goal of our research. We are currently working on assessing them on various actinide dioxides, as part of an overall effort to theoretically describe *f*-electron systems. Defects and distortions of actinide oxide lattices are also under investigation.

References to work supported by this project

1. K. N. Kudin, G. E. Scuseria, and R. L. Martin, (2003), Hybrid density-functional theory and the insulating gap of UO_2. *Phys. Rev. Lett.* **89**, 266402.
2. I. D. Prodan, J. A. Sordo, K. N. Kudin, G. E. Scuseria, and R. L. Martin, Non-stoichiometry and magnetic ordering in plutonium oxides: A hybrid density functional theory study of strongly correlated materials. *Phys. Rev. Lett.* (submitted).

Other references

3. M. Ernzerhof and G. E. Scuseria, (1999), Assessment of the Perdew-Burke-Ernzerhof exchange-correlation functional. *J. Chem. Phys.* **110**, 5029-5036.

Spectroscopic probing of the function of membrane proteins

Mary J. Wirth
Jason W. Coym
University of Arizona
mwirth@email.arizona.edu
www.chem.arizona.edu/wirth

Overall research goals: Our program is directed toward creating an enabling technology for engineering of membrane proteins for solar energy conversion by investigating the science that limits these developments. Our work focuses on the rhodopsin family of integral membrane proteins, with the idea that these are candidates for photovoltaic devices that require informed genetic engineering of the protein. The enabling tools needed are a means of performing chemical separations of membrane proteins without losing their function, and of probing function after separation. We are investigation the ability to insert functional membrane proteins into supported lipid bilayers, which we will then use as an electrophoretic medium for separation without loss of function.

Significant achievements in 2003-2005: Our specific achievements in this past year is that we have learned how to coax electrically neutral lipid bilayer onto an electrically neutral polymer surface, and we determined that we can insert functional rhodopsins into the supported lipid bilayer, and that these functional rhodopsins undergo electromigration.

Our research has progressed from the initial invention of polymer brush phases, through exploring their use in chemical separations, and now to investigation of their novel ability to support neutral lipid bilayers that are decoupled from the substrate. We established that the neutral polymer spontaneously attracts and support a neutral lipid bilayer. We investigated the ability of the bilayer to incorporate integral membrane proteins of the rhodopsin family. We took advantage of collaborators on campus (Victor Hruby and Hank Yamamura) who have experience with the delta-opioid receptor, which is a protein in the rhodopsin family. When in its functional conformation, the delta opioid receptor binds to certain small peptides that then exert force to change the receptor conformation. By labeling the peptide with rhodamine, its binding can be probed directly to assess whether the rhodopsin in the membrane is in a functional form. Our results establish that the protein is functional.

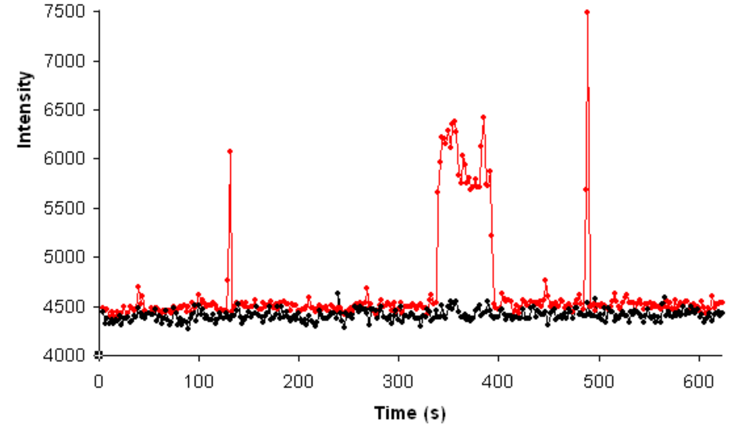


Figure 1. Single-molecule fluorescence from one receptor showing transient binding events (140, 490 s) and a stable binding event .

Single-molecule movies of delta-opioid receptors in the lipid bilayer in the presence of 5 nM solution of rhodamine-labeled peptide were acquired with a 2-s acquisition time. The temporal behavior is described in detail in Figure 1, which shows a receptor that adsorbs transiently at 140 and 490 s, and adsorbs stably from 340 to 400 s. This shows that ligands attempt to bind often without successful binding: the collision cross section for ligand recognition is less than 50%. The results also give a fascinating glimpse into the behavior of the bound ligand, where indeed its behavior evolves over time. The intensity changes between two levels, indicating discrete binding states. Multiple discrete states are common for the many receptors studied here. The single-molecule experiment gives a unique view of the sequence of events after binding.

We have made our firsts steps toward electrophoresis in the lipid bilayer. The receptors are indeed mobile in an applied electric field, and they remain functional as they electromigrate. The mobility is low: $3\text{x}10^{-8}$ cm^2/Vs. We have an indication of what slows the mobility: it decreases markedly with increasing polymer thickness, indicating it is the residual molecular scale roughness of the polymer, and not coupling to the substrate, that limits mobility. This is an exciting result because one can control the interfacial tension of the lipid bilayer with cholesterol to smooth the bilayer over such roughness features.

Specific objectives for 2005-2006: Our specific objective is to understand the factors that control protein mobility in the membrane in order to achieve significantly faster electromigration of bacteriophodopsin. The research described here points to the free energy penalty a bilayer pays when it crosses roughness features, and our approach will be to investigate the use of cholesterol and the use of other lipids and mixtures to ultilize the known relations between bilayer composition and interfacial tension. Our research will also use bacteriorhodopsin itself, rather than similar receptors, since we now have sufficient expertise with integral membrane proteins.

References of work that were supported by this project

Publications.
1. Surface Initiated Radical Polymerization of Acrylamide on Silica at Room Temperature, D. Xiao and Mary J. Wirth, *Macromolecules*, 35, 2919-2925 (2002).
2. Chemical Modification of the Surface of Poly(dimethysiloxane) by Atom-Transfer Radical Polymerization of Acrylamide, Deqing Xiao, Hui Zhang, and Mary Wirth, *Langmuir,* 25, 9971-9976 (2002).
3. Surface Modification of the Channels of PDMS Microfluidic Chips with Polyacrylamide for Fast Electrophoretic Separations of Proteins, Deqing Xiao, Thai Van Le, and Mary J. Wirth, *Analytical Chemistry*, 76, 2055-2061 (2004).
4. Single-Molecule Binding Events at a G-Protein Coupled Receptor in a Lipid Bilayer", Jason W. Coym, Emily A. Smith, Scott M. Cowell, Victor J. Hruby, Henry I. Yamamura, Mary J. Wirth, submitted.
5. Lipid Bilayers on Polyacrylamide Brushes for inclusion of integral membrane proteins, Jason W. Coym, Emily A. Smith, Scott M. Cowell, Victor J. Hruby, Henry I. Yamamura, Mary J. Wirth, submitted.

Presentations at Conferences.
2002 Eastern Analytical Symposium, "Nanoscale Interactions of Analytes and ChemicallyModified Surfaces"
2003 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, "Chemical Modification of Surfaces with Uniform Polymer Chains", presented by Deqing Xiao
2004 Gordon Research Conference on Bioanalytical Sensors, Oxford, UK, "Nanoscale Transport of Single Biomolecules: Integral Membrane Proteins"
2004 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, "Surface Modification of PDMS Microchips for Protein Electrophoretic Separations" Mary J. Wirth and Deqing Xiao

Oral Session 3:

Synthesis

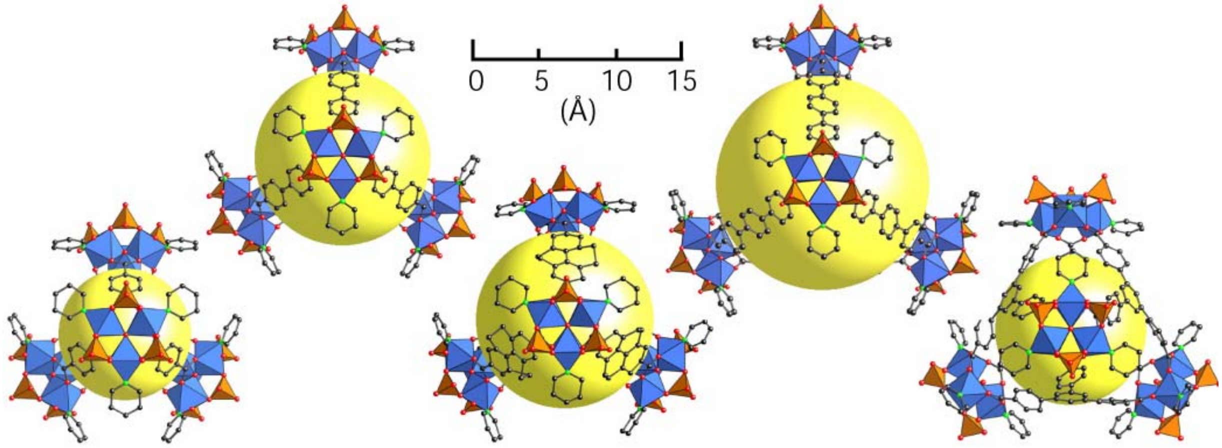
Metal-Organic Frameworks and Polyhedra for Separation of Gases and Organic Molecules

Omar M. Yaghi
Andrew Millward, Andrea Sudik
University of Michigan
oyaghi@umich.edu
http://www.umich.edu/~yaghigrp/

Overall research goals: The objectives of this project are three: First, to continue studying the sorption behavior of organic molecules in MOFs for its relevance to the recovery/removal of toxic organic molecules from liquid and gas streams. Second, to develop rational means to building porous structures that are amenable to design of *large* pores in order to separate larger organic molecules (for example, larger petroleum fragments) in a size and shape selective fashion. Third, functionalize the pores in MOFs with organic moieties and/or with periodic arrays of site isolated metal ions for highly selective separations. This presentation will show how MOFs can be used as platforms for functionalization and sorption of voluminous amounts of gases and organic vapors.

Significant achievements in 2003-2005: 1. One of the outstanding challenges in the field of porous materials is the design and synthesis of chemical structures with exceptionally high surface areas. Until recently the highest surface area for a disordered structure was that of carbon (2,030 m^2/g), and for an ordered structure was that of zeolite Y (904 m^2/g). More recently we, and others, have reported crystals of metal-organic frameworks (MOFs) with similar or somewhat higher surface areas. Despite this progress and the critical importance of high surface area to many applications involving catalysis, separation and gas storage, no strategy has yet been outlined to answer the question of what the upper limit in surface area for a material is, and how it might be achieved. We have developed a general strategy that has allowed us to realize several structures having, by far, the highest surface area reported to date. Specifically, we report on the design, synthesis and properties of crystalline $Zn_4O(Link)_2$ (Link: BTB = 1,3,5-benzenetribenzoate, BBC = 1,3,5-benzenetribiphenyltricarboxylate), new metal-organic framework (named MOF-177 and MOF-200, shown here) with a surface area of 4,500-5,000 m^2/g. We also showed that MOF-177 combines this exceptional level of surface area with an ordered structure that has extra-large pores capable of binding polycyclic organic guest molecules–attributes heretofore unrealized in one material.

2. In another development, we have designed a series of porous molecules with discrete structures. Here we used as nodes the common oxygen-centered trinuclear cluster, $Fe_3O(CO_2)_6$ (Figure below). The carboxylate carbon atoms are the points-of-extension that represent the vertices of a trigonal prismatic secondary building unit. We showed that this SBU can be linked at all six points-of-extension by ditopic links to give 3-D extended MOFs. In this study, three sites on the SBU have been capped by sulfate groups to yield a triangular SBU which predisposes the carboxylates at 60° to each other. Thus linking these SBUs together by either ditopic links such as 1,4-benzenedicarboxylate (BDC), 4,4'-biphenyldicarboxylate (BPDC), tetrahydropyrene-2,7-dicarboxylate (HPDC), and 4,4-terphenyldicarboxylate (TPDC) or a tritopic link such as 1,3,5-tris(4-carboxyphenyl)benzene (BTB) gives porous truncated tetrahedra. Within this series of compounds, the pore size and its opening have been systematically varied without changing their overall tetrahedral topology. We described the synthesis and X-ray single crystal structures of each member of this series and, for three



members, also show that their structures are architecturally robust and are indeed capable of gas adsorption typical of materials with permanent porosity.

Specific objectives for 2005-2006: 1. Characterize more precisely the gas sorption characteristics of this series of compounds including study of their application to selective separations of methane/carbon dioxide, and ethane/ethylene. 2. Examine the selective sorption of hydrogen disulfide, hydrogen, methane (including polychlorinated organics) in both the impregnated and non-impregnated MOF-177. 3. Functionalize the pores in the tetrahedral series with organic groups that would produce openings tailored for the selective removal aryl and naphthalene based organics.

References of work that were supported by this project

1. N. Rosi, J. Kim, B. Chen, M. Eddaoudi, M. O’Keeffe, O. M. Yaghi, (2005) Rod-Packings and the Metal-Organic Frameworks with Rod-Like Secondary Building Units, *J. Am. Chem. Soc.*, **127**, 1504-1518.
2. J. Rowsell, O. M. Yaghi , Metal-Organic Frameworks: A New Class of Porous Materials, (2004) *Micro- and Mesoporous Mater*., **73**, 3-16.
3. J**.** Rowsell, A. Millward, K. Park, O. M. Yaghi, (2004) Hydrogen Sorption in Functionalized Metal-Organic Frameworks**,** *J. Am. Chem. Soc.*, 126, 5666-5668.
4. T. Duren, L. Sarkisov, O. M. Yaghi, R. Q. Snurr, (2004), Design of New Materials for Methane Storage, *Langmuir*, **20**, 2683-2689.
5. H. Chae, D. Y. Siberio-Perez, J. Kim, Y. Go, M. Eddaoudi, A. Matzger, M. O’Keeffe, O. M. Yaghi, (2004) A Route to High Surface Area, Porosity and Inclusion of Large Molecules in Crystals, *Nature*, 427, 523-527.
   Featured in (1) Chemical & Engineering News magazine, Feb. 9, 2004, (2) BBC World Service, Feb. 04, (3) New Scientist, Feb. 04, and (4) several science magazines and local papers.
6. O. M. Yaghi, M. O’Keeffe, N. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim**,** (2003) Reticular Synthesis and the Design of New Materials, *Nature***,** *423***,** 705-712**.**
7. N. Rosi, M. Eddaoudi, D. Vodak, J. Eckert, M. O’Keeffe, O. M. Yaghi, (2003) Metal-Organic Frameworks as New Materials for Hydrogen Storage, *Science*, **300**, 1127-1132.
   Featured in (1) Chemical &Engineering News magazine, May 19, 2004, and (2) Technology Research News Magazine, May 21, 03.

The Synthesis, Structures and Chemical Properties of Macrocyclic Ligands Covalently Bonded into Layered Arrays

Principle Investigator: Prof. Abraham Clearfield
Assistant Research Scientist: Dr.Deyuan Kong
Department of Chemistry, Texas A&M University, College Station, TX 77843-3255
clearfield@mail.chem.tamu.edu

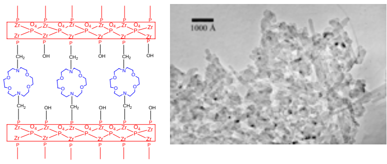
Dr. Naima Bestaoui, Texas A&M University; Dr. Hari Gali, Lynntech. Inc. College Station

Overall research goals:

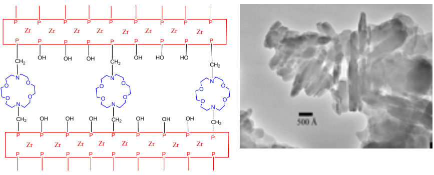
Having prepared azacrowns with multiple phosphonic acid groups we will utilize the concepts of crystal engineering to synthesize three-dimensional porous nanoaggregates of crown ethers. The objective is to determine the effect of structure on selectivity and binding strength of metals. Potential uses are as sorbents for separation of radionuclides for medical uses. We have had preliminary success in separating α-emitters such as ^{207}Bi from ^{88}Y and Ba from La acting as surrogates for ^{223}Ra and Ac. Our phosphonates will also be examined for use in bone cancer treatment and as radiopharmaceuticals.

Significant achievements in 2003-2005:

1. Synthesis of cross-linked layered compounds (186211, 186214) and bilayered Zirconium phosphonates-15111 were carried out and characterized by XRD, IR, EA, TGA and Microprobe analysis. TEM and SEM have been done for all three compounds and they show a lamellar morphology and are in the range of nano-sized materials. Surface areas have been measured, 186211 and 186214 have 90, 40 m^2/g, respectively. 186211 is mostly mesoporous with pore size in the range of 80-100 Å. All those materials have been subjected for ion exchange of Cu(II).



186211



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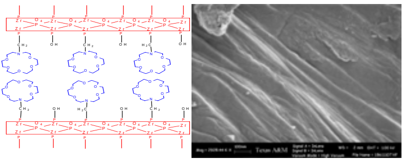
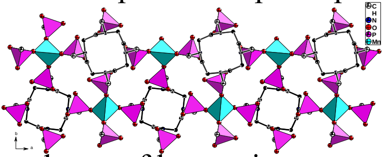
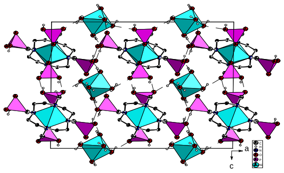


15111

DOTP 1,4,7,10-tetrakis(methylene phosphonic acid)-1,4,7,10-tetraaza-cyclododecane has been synthesized with Mn^{2+} and Ni^{2+}. Mn-DOTP forms 2D sheets with four phosphonic acid groups involved in coordination. The nickel compound crystallized as an ion pair with two phosphonic pendent groups coordinated to the central nickel atoms. The charge is balanced by Ni(H$_2$O)$_6$$^{2+}$. The Mn compound did pick up Cs$^+$ in our preliminary experiments.



Mn-DOTP



Ni-DOTP

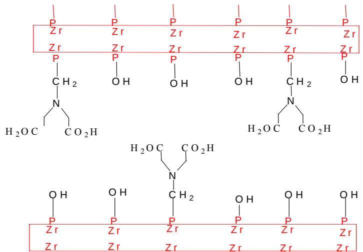
2. Syntheses of larger size macrocyclic ring systems

To develop the ring system, ten novel macrocyclic complexing rings ranging from 24-32 membered have been synthesized and characterized by NMR, IR, EA and ESI-MS. All macrocyclic ligands were synthesized by a high dilution technique and optimized Mannich reactions. Final products contained 6-8 dangling phosphonic groups attached to imino nitrogen atoms. Three final products have been structurally characterized by x-ray structure determination together with three intermediate rings as HBr salts. Interesting hydrogen bonding characterized these compounds.

3. Synthesis of Zr-PMIDA layered complexes

Table 1: Dissociation constants for La and Bi

Compound	KdLa	KdBi	KdLa/KdBi	H_3PO_4/ $H_2PMIDAH_2$
NB-I-35	**9,743**	**112.6**	**86.5**	**5/1**
NB-I-36	5,406	1,164	4.64	1/1
NS-I-49-1	11,498	21,834	0.52	3/2
NS-I-49-2	8,441	13,286	0.387	2/1
NS-I-49-3	7,388	4,032	0.556	7/3
HG-1-71	1,011	535.6	1.88	1/2.5



Schematic structure of the layered Zr-PMIDA

Representative samples were characterized using X-ray diffraction, MAS NMR, CHN analysis, TGA, and ICP-AES. Synthetic conditions were optimized for scale-up synthesis and to produce materials in a pelletized form suitable for the column applications.

Specific objectives for 2005-2006:

We have synthesized several classes of new hexa and octaazacrown ethers with 24 to 32 membered ring systems and converted them to phosphonic acid derivatives. Potentiometric titrations of those phosphorylated crowns will be carried out in the presence and absence of divalent metal ions to yield stability constants of the metal complexes. We propose to carry out similar studies for the linear chain and layered compounds to determine how the immobilized aggregated crown ethers behave relative to their soluble unphosphonated forms. All those synthesized materials will be examined for the separation of Bi/La and other heavy metal ions uptake.

References of work that were supported by this project (10 publications listed below)

10. Deyuan Kong and Abraham Clearfield "Supramolecular Hydrogen Bonded Framework with 6-phosphonopyridine-2-carboxylic acid Ligand and Transitional Metal Ions" *Cryst. Growth & Design*. (in press) 2005

9. Deyuan Kong, Jennifer McBee and Abraham Clearfield "Crystal Engineered Acid-Base Complexes with 2D and 3D Hydrogen Bonding Systems Using Bisphosphonic Acid as Building Block" *Cryst. Growth & Design*. (in press) 2005

8. Deyuan Kong and Abraham Clearfield "Novel Copper Macroleaflet with N-methylenephosphonic acid-18-crown-6" *Chem. Commun*. 1005-1006, 2005

7. Deyuan Kong, Yang, Li, Xiang Ouyang, Andrey Prosvin, Hanhua Zhao, Joseph H. Ross, Kim Dunbar and Abraham Clearfield " Syntheses, Structures and Magnetic Properties of New Types of Cu(II), Co(II) and Mn(II) Organophosphonate Materials: 3D-Frameworks and a 1D-chain Motif " *Chem. Mater*. **16**, 3020-3031, 2004

6. Deyuan Kong, Dmitri Medvedev and Abraham Clearfield "DOTP-Manganese and Nickel complexes: from tetrahedra network with 12-memered rings toward single molecular phosphonate" *Inorg. Chem***.** **43**, 7308-7314, 2004

5. Mingzhang Gao, Deyuan Kong, Abraham Clearfield, Ralph Zingaro "Structure-defined chiral bis(oxazolinyl)thiophenes for Ru-catalyzed asymmetric cyclopropanation" *Tetrahedron Lett*. **56**, 5649-5653, 2004

4. Deyuan Kong, Joseph Reibenspies, Abraham Clearfield and A. E. Martell "Synthesis and crystal structure of nickel and cobalt complexes with tetraazamacrocyclic ligand attached four pyridinyl groups " *Inorg. Chem. Commun*., **7,** 195-200, 2004

3. Deyuan Kong, Yang, Li, Joseph H. Ross and Abraham Clearfield "A novel copper organophosphonate with a pore-like 3D framework and Cu-Cu magnetic ordering" *Chem. Communication*. 1720-1721, 2003**.**

2. Deyuan Kong**,** Xiang Ouyang, Arthur E. Martell, Abraham Clearfield "Novel Dioxotetrazamacrocyclic "Sandwich" Complexes-Synthesis and Structural Characterization" *Inorg. Chem. Commun*. **6**, 317-321, 2003

1. Deyuan Kong, Jianggao Mao, Arthur E. Martell and Abraham Clearfield "A new oxo-azamacrocyclic Ligand:13,27-dimethyl-6,20-dioxa-3,9,17,23-tetraaza-tricyclo[23.3.1.1^{11,15}]triaconta-1(29),11, 13,15(30),25,27-hexaene-29,30-diol and A dinuclear Copper (II) Complex: Syntheses, Characterization and Binding Ability" *Inorg. Chim. Acta* **342,** 260-266**,** 2003.

O3-3

Investigation of Size-Selective Separations and Mitigation of Fouling by Multilayer Polyelectrolyte Membranes

Merlin L. Bruening
Malaisamy Ramamoorthy, Matthew Miller, Christin Lott
Michigan State University
bruening@cem.msu.edu
http://www.chemistry.msu.edu/faculty/bruening/

Overall research goals: The first goal of this project is to control and understand size-selective transport through multilayer polyelectrolyte membranes (MPMs). Knowledge of how film composition and deposition conditions affect swelling, partitioning, effective pore size, selectivity, and flux will permit development of new, high-flux MPMs that can rapidly separate organic molecules with a wide range of molecular weights. The variety of available polyelectrolytes, as well as the ability to vary deposition conditions such as pH and ionic strength, make MPMs an extremely attractive platform for examining size-exclusion by polymer films. Our second objective is development of a membrane regeneration procedure involving desorption of the top bilayer of a MPM (along with foulants) and subsequent readsorption of a fresh bilayer. This method is distinctive because it provides a completely *new* surface upon regeneration. Such a regeneration strategy is unique to MPMs because of the simple adsorption procedure (Figure 1) employed in their formation.

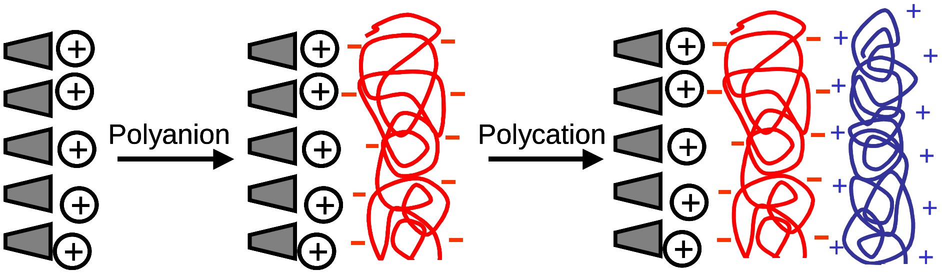


Figure 1. Alternating adsorption of a polycation and a polyanion to form a multilayer polyelectrolyte membrane on a porous support. Interweaving of polyelectrolytes is not shown for figure clarity.

Significant achievements in 2003-2005: In the last two years, we have investigated how size exclusion by MPMs deposited on porous alumina varies with changes in polyelectrolyte composition. Remarkably, judicious selection of constituent polyelectrolytes yields membranes capable of separating molecules with molecular weights ranging from 100 to ~30,000. Water fluxes through these ultrathin films are >2 $m^3/(m^2day)$ at a pressure of only 4.8 bar, and such fluxes are about twice those through typical nanofiltration membranes. Selectivities in separations of glucose and raffinose reach 40, with 40% passage of glucose.

Based on previous ion dialysis and pervaporation studies, we thought that the molecular weight cutoffs (MWCOs) of MPMs would correlate with the degree of ionic cross-linking in these membranes, and that the density of ionic cross-links should, in turn, depend on the charge density of the constituent polyelectrolytes. Nanofiltration data strongly suggest that this is the case. For example,

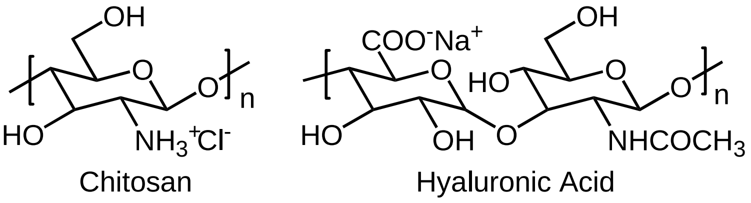


Figure 2. The structures of chitosan and hyaluronic acid. Their open structure and low charge density lead to highly permeable films.

films prepared from chitosan and hyaluronic acid (1 ion pair per 37 non-hydrogen atoms, Figure 2) exhibit a MWCO of ~40,000, while some poly(styrene sulfonate)/poly(allylamine hydrochloride) films (1 ion pair per 16 non-hydrogen atoms) have MWCOs of ~100. *In situ* ellipsometry measurements show that the chitosan/hyaluronic acid films swell by 260% upon immersion in water, while poly(styrene sulfonate)/poly(allylamine hydrochloride) swells by only 50%. Greater swelling, which is likely due to fewer ionic cross-links, yields a more open membrane with a lower MWCO.

In another major achievement, we demonstrated the formation of MPMs on polymeric ultrafiltration membranes. Interactions between an initial poly(styrene sulfonate) layer and the ultrafiltration substrate may be crucial for good adhesion of the films to these polymer supports. The use of ultrafiltration membranes as supports is advantageous in that they are both less fragile and less expensive than the porous alumina that we employed previously. Remarkably, films containing only 1.5 bilayers of polyelectrolytes are capable of changing the MWCO of a membrane from 50 kDa to 500 Da. The decreased number of layers needed to cover these supports will make membrane formation with polyelectrolyte multilayers much more practical. Although most inorganic ions have molecular weights <500, electrostatic exclusion of multivalent ions by MPMs on ultrafiltration supports allows rapid separations of chloride and sulfate with a selectivity of 30.

Specific objectives for 2005-2006: Our objectives for the next two years include examining the fouling tendencies of MPMs in solutions containing humic acids and proteins. Fouling by these species will vary with both the surface charge and composition of the polyelectrolyte film, and an understanding of the interactions between films and foulants will allow design of membranes with longer duty cycles and gentler cleaning regimens. Additionally, we aim at developing regeneration methods that will include removal of the polyelectrolyte film along with the fouling layer and deposition of a replacement film to give a completely new membrane. Finally, we will continue examining transport through polyelectrolyte films with a focus on understanding partitioning and how swelling and selectivity vary with solvent polarity.

References of work that were supported by this project

1. D.M. Sullivan and M.L. Bruening, “Ultrathin, Cross-linked Polyimide Pervaporation Membranes Prepared from Polyelectrolyte Multilayers”, *J. Membrane Sci.*, **248**, 161-170 (2005).
2. M.D. Miller and M.L. Bruening, “Controlling the Nanofiltration Properties of Multilayer Polyelectrolyte Membranes through Variation of Film Composition”, *Langmuir*, **20**, 11545-11551 (2004).
3. S. Kidambi, J. Dai, J. Li, and M.L. Bruening, “Selective Hydrogenation by Pd Nanoparticles Embedded in Polyelectrolyte Multilayers”, *J. Am. Chem. Soc.*, **126**, 2658-2659 (2004).
4. X. Liu and M.L. Bruening, “Size-Selective Transport of Uncharged Solutes through Multilayer Polyelectrolyte Membranes”, *Chem. Mater.*, **16**; 351-357 (2004).
5. B.W. Stanton, J.J. Harris, M.D. Miller, and M.L. Bruening, “Ultrathin, Multilayered Polyelectrolyte Films as Nanofiltration Membranes”, *Langmuir*, **19**, 7038-7042 (2003).
6. D.M. Sullivan and M.L. Bruening, “Ultrathin, Gas-selective Polyimide Membranes Prepared from Multilayer Polyelectrolyte Films”, *Chem. Mater.*, **15**, 281-287 (2003).
7. B.Y. Kim and M.L. Bruening, “pH-Dependent Growth and Morphology of Multilayer Dendrimer/Poly(acrylic acid) Films”, *Langmuir*, **19**, 94-99 (2003).

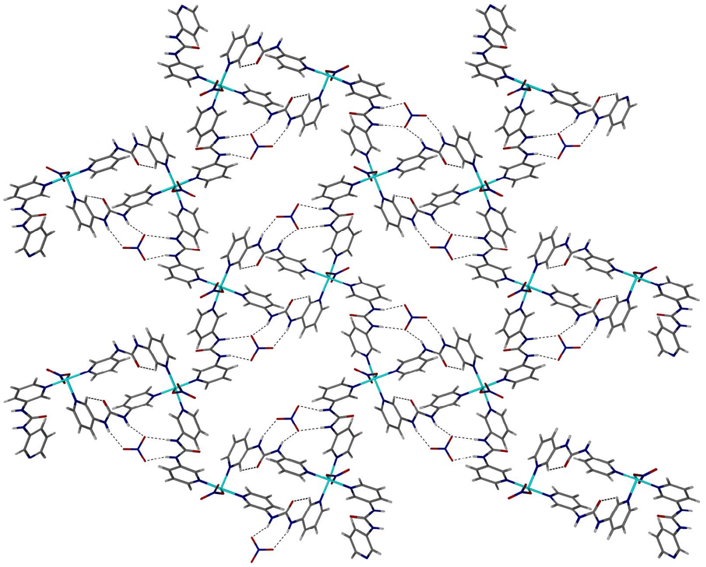
Principles of Chemical Recognition and Transport in Extractive Separations: Metal-Organic Frameworks as Solid-Phase Anion Exchangers

Radu Custelcean, PI
Maryna G. Gorbunova, Postdoctoral
Chemical Sciences Division, Oak Ridge National Laboratory
custelceanr@ornl.gov
http://www.ornl.gov/sci/casd/csg/

Collaborators: Bruce A. Moyer, Peter V. Bonnesen, Lætitia H. Delmau, ORNL; Benjamin P. Hay, PNNL

Overall research goals: A new thrust has been initiated in 2004, aiming at the understanding of anion recognition and separation by novel solid-state materials. In particular, this research involves metal-organic frameworks (MOFs) as scaffolds for the attachment of anion binding sites. Thus, hydrogen-bonding groups such as –OH, –COOH, –CONH, or urea are being incorporated into MOFs via organic synthesis of building blocks containing traditional pyridine or PhCN metal coordinating groups. The MOFs resulting from the self-assembly of these organic ligands with transition metal salts are being analyzed by single-crystal X-ray diffraction as a first step toward understanding their potential anion-recognition abilities. Selected MOFs identified by structural analysis will be subjected to further thermodynamic and kinetic studies to assess their anion-separation properties.

Significant achievements in 2003–2005: The binding of oxyanions such as NO_3^-, SO_4^{2-}, $CH_3SO_3^-$, or $CF_3SO_3^-$ by novel MOFs built from simple ligands containing urea groups has been demonstrated by single-crystal X-ray structural analysis. The ligands were designed so that the C=O group from urea forms relatively strong intramolecular C-H···O hydrogen bonds, thus inhibiting intermolecular urea···urea interactions that would otherwise render the anion-binding sites unusable. The urea group has been found to bind the anions via the expected bidentate hydrogen bonding, as exemplified by nitrate in the figure below. Remarkably, no self-association between urea molecules has been observed in most of the MOFs synthesized, despite the known persistance of this group in self-assembling into one-dimensional hydrogen-bonding chains in the solid state.



Crystal structure of $Cu(NO_3)_2 \cdot (DPU)_2$ (DPU = N, N'-di-*m*-pyridylurea) showing nitrate binding via bidentate hydrogen bonding

A different design strategy being pursued is based on 4,4'-bipyridine (bpy), a versatile ligand frequently utilized in the synthesis of MOFs. The synthesis of bpy ligands decorated with hydrogen-bonding groups for anion binding, such as –COOH, $-CONH_2$, –OH, or urea, is currently under way. A prototype MOF functionalized with –COOH groups has been synthesized and structurally characterized. The presence of free carboxylic groups pointing inside the pores of this MOF is remarkable and unprecedented, as such reactive groups typically participate in the network assembly and thus are not available for guest binding. Preliminary competition experiments demonstrated selective inclusion of halide anions against larger oxyanions such as NO_3^-, SO_4^{2-}, ClO_4^-, or AcO^-.

Specific objectives for 2005–2006: The design, synthesis, structural characterization, and separation properties of MOFs functionalized for anion binding will continue with focus on how to achieve greater control of the organization of functional groups within the binding cavity. A particular emphasis will be placed on the introduction in MOFs of multiple urea groups positioned complementarily around oxyanions for shape recognition, which is expected to result in enhanced selectivity. The design of the ligands will be aided by molecular modeling at ORNL and through collaboration with Ben Hay at PNNL. Thus, the top synthetically accessible candidate ligands identified by the HostDesigner software program developed at PNNL will be synthetically modified with pyridine or PhCN end groups that provide for transition metal coordination and incorporation into MOFs. The synthesis of one such ligand, containing an adamantine link, is currently under way through collaboration with Peter Bonnesen at ORNL.

References of work that were supported by this project in 2003–2005:

(1) R. Custelcean and M. G. Gorbunova (2005), "Pore Functionalization in Metal-Organic Frameworks: A Flexible Microporous Coordination Polymer with Free Carboxylic Groups Attached to the Pore Walls", submitted to *Angew. Chem. Int. Ed.*

(2) R. Custelcean and M. G. Gorbunova (2005), "Protonation-Assisted Spontaneous Resolution: Formation of a Homochiral 2D Interpenetrated Hydrogen-Bonded Network from 4,4'-Binicotinic Acid under Highly Acidic Conditions", submitted to *CrystEngComm*.

(3) R. Custelcean, L. H. Delmau, B. A. Moyer, J. L. Sessler, W.-S. Cho, D. Gross, G. W. Bates, S. J. Brooks, M. E. Light and P. A. Gale (2005), "Calix[4]pyrrole: An old yet new ion-pair receptor", *Angew. Chem. Int. Ed., in press.*

(4) B. A. Moyer, P. V. Bonnesen, R. Custelcean, L. H. Delmau, and B. P. Hay (2005), "Strategies for Using Host-Guest Chemistry in the Extractive Separation of Ionic Guests." *Kem. Ind.*, in press.

(5) R. Custelcean, M. G. Gorbunova, and P. V. Bonnesen (2005), "Steric Control over Hydrogen Bonding in Crystalline Organic Solids: A Structural Study of N,N'-Dialkylthioureas" *Chem. Eur. J.*, *11*, 1459.

O3-5

Synthesis, Structure, and Ion-Exchange Properties of Open-Framework Actinyl Materials

Thomas E. Albrecht-Schmitt
Dr. Jonathan D. Woodward, Tyler A. Sullens, Tatiana Shvareva, J. Travis Brown
Auburn University
albreth@auburn.edu
http://www.auburn.edu/academic/science_math/chemistry/docs/faculty_staff/albrechtnew.html

Collaborators: Lynne Soderholm (ANL), S. Skanthakumar (ANL), Richard G. Haire (ORNL), Richard E. Sykora (ORNL), Zerihun Assefa (ORNL)

Overall research goals: The one-dimensional nature of the majority of the uranyl iodates prepared in our group has caused us to ask the question: How can we reverse this trend and increase the likelihood of uranyl compounds forming three-dimensional, open-framework structures? These compounds will be of interest not only because of their unusual structures, but because their structures lend themselves to ion-exchange studies. We propose that uranyl compounds containing octahedral building units such as GaO_6, TeO_6, and IO_6 will adopt three-dimensional structures because unlike uranyl polyhedra these octahedral units can bridge in all three dimensions.

Significant achievements in 2003-2005: Our most recent achievement is the syntheses, structures, and ion-exchange properties of the three-dimensional open-framework uranyl gallium phosphates, $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ (**UGaP-1**) and $Cs[UO_2Ga(PO_4)_2]$ (**UGaP-2**). The reaction of $UO_2(NO_3)_2\cdot 6H_2O$ with Cs_2CO_3 or CsCl, H_3PO_4, and Ga_2O_3 under mild hydrothermal conditions results in the formation of **UGaP-1** or **UGaP-2**. The structure of **UGaP-1** was solved from a twinned crystal revealing a three-dimensional framework structure consisting of one-dimensional ${}^{1}_{\infty}[Ga(OH)(PO_4)_2]^{4-}$ chains composed of corner-sharing GaO_6 octahedra and bridging PO_4 tetrahedra that extend along the *c* axis. The phosphate anions bind the UO_2^{2+} cations to form UO_7 pentagonal bipyramids. The UO_7 moieties edge-share to create dimers that link the gallium phosphate substructure into a three-dimensional ${}^{3}_{\infty}[(UO_2)_2(GaOH)_2(PO_4)_4]^{4-}$ anionic lattice (Figure 1.) that has intersecting channels running down the *b* and *c* axes. Cs^+ cations and water molecules occupy these channels. The structure of **UGaP-2** is also three-dimensional and contains one-dimensional ${}^{1}_{\infty}[Ga(PO_4)_2]^{3-}$ gallium phosphate chains that extend down the *a* axis. These chains are formed from fused eight-membered rings of corner-sharing GaO_4 and PO_4 tetrahedra. The chains are in turn linked together into a three-dimensional ${}^{3}_{\infty}[UO_2Ga(PO_4)_2]^{1-}$ framework by edge-sharing UO_7 dimers as occurs in **UGaP-1**. There are channels that run down the *a* and *b* axes through the framework. These channels contain the Cs^+ cations. Ion-exchange studies indicate that the Cs^+ cations in **UGaP-1** and **UGaP-2** can be exchanged for Ca^{2+} and Ba^{2+}.

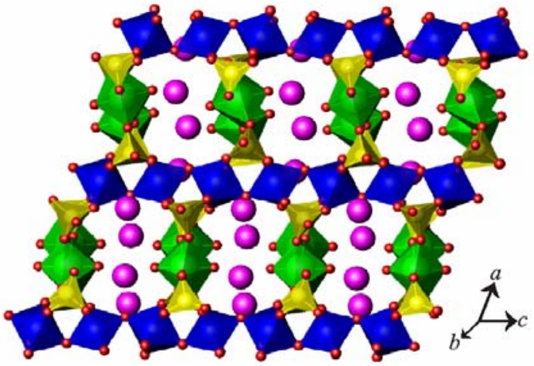


Figure 1. An illustration of the three-dimensional ${}^{3}_{\infty}[(UO_2)_2(GaOH)_2(PO_4)_4]^{4-}$ anionic lattice of **UGaP-1**.

Specific objectives for 2005-2006: Our primary objectives are to prepare open-framework uranyl gallium phosphates, uranyl antimony phosphates, and uranyl titanium phosphates, to determine their structures, and to measure their ion-exchange properties.

Selected References of work that were supported by this project in 2004-05

1. T. Y. Shvareva, P. M. Almond, and T. E. Albrecht-Schmitt (2005) "Crystal chemistry and ion-exchange properties of the layered uranyl iodate $K[UO_2(IO_3)_3]$," *J. Solid State Chem., in press*.
2. T. A. Sullens and T. E. Albrecht-Schmitt, (2005) "Structure and Properties of the Thorium Vanadyl Tellurate, $Th(VO_2)_2(TeO_6)(H_2O)_2$," *Inorg. Chem.* **2005**, *in press*.
3. T. Y. Shvareva, T. A. Sullens, T. C. Shehee, and T. E. Albrecht-Schmitt, (2005) "Syntheses, Structures, and Ion-Exchange Properties of the Three-Dimensional Framework Uranyl Gallium Phosphates, $Cs_4[(UO_2)_2(GaOH)_2(PO_4)_4]\cdot H_2O$ and $Cs[UO_2Ga(PO_4)_2]$," *Inorg. Chem.*, **44**, 300-305.
4. R. E. Sykora, Z. Assefa, R. G. Haire, and T. E. Albrecht-Schmitt, (2004) "Hydrothermal Synthesis, Structure, Raman Spectroscopy, and Self-Irradiation Studies of $^{248}Cm(IO_3)_3$," *J. Solid State Chem.*, **177**, 4413-4419.
5. R. E. Sykora and T. E. Albrecht-Schmitt, (2004) "Hydrothermal Synthesis and Crystal Structure of $Cs_6[(UO_2)_4(W_5O_{21})(OH)_2(H_2O)_2]$: A New Polar Uranyl Tungstate," *J. Solid State Chem.*, **177**, 3729-3734.
6. E. Jobiliong, Y. Oshima, J. S. Brooks, T. E. Albrecht-Schmitt, (2004) "Magnetism and Electron Spin Resonance in Single Crystalline β-$AgNpO_2(SeO_3)$," *Solid State Comm.*, **132**, 337-342.
7. J. D. Woodward, P. M. Almond, and T. E. Albrecht-Schmitt, (2004) "Synthesis and Crystal Structures of the Layered Uranyl Tellurites $A_2[(UO_2)_3(TeO_3)_2O_2]$ (A = K, Rb, Cs)," *J. Solid State Chem.*, **177**, 3971-3976.
8. T. A. Sullens, R. A. Jensen, T. Y. Shvareva, and T. E. Albrecht-Schmitt, (2004) "Cation-Cation Interactions Between Uranyl Cations in a Polar Open-Framework Uranyl Periodate," *J. Am. Chem. Soc.*, **126**, 2676-2677.
9. P. M. Almond, R. E. Sykora, S. Skanthakumar, L. Soderholm, and T. E. Albrecht-Schmitt, (2004) "Hydrothermal Synthesis, Structure, and Magnetic Properties of the Mixed-Valent Np(IV)/Np(V) Selenite, $Np(NpO_2)_2(SeO_3)_3$," *Inorg. Chem.*, **43**, 958-963.
10. R. E. Sykora, J. King, A. Illies, and T. E. Albrecht-Schmitt, (2004) "Hydrothermal Synthesis, Structure, and Catalytic Properties of $UO_2Sb_2O_4$" *J. Solid State Chem.*, **177**, 1717-1722.
11. P. M. Almond and T. E. Albrecht-Schmitt, (2004) "Hydrothermal synthesis and crystal chemistry of the new strontium uranyl selenites, $Sr[(UO_2)_3(SeO_3)_2O_2]\cdot 4H_2O$ and $Sr[UO_2(SeO_3)_2]$" *Am. Mineral.*, **89**, 976-980.
12. R. E. Sykora, S. M. McDaniel, and T. E. Albrecht-Schmitt, (2004) "Hydrothermal Synthesis and Structure of $K_6[(UO_2)_4(CrO_4)_7]\cdot 6H_2O$: A Layered Uranyl Chromate with a New Uranyl Sheet Topology," *J. Solid State Chem.*, **177**, 1431-1436.
13. A. C. Bean,* B. L. Scott, T. E. Albrecht-Schmitt, and W. Runde, (2004) "Intercalation of KCl Into Layered Neptunyl and Plutonyl Iodates," *J. Solid State Chem.*, **176**, 1346-1351.
14. R. E. Sykora, A. C. Bean, B. L. Scott, W. Runde, and T. E. Albrecht-Schmitt, (2004) "New One-Dimensional Uranyl and Neptunyl Iodates: Crystal Structures of $K_3[(UO_2)_2(IO_3)_6](IO_3)\cdot H_2O$ and $K[NpO_2(IO_3)_3]\cdot 1.5H_2O$," *J. Solid State Chem.*, **177**, 725-730.

O3-6

Actinide Transition-Metal Chalcogenides and Pnictides

James A. Ibers
Jong-Young Kim
Danielle Gray
Northwestern University
ibers@chem.northwestern.edu
http//www.chem.northwestern.edu/~ibers/

Lynda Soderholm, Argonne National Laboratory

Overall research goals: To synthesize new chalcogenides and pnictides of U and Np, to characterize them structurally as single crystals, to determine selected physical properties, and to develop theoretical insights into these properties.

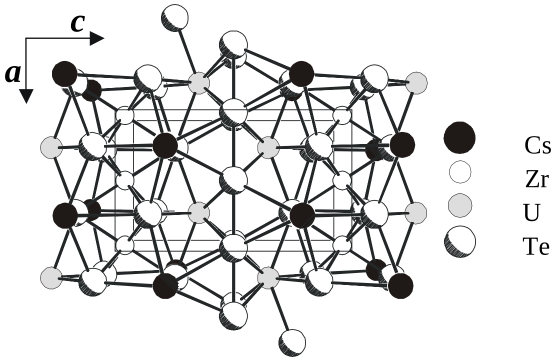


Figure 1. Structure of $CsZrUTe_5$

Significant achievements since July 2004: The target compound $CsZrUTe_5$ was synthesized at 1223 K by the reaction of Cs_2Te_3, Zr, U, and Te with CsCl as a flux. $CsZrUTe_5$ is isostructural with $CsTiUTe_5$ [1]. $CsZrUTe_5$ has a layered structure (Fig. 1) in which UTe_8 bicapped trigonal prisms share common edges with $ZrTe_6$ octahedra. Cs^+ cations separate the layers. The structure contains an infinite linear chain of Te atoms in which the Te!Te separation is 3.1551 (4) Å.

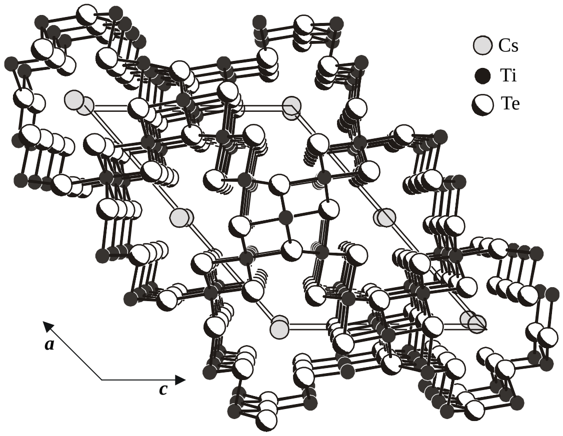


Figure 2. Structure of $CsTi_5Te_8$

$CsTi_5Te_8$ has been synthesized by an "U-assisted" solid-state synthesis. $CsTiUTe_5$ was originally synthesized at 1173 K by the reaction of Cs_2Te_3, Ti, U, and Te. An attempt to re-synthesize $CsTiUTe_5$ with CsCl added as a flux failed; rather the new ternary compound $CsTi_5Te_8$ was isolated. Attempts to make this compound in a rational manner failed; it appears that the presence of U is essential for its formation. The structure (Fig. 2) contains a network of $TiTe_6$ octahedra with Cs-containing channels. This structure is similar to that of $CsCr_5S_8$ [2]. However, the channels differ.

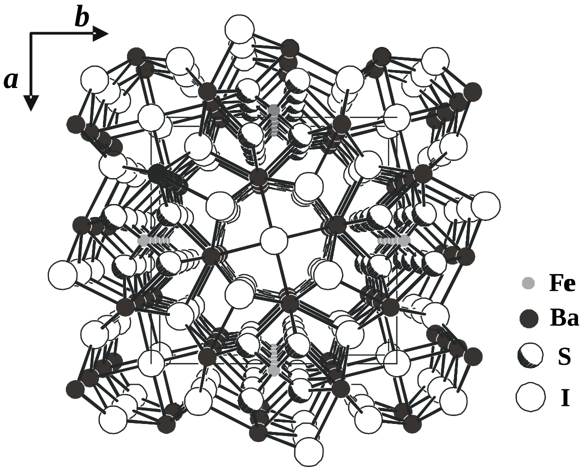


Figure 3. Structure of $Ba_4Fe_2I_5S_4$

$Ba_4Fe_2I_5S_4$ is another new compound made in an "U-assisted" solid-state synthesis. In an attempt to synthesize a Ba/U/Fe/S quaternary the reaction of FeS, BaS, S, and U with BaI_2 as a flux was carried out at 1173 K. The compound $Ba_4Fe_2I_5S_4$ resulted! This synthesis is reproducible. A more rational synthesis has not been found; the presence of U appears to be essential. The structure (Fig. 3) contains what we believe is the first example of infinite chains of edge-sharing FeS_4 tetrahedra.

We have devised methods to make pure samples of some of the U/Q binaries. To prepare U_2Q_3, stoichiometric amounts of U and Q with CsCl as a flux are sealed and heated at 973 K. To prepare U_3Q_5, stoichiometric amounts of U and Q with I_2 as a transport agent are sealed and placed in a two-zone furnace at 1073/1173 K.

Specific objectives for 2005-2006: The first objective is to get Np solid-state chemistry underway at ANL. Progress has been slow, in part because this work will entail techniques, apparatus, and procedures that are new to the Actinide Facility. Currently, the first version of the Safety Plan is being reviewed. The second objective is to synthesize at Northwestern new U/M/Q and U/M/T compounds, where M is a transition metal, Q is a chalcogen and T is a pnictogen. Successful syntheses in the past have involved U powder. Unfortunately, the only U now available to us is in the form of turnings. This has greatly hampered our progress. Consequently, a specific objective is to find ways to live more peacefully with U turnings. The U/Q binaries noted above will be reacted with M/Q and M/T compounds. Metathesis reactions between UCl_4 or UCl_3, and A/Q or A/T salts, where A is an alkali metal, will be carried out. Arc melting U turnings with M to make alloys will be attempted. If such alloys can be made they will be reacted with Q or T to form UMQ or UMT ternaries.

References of work that were supported by this project: None.

Other references

[1] J. A. Cody and J. A. Ibers, Inorg. Chem. 34 (1995) 3165.
[2] J.Huster, Z. Anorg. Allg. Chem. 447 (1978) 89.

Keynote Lecture 2:

Mike Ramsey – Molecular Transport Through Fabricated Nanoscale Channels

Molecular Transport Through Fabricated Nanoscale Channels

J. Michael Ramsey
Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290
Email: jmramsey@unc.edu; Web: www.chem.unc.edu/people/faculty/ramseyjm/jmrindex.html

The transport of fluids through nanoscopic conduits is an area of study that has received relatively little attention although it is fundamental to life. We call the fabrication of such conduits and the active transport of fluid through them nanofluidics. Studies leading to detailed understanding of nanofluidic transport will likely result in revolutionary technological capabilities. For example, the design of artificial cellular receptors may be possible that could result in sensitive and inexpensive sensors for chemical and biological agents or the ability to sequence *single* molecules of DNA at rates many orders of magnitude faster than presently possible. We have been investigating electrokinetic transport of fluids and polyelectrolytes through fabricated nanochannels formed in various hard materials using top-down nanofabrication methods. Interesting phenomena become apparent as channel dimensions are reduced from the 1-µm scale to ≈ 100 nm. Electroosmotic transport, under double-layer overlap conditions, has been studied and to our knowledge, this is the first experimental investigation that is directly comparable to existing continuum theories for such transport. We have also discovered that that new mechanisms arise for separating polyelectrolytes in free solution once the channel dimensions approach the hydrodynamic radius of the molecules. Recent experiments and future possibilities will be discussed.

Oral Session 4:

Theory and Bonding

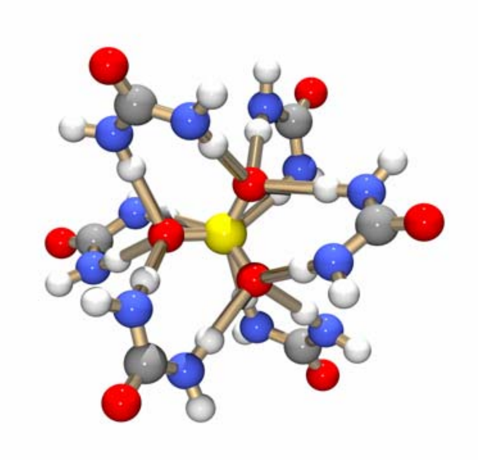
Principles of Chemical Recognition and Transport in Extractive Separations: Molecular Modeling and Host Design

Benjamin P. Hay, Principal Investigator
Vyacheslav S. Bryantsev, Postdoctoral
Chemical Sciences Division, Pacific Northwest National Laboratory
ben.hay@pnl.gov
http://emslbios.pnl.gov, http://hostdesigner.emsl.pnl.gov

Collaborators, Bruce A. Moyer, Peter V. Bonnesen, Laetitia H. Delmau, and Radu Custelcean, Oak Ridge National Laboratory

Overall research goals: Ion-recognition through discovery and exploitation of host-guest principles in extractive separations constitutes the primary objective of this research. The core question addresses how the structure of host molecules governs their ability to recognize ionic species and effect selective, efficient separations as modulated by matrix interactions. A major focus is the deliberate design of receptors for anions, both to learn how to enhance salt extraction and to understand factors determining anion selectivity. Representing the theoretical component of the multi-disciplinary team led by Oak Ridge National Laboratory, our research centers on the use of molecular modeling to address fundamental questions concerning the design of superior extractive materials. The theoretical objectives are (1) to develop sufficient structural criteria to allow the deliberate design of candidate host structures with optimal organization for coordination to targeted ionic species and (2) to generalize the design process computationally. Ultimately, we hope to design molecular architectures in which anion– and cation–receptor functions are combined into a single ditopic host for the recognition of complete ion pairs.

Significant achievements in 2003-2005: The deliberate design of ion receptors requires the capability to distinguish hosts that efficiently complement guest ions. Accurate electronic-structure calculations can be coupled with experimental data to provide fundamental knowledge about host structure and the nature of ion–binding site interactions. Examination of hydrogen bonds in crystal structures has revealed a distinct and general directionality for the oxygen atom acceptors of trigonal planar and tetrahedral oxyanions. Optimized geometries obtained from electronic– structure calculations on one–to–one hydrogen bonded complexes between oxyanions, such as nitrate and sulfate, and various unidentate donor groups exhibit structural features that are consistent with those observed in the solid state.[4,5] By extending these studies to a bidentate hydrogen-bond donor group, we identified differences and similarities in the optimal placement of urea about spherical, trigonal planar, and tetrahedral anions to ascertain instances where host architecture might be exploited to achieve recognition on the basis of anion shape.[7] In addition, a study of the structure and potential energy surfaces of simple urea derivatives has provided a basis for predicting the geometries of urea-based receptors.[8]



This structure, local minimum obtained via geometry optimization with B3LYP/DZVP2, shows how six urea groups can be arranged about sulfate to form a stable complex [ref 7].

The ability to evaluate potential host structures is only half of the design process. The other half is identifying a set of host structures for evaluation. We have devised novel algorithms for building potential host structures from molecular fragments and rapid methods for quantifying the complementarity of the resulting candidates for a targeted ion guest. The algorithms are embodied in a computer software program, called HostDesigner, which can generate and evaluate millions of new molecular structures per minute on a desktop personal computer. An updated version of HostDesigner, completed April 2003, contains modifications that improve the performance and extend the application.[3,4,6] The changes include: (1) ability to treat any guest, (2) ability to vary input geometries, (3) incorporation of a larger link fragment library, (4) addition of an algorithm to prioritize structures with respect to degree of preorganization based on conformational energy estimates. In December 2004, we automated the scoring of HostDesigner output via force field methods, using computed binding energies and conformational energies to reprioritize the results. This code has been adapted to execute on parallel systems and is now being tested.

Specific objectives for 2005-2006: Research will focus on the computational design of anion host molecules constructed by assembling hydrogen–bonding urea, thiourea, guanidinium, and related groups to obtain complementary and preorganized architectures. One objective is the application of computational design methods to identify candidate host architectures for synthesis and testing. Synthesis and evaluation of designed structures, performed by collaborators at ORNL, will provide valuable structure-function data needed to test the validity of the theoretical approach. A second objective is to continue to develop further structural criteria to allow the deliberate design of candidate host structures with maximum organization for coordination to targeted anions.

References of work that was supported by this project in 2003 - 2005:

(1) J. C. Bryan, R. A. Sachleben, C. T. Eagle, B. P. Hay, C. Zhang, and P. V. Bonnesen (2003), “Design, Synthesis, and Structure of Novel Cesium Receptors,” *J. Chem. Crystallogr.* **33**, 349-355.

(2) R. A. Sachleben, J. C. Bryan, G. M. Brown, R. Dabestani, N. L. Engle, T. J. Haverlock, B. P. Hay, H.-F. Ji, A. Urvoas, and B. A. Moyer (2003), “Rational Design of Cesium-Selective Ionophores and Chemosensors: Dihydrocalix[4]arene Crown-6 Ethers,” *Eur. J. Org. Chem.*, 4862-4869.

(3) B. P. Hay and T. K. Firman (2003), “HostDesigner, Version 2.0, User’s Manual.” PNNL-13850, Richland, Washington. Manual and software are available at no cost from the Internet at http://hostdesigner.emsl.pnl.gov

(4) B. P. Hay, D. A. Dixon, G. J. Lumetta, R. Vargas, and J. Garza (2004), “Structural Aspects of Hydrogen Bonding with Nitrate and Sulfate: Design Criteria for Polyalcohol Hosts,” in *Fundamentals and Applications of Anion Separations*; Singh, R. P. and Moyer, B. A., Eds.; Proceedings of an ACS Symposium, Kluwer Academic/Plenum: New York, Ch 3, 43-45.

(5) B. P. Hay, M. Gutowski, D. A. Dixon, J. Garza, R. Vargas, and B. A. Moyer (2004), “Structural Criteria for the Rational Design of Selective Ligands. Convergent Hydrogen Bonding Sites for the Nitrate Anion.” *J. Am. Chem. Soc.* **126**, 7925-7934.

(6) B. P. Hay, T. K. Firman, G. J. Lumetta, B. M. Rapko, P. A. Garza, S. I. Sinkov, J. E. Hutchison, B. W. Parks, R. D. Gilbertson and T. J. R. Weakley (2004), “Toward the Computer-Aided Design of Metal Ion Sequestering Agents,” *J. Alloys Comp.* **374**, 416-419.

(7) B. P. Hay, T. K. Firman, and B. A. Moyer (2005), “Achieving Anion Shape Recognition through the Complementary Placement of Urea Donor Groups,” *J. Am. Chem. Soc.*, **127**, 1810-1819.

(8) V. S. Bryantsev, T. K. Firman, and B. P. Hay (2005), “Conformational Analysis and Rotational Barriers of Alkyl- and Phenyl-Substituted Urea Derivatives,” *J. Phys. Chem. A*, **109**, 832-842.

(9) B. A. Moyer, P. V. Bonnesen, R. Custelcean, L. H. Delmau, and B. P. Hay (2005), “Strategies for Using Host-Guest Chemistry in the Extractive Separation of Ionic Guests.” *Kem. Ind.*, in press.

Theoretical Studies of Thermochemistry and Excited States of Actinide Complexes

Principal Investigators: Richard L. Martin, P. Jeffrey Hay
Post-doctorals: Enrique R. Batista[‡], Aurora E. Clark
Graduate Student: Jason L. Sonnenberg

Institution: Los Alamos National Laboratory, Theoretical Division, MS B268, Los Alamos, NM 87545

E-mail: erb@lanl.gov

Our poster presents several theoretical studies illustrative of chemistry in actinide complexes. The simulations were carried out using hybrid density functional theory and relativistic effective core potentials were employed. The excited states of the molecules were studied via density functional response theory (TDDFT) and analyzed using natural transition orbitals (NTOs). Four physical systems will be shown: (1) uranium halides, (2) organometallic actinide complexes, (3) uranyl in solution, and a (4) metal-oxo complex (NpO_4^-). We show that for the first time very good agreement between the computed thermochemistry of UF_n and UCl_n (n=1,...,6) with the experimental measurements can be achieved. The electronic structure and geometries of all the molecules were characterized. We were able to explain the nature of the spectroscopic peaks in the absorption UV-vis spectrum as well as the photoelectron spectrum in bis(ketimido) complexes (M=Th, U, Zr). We present a careful analysis of the molecular bonding for UO_2L_n systems in solution, and in NpO_4^- a solid environment. A description of forbidden excitations observed in the UV-vis absorption spectrum of NpO_4^- will also be presented.

References

[1] E. R. Batista, R. L. Martin, P. J. Hay, J. E. Peralta, and G. E. Scuseria. "*Density functional investigations of the properties and thermochemistry of UF_6 and UF_5 using valence-electron and all-electron approaches*", J. Chem. Phys, **121,** 2144, (2004).

[2] E. R. Batista, R. L. Martin, and P. J. Hay. "*Density functional investigations of the properties and thermochemistry of UF_n and UF_n ($n = 1, \ldots, 6$)*", J. Chem. Phys, **121,** 11104, (2004).

[3] J. L. Sonnenberg, P. J. Hay, R. L. Martin and B. E. Bursten. "*Theoretical Investigations of Uranyl-Ligand Bonding: Four- and Five-Coordinate Uranyl Cyanide, Isocyanide, Carbonyl, and Hydroxide Complexes*", Inorg. Chem., *(in press).*

[‡] Presenter

All-electron relativistic methods for molecules and extended systems

Principal Investigator: Gustavo E. Scuseria.
Postdoctoral: Juan E. Peralta.
Institution: Department of Chemistry, Rice University.
Email: guscus@rice.edu
Web site: http://python.rice.edu/~guscus/
Collaborators: Enrique R. Batista, Richard L. Martin, and P. Jeffrey Hay, Los Alamos National Laboratory, Theoretical Division T-12.

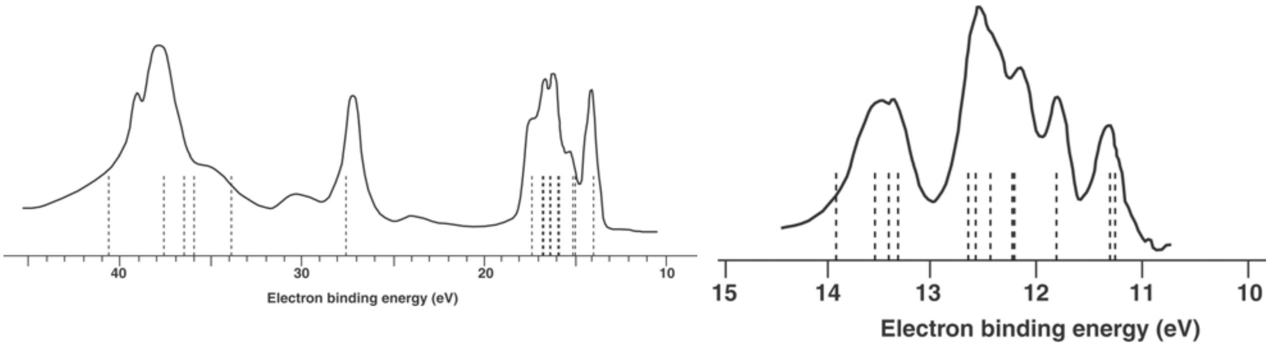
Overall research goals:

The methodological development and computational implementation of quantum chemistry methods for the accurate calculation of electronic structure and properties of molecules, solids, and surfaces, which contain actinides and other heavy atoms. In this abstract, we focus on the development of all-electron methods based on the Douglas-Kroll-Hess quasi-relativistic approximation.[a,b]

Significant achievements in 2003-2005:

Traditionally, electronic structure computer simulations on heavy elements have been carried out without explicitly taking the inner-shell electrons into account. This is due mainly to the high computational demand of all-electron approaches. However, for an accurate treatment of relativistic effects, all electrons must be included in the calculation. Considering that state-of-the-art density functional theory (including hybrid density functionals) is nowadays able to deliver accurate properties in molecules and extended systems,[c,d,e] we have implemented a relativistic all-electron two-component density functional program that includes scalar and spin-orbit effects for molecules.[1] Using a similar scheme than the one employed for the molecular case, we have also included all-electron scalar relativistic effects in our periodic boundary conditions (PBC) quantum chemistry computational program.[2] Even though relativistic effective core potentials have been shown to perform reasonably well in solids, this code provides the possibility of testing and benchmarking valence-only based approximations against all-electron approximations. With these approaches, we are able to accurately predict properties of molecules and solids containing heavy elements, such as thermochemical data of molecules and band gaps of bulk systems.

Here, we report on the structural properties and thermochemistry of uranium hexafluoride (UF_6) and uranium pentafluoride (UF_5) that we have investigated using several density functional theory approximations, including hybrid functionals, in combination with relativistic effective core potentials and the all-electron approximation described above.[3] Even though there exists experimental data for most of the UF_n and UCl_n (n=1-6) species of both series of uranium halides, only a few of them have been studied from a computational point of view. It should be pointed out that some of these compounds play a key role in the nuclear fuel cycle and in waste management. We have studied the electronic structure and thermochemistry of these challenging series of molecules using our all-electron approximation and reliable hybrid density functionals.[4]



(a) (b)

FIG. 1: Photoelectron spectrum of UF_6 (a) and UCl_6 (b) from Refs. f and g (solid lines) and calculated orbital energies (dashed lines). The orbital energies have been shifted so that the highest occupied molecular orbital matches the ΔSCF calculation of the first ionization potential.

Specific objectives for 2005-2006:

- To extend the all-electron PBC code to include spin-orbit effects.
- To compare the effects of relativity on the electronic structure (density of states and band structure) of bulk systems containing heavy elements using effective core potentials and all-electron methods.
- To develop a prototype code for 4-component Dirac-Hartree-Fock and Dirac-Kohn-Sham calculations in molecules.

References of work that were supported by this project

1. J. E. Peralta and G. E. Scuseria, *J. Chem. Phys.* **120**, 5875 (2004).
2. J. E. Peralta, J. Uddin, and G. E. Scuseria, *J. Chem Phys.* **122**, 084108 (2005).
3. E. R. Batista, R. L. Martin, P. J. Hay, J. E. Peralta, and G. E. Scuseria, *J. Chem. Phys.* **121**, 2144 (2004).
4. J. E. Peralta, E. R Batista, G. E. Scuseria, and R. L. Martin, submitted.

Other references

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a. M. Douglas and N. M. Kroll, *Ann. Phys.* **82**, 89 (1974).
b. B. A. Hess, *Phys. Rev. A* **32**, 756 (1985); *Ibid.* **33**, 3742 (1986).
c. M. Ernzerhof and G. E. Scuseria, *J. Chem Phys.***110**, 5029 (1999).
d. V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, *J. Chem Phys.***119**, 12129 (2003).
e. J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003).
f. N. Mårtensson, P.-Å Malmquist, S. Svensson, and B. Johansson, *J. Chem Phys.* **80**, 5458 (1984).
g. G. Thornton, N. Edelstein, N. Rösch, R. G. Egdell, and D. R. Woodwark, *J. Chem Phys.* **70**, 4218 (1979).

A Fully-Relativistic Density Functional Study of the Role of 5f Electrons in Chemical Bonding in Transuranium Elements

Dr. Asok K. Ray, Principal Investigator
Dr. M. N. Huda; Dr. H. R. Gong; Dr. D. Gao; Mr. M. L. Mayo; Mr. P. Dholabhai
Department of Physics, University of Texas at Arlington, Texas 76019
akr@uta.edu; http://www.uta.edu/faculty/asok/
Collaborators: Dr. J. C. Boettger, Los Alamos National Laboratory, New Mexico 87545

Overall research goals: The various goals in the project are as follows: a) Implementation of the LDA+U method and Orbital Polarization in the LCGTO-FF code GTOFF; b) Electronic structure studies of actinide surfaces and possibilities of surface reconstructions and surface magnetic phase transitions, using LCGTO-FF and FP-LAPW; c) Studies of molecular adsorptions on trans-uranium actinide surfaces; d) Understanding and establishing the extent of the validity of density functional theory (DFT) in regards to surface chemistry processes.

Significant achievements in 2003-2005: We have studied up to 5-layer films of Pu in hexagonal and square symmetries, both at the scalar-relativistic and fully-relativistic levels using GTOFF. For the (111) surface, the surface energy is found to be rapidly convergent, while the work function exhibits a strong quantum size effect for all thicknesses considered. From these results, we infer that a 3-layer film may be sufficient for atomic and molecular adsorption studies on Pu films, if the primary quantity of interest is chemisorption energy. The surface energy and work function of the (111) surface are predicted to be 1.12 J/m^2 and 2.85 ± 0.20eV, respectively, in good agreement with experimental results. For square symmetry, same trends are observed, with (001) surface energies notably larger than (111) surface energies.

We have also studied, at the scalar-relativistic non-spin-polarized and spin-polarized levels, atomic and molecular oxygen and hydrogen adsorptions on δ-Pu (100) and (111) surfaces. Also investigated is oxygen molecule adsorption on uranium (100) surface. O_2 chemisorption energy for the most favorable adsorption site on uranium surface has higher chemisorption energy, 9.492eV, than the corresponding plutonium site, 8.787eV. In almost all cases, the most favorable adsorption sites are found where the coordination numbers are higher. In general, oxygen reacts more strongly with plutonium surfaces than hydrogen. For example, atomic oxygen adsorption energy on (100) surface is 3.613eV higher than that of the hydrogen adsorptions, considering only the most favorable site. This is also true for molecular adsorptions, as the oxygen molecules on both (100) and (111) plutonium surfaces dissociate almost spontaneously, whereas hydrogen needs some activation energy to dissociate (see figure below). Comparison of DOS plots between bare and hydrogen/oxygen adsorbed plutonium layers may imply that the adsorption makes 5f electrons more localized. In spin-polarized layers, electronic localizations are higher than that of the non-spin-polarized layers. We found both (100) and (111) plutonium surfaces have layer by layer alternating spin-magnetic behavior, which might be a precursor of anti-ferromagnetic behavior. In general, adsorptions of H_2 and O_2 do not change this feature.

Using WIEN2K software, we have studied bulk δ-Plutonium and the fcc (001) ultra-thin films up to 7 layers. Spin-orbit coupling and spin-polarization play important roles in determining the equilibrium atomic volume and bulk modulus for δ-Pu. Our calculated equilibrium atomic volume of 178.3 a.u.^{3} and a bulk modulus 24.9 GPa at the level of spin-polarized and spin-orbit coupling approximations combined are in good agreement with the experimental values of 168.2 a.u.^{3} and 25 GPa (593°K), respectively. 5f electrons are more itinerant when δ-Pu is compressed and they are more localized when δ-Pu expands, which might provide evidence to explain the origin of the volume expansion between the α- and δ-phases. We have used the calculated equilibrium bulk lattice constants at different levels of approximations to study the surface properties calculations for thin films. Using WIEN2K, we have also carried out calculations on the bulk fcc structure of americium (AmII).

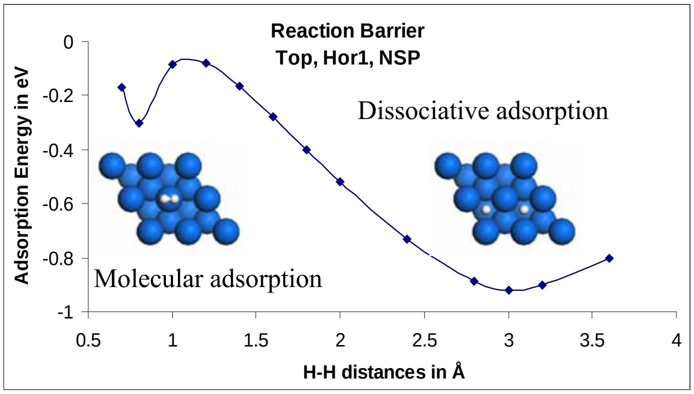


Figure 1: Reaction barrier for most favorable adsorption configuration of H_2 on plutonium (111) surface at the non-spin-polarized (NSP) level. The activation energy for this curve is 0.216eV. Similar curve for the spin-polarized case gives an activation energy of 0.305eV.

Specific objectives for 2005-2006:

______We are currently expanding our work to atomic and molecular adsorptions on Pu and Am surfaces in various symmetries.

References of work that were supported by this project:

1. A. K. Ray and J. C. Boettger (2004), A First-Principles Electronic Structure Study of the Quantum Size Effects in (111) Films of δ – Plutonium, Physical Review B, **70**, 085418-1-6.
2. M. N. Huda and A. K. Ray (2004), Electronic Structures and Bonding of Oxygen on Plutonium Layers, *European Physical Journal B*, **40**, 337-346.
3. M. N. Huda and A. K. Ray (2004), A Density Functional Study of Atomic Hydrogen Adsorption on Plutonium Layers, *Physica B*, **352**, 5-17.
4. M. N. Huda and A. K. Ray (2004), A Density Functional Study of O_2 Adsorption on (100) Surface of γ-Uranium, *International Journal of Quantum Chemistry*, **102**, 98-105.
5. M. N. Huda, *A Relativistic Density Functional Study of Atomic and Molecular Adsorptions on Actinide Surfaces,* Ph. D. Dissertation, The University of Texas at Arlington (2004).
6. M. N. Huda and A. K. Ray (2005), A Density Functional Study of Molecular Oxygen Adsorption and Reaction Barrier on Pu (100) Surface, *European Physical Journal B*, accepted for publication.
7. X. Wu and A. K. Ray, A Full-Potential-Linearized-Augmented-Plane-Wave Electronic Structure Study of δ - Plutonium and the (001) Surface, *Physical Review B*, submitted.
8. M. N. Huda and A. K. Ray, An *Ab Initio* Study of H_2 Interaction with the Pu (100) Surface, *Physica B*, submitted.
9. M. N. Huda and A. K. Ray, Molecular Hydrogen Adsorption and Dissociation on the Pu (111) Surface, *Physical Review B*, submitted.
10. M. N. Huda and A. K. Ray, An *Ab Initio* Study of Molecular Oxygen Adsorption on Pu (111) Surface, *Journal of Physics: Condensed Matter,* submitted for publication.
11. J. C. Boettger and A. K. Ray, Relativistic LCGTO-FF Calculations of Quantum-Size-Effects in Plutonium Films, *International Journal of Quantum Chemistry,* submitted for publication.

Intrinsic Nanoscience: Nanoscale Heterogeneity and Collective Properties of Complex Materials

Steven D. Conradson
Rafael C. Howell,Angel J. Garcia-Adeva, Dylan R. Conradson, Francisco J. Espinosa-Faller, Phillip M. Villella
Materials Science and Technology Division, Los Alamos National Laboratory
conradson@lanl.gov

Luis A. Morales: Nuclear Materials Technology Division, Los Alamos National Laboratory
David L. Clark: Nuclear Materials Technology Division, Los Alamos National Laboratory
Gerard Lander, Franck Wastin: Institute for Transuranium Elements, Karlsruhe, Germany
Bruce D. Begg: Australian Nuclear Science and Technolgy Organisation, Menai, Australia
Nancy J. Hess: Pacific Northwest National Laboratory, Richland, WA
Peter K. Dorhout: Colorado State University, Fort Colllins, CO
Christophe den Auwer: Commissariat a l'Energie Atomique, Marcoule, France
Richard G. Haire: Oak Ridge National Laboratory, Oak Ridge, TN

Overall research goals: Complex materials, which are often characterized by inhomogeneities resulting from bulk stoichiometries that deviate from the chemical formulas of their unit cells, frequently exhibit local lattice distortions with associated elastic forces and intragap electronic states. Collective behavior among these strained sites coupled to competing conformational states may be enhanced by cooperative effects and can therefore produce nanoscale heterogeneity. This may be a characteristic of many complex solids and will contribute to their correlated electronic and transformational properties. Consideration of these local strains shows that such sites utilize an effective potential between the atoms that can be radically modified by, e.g., changes in charge distribution with negligible changes in the atom positions so that local chemical speciation is associated with soft modes and minimal Franck-Condon barriers. These types of effects may also be critical in determining the properties of these types of materials. The goal of this project is to use a combination of experiment, theory, and modeling to understand how inhomogeneities in crystalline solids interact and the resultant effects on structure, properties, and function. Both actinide-containing and other types of correlated materials will be studied.

Significant achievements in 2003-2005: Significant progress was made in the areas of magnetic materials, modeling of crystal and electronic structures modified by local elastic forces, alloy structures and PuGa, correlated materials, XANES, and dynamic energy landscapes. The presentation will focus on work on the AnO_{2+x} systems:

Chemical Speciation and Local and Nanoscale Structure in AnO_{2+x}, An = U, Pu

The AnO_2 binary oxides are arguably not only the most important compounds of the light actinides but also scientifically challenging, exhibiting unusual stability so that they form even for elements that do not display the (IV) valence in molecular complexes and retaining the An sublattice across a wide range of O stoichiometries that are continuous from An:O = 1.6–2.25+. Although 60 years of research on these materials would suggest that all that remains to be done are further refinements of our current knowledge, the entire $AnO_{2\pm x}$ field is actually experiencing a renaissance. Recent work has demonstrated that PuO_2 also forms superstoichiometric oxides up to an excess of 0.25 O atoms. Consistent with diffraction based models for UO_{2+x} and supported by calculations, this adventitious O was supposed to be located in the octahedral holes in the structure and it was also postulated that the higher valence would result in enhanced solubility. Although this type of structure involving distribution of the excess charge over many An sites and stabilizing it with large numbers of near neighbor anions at relatively long distances had been accepted, there remained the problem that in both molecular species and actinates higher charges are stabilized by short An-O distances in complexes involving reduced numbers of ligands and charge localization. We have now performed X-ray Absorption Fine Structure spectroscopy measurements on both UO_{2+x} and PuO_{2+x} that contradict the model and the calculations by clearly showing that increased x is correlated with the formation of oxo groups and, most likely, U(VI) and Pu(V). With Pu, this oxidation occurs under especially mild conditions so that the mixed valence form is often observed even in PuO_2-type compounds prepared by precipitation in aqueous solution, belying the idea that the Pu(V) sites are more soluble. PuO_2 also always shows a multisite Pu-O distribution consistent with forming highly stable adducts with OH^- and other H_2O-derived ligands, so that the crystallographic form is produced only with unusual conditions. There may also be different stereochemical forms of the local environments. These characteristics, that ostensibly contradict the mononuclear and molecular chemistry, point to cooperative behavior and the presence and significance of nanoscale heterogeneity in these materials.

Specific objectives for 2005-2006:
Improve and enhance structure modeling algorithms
Expand electronic structure calculations
Expand modeling to include other parameters, e.g., phonons
Continue experimental work

References of relevant work that were supported by this project

1. S. D. Conradson, et al. (2005), Charge distribution and local structure and speciation in the UO_{2+x} and PuO_{2+x} binary oxides for $x \leq 0.25$, *Journal of Solid State Chemistry,* **178,** 521-535.

2. F. J. Espinosa-Faller, et al. (2005), Local atomic structure of partially ordered NiMn in NiMn/NiFe exchange coupled layers: I. XAFS measurements and structural refinement, *Journal of Physical Chemistry B*, in press.

3. A. J. Garcia-Adeva et al., Local atomic structure of partially ordered NiMn in NiMn/NiFe exchange coupled layers: II. Electronic structure calculations, *Journal of Physical Chemistry B*, in press.

4. S. D. Conradson, et al. (2004), Local structure and charge distribution in the UO2-U4O9 system, *Inorganic Chem*istry, **43**, 6922-6935.

5. S. D. Conradson, et al. (2004), Local and nanoscale structure and speciation in the $PuO_{2+x-y}(OH)_{2y}\cdot zH_2O$ system, *Journal of the American Chemical Society*, **126**, 13443-13458.

6. S. D. Conradson, et al. (2004), Higher order speciation effects on plutonium L-3 X-ray absorption near edge spectra, *Inorganic Chem*istry, **43**, 116-131.

10. A. J. Garcia-Adeva, et al. (2003), Signatures of collective local and nanoscale distortions in diffraction experiments, *Journal of Physical Chemistry B*, **107**, 6704-6716.

11. S. D. Conradson, et al. (2003), Speciation and unusual reactivity in PuO_{2+x}, *Inorganic Chem**istry,*** **42**, 3715-3717.

Understanding Bonding in Actinide-Soft Donor Complexes

Mark P. Jensen, Guokui Liu
Xueyuan Chen, Philip Almond Postdoctoral Scientists
Chemistry Division, Argonne National Laboratory
mjensen@anl.gov

Collaborators: Thomas Albrecht-Schmitt, Auburn University; Manuel Miguirditchian, CEA

Overall research goals: Our research program focuses on understanding the specific origins of the greater affinity of ligands containing donor atoms softer than oxygen for actinide ions as compared to equivalent lanthanide ions. This chemistry is critical to separating trivalent lanthanide (Ln) and actinide (An) ions. Employing experimental measurements, we are testing the hypothesized electronic origins of this effect using complexes of trivalent lanthanide and transuranic actinide ions, attempting to link thermodynamic, structural, and spectroscopic information into a predictive picture of bonding in actinide-soft donor complexes.

Significant achievements in 2003-2005: Despite the great chemical similarity of the trivalent lanthanide and actinide cations, it is well known that the trivalent actinides form thermodynamically stronger complexes with ligands containing nitrogen or sulfur donors than the equivalent trivalent lanthanides do. This is often attributed, with little experimental evidence, to participation of the 5f orbitals in forming more covalent actinide-ligand bonds.

To investigate this we have examined the mixed N,N-diethyldithiocarbamate ($Et_2NCS_2^-$) – 2,2'-bipyridyl (bipy) complexes of Ln(III) and An(III) ions. These complexes contain ligands incorporating the two most common types of soft donors used in An/Ln separations, nitrogen and sulfur. Using X-ray crystallography, we have extended the range of structurally characterized $Ln(Et_2NCS_2)_3(bipy)$ complexes to include all of the stable trivalent light lanthanides from La through Gd and Yb. We have also shown that trivalent transuranic ions have equivalent crystal and molecular structures as the lanthanides in these complexes. The Ln and An complexes were compared to look for evidence of a covalent contraction in the actinide-ligand bonds. None was apparent in the Am and Cm complexes despite the apparently stronger actinide-ligand bonds. This is in contrast to the observations for numerous soft donor complexes of U(III), where significant (> 0.04 Å) contractions in the uranium-ligand bonds, relative to Ln complexes, are observed. Spectroscopic studies of the $Ln(Et_2NCS_2)_3(bipy)$ complexes were used to examine the interaction between the metal-centered 4*f* states and ligand-based orbitals. The optical spectra can be interpreted using a modified crystal-field approach, and they point to a measurable covalent interaction between the metal and these soft donor ligands even in the case of the lanthanide ions.

Specific objectives for 2005-2006: Our objectives for the next fiscal year are to measure and interpret the electronic spectra of the dithiocarbamate-bipyridine complexes of trivalent transuranic actinides and to obtain information on the complexation thermodynamics of relevant actinide and lanthanide dithiocarbamate complexes in order to create a comprehensive and understandable experimental picture of the bonding in actinide-soft donor complexes.

References of work that were supported by this project

1. M. Miguirditchian, D. Guillaneux, D. Guillaumont, P. Moisy, C. Madic, M. P. Jensen, K. L. Nash (2005). Thermodynamic Study of the Complexation of Trivalent Actinide and Lanthanide Cations by ADPTZ, a Tridentate N-Donor Ligand. *Inorganic Chemistry* **44**, 1404-1412.

Gas-Phase Actinide Ion Chemistry—Reaction Kinetics and Molecular Thermodynamics

John K. Gibson
Oak Ridge National Laboratory
gibsonjk@ornl.gov
http://www.ornl.gov/sci/csd

Collaborators:
R. G. Haire, D. C. Duckworth—ORNL
J. Marçalo, M. Santos, A. Pires de Matos—Instituto Tecnológico e Nuclear, Portugal

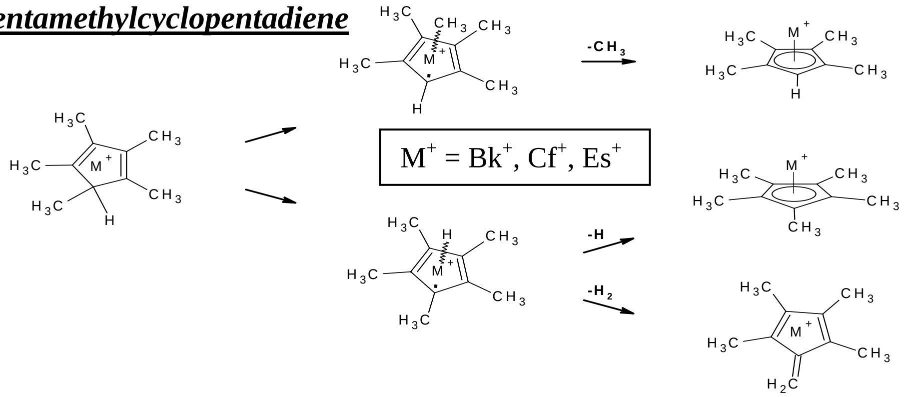
Overall research goals

The program's central objective is to perform basic experimental research to provide information for the overall understanding of the underlying science, properties and behavior of actinides. Gas-phase actinide ion chemistry is a valuable approach for obtaining such fundamental information and insights. These studies focus on experimental molecular actinide chemistry, but also provide a basis to develop and validate theoretical concepts of actinide chemistry. An underlying theme is the role of the 5f electrons/orbitals in molecular chemistry.

Selected recent accomplishments

- Gas-phase actinide ion reactions have revealed new transcurium organometallic chemistry.[3]

Activation of Pentamethylcyclopentadiene



- Ionization energies of AnO_2 (An = Np, Pu, Am) were determined by electron transfer.[1,8] Substantial corrections to previously available values.[10]

	IE[AnO_2] / eV	
U	6.13[a]	5.5±0.5[c]
Np	6.33±0.18[b]	5.0±0.5[c]
Pu	7.02±0.12[b]	9.4±0.5[c]
Am	7.23±0.15[b]	-

[a] Ref. 9—photoionization
[b] This project—electron transfer[1,8]
[c] Ref. 10—electron impact

- Synthesis and characterization of bare actinyls: UO_2^{2+}(g), NpO_2^{2+}(g), PuO_2^{2+}(g).[2] Determined AnO_2^{2+} hydration enthalpies of ca. -1670 kJ mol^{-1} (same as from DFT[11]).
- Assessment of bonding in monoxides indicated a requirement for two metal d-electrons at the actinide metal center.[6]

Selected objectives for 2005-2006

- Study the oxidation chemistry of Pa^+ and Pa^{2+}, and determine bond energies and ionization energies of Pa oxides. Examine organometallic reactions of bare and oxo-ligated Pa ions.
- Determine ionization energies of UF_2 and UF_3, and the reactivities of UF_2^+ and UF_3^+. These fluorides are of particular interest for comparison with uranium oxides.
- Systematic examinations of reactions of An^{2+} with organic molecules (An = Th through Cm).
- Perform electrospray ionization mass spectrometry studies with transuranics to explore actinide solution speciation and gas-phase complexation.
- Carry out the first quantitative studies of gas-phase curium ion chemistry by FTICR-MS. Establish thermodynamics of molecular curium oxides.
- Explore comparative chemistries of particular ligated actinide ions to experimentally probe the concept of "autogenic isolobality".[12]

References of work supported by this project

1. J. K. Gibson, R. G. Haire, J. Marçalo, M. Santos, J. P. Leal (2005), "Determination of the Ionization Energy of NpO_2 and Comparative Ionization Energies of Actinide Oxides," *J. Nucl. Materials* (in press).
2. J. K. Gibson, R. G. Haire, M. Santos, J. Marçalo, A. Pires de Matos (2005), "Oxidation Studies of Dipositive Actinide Ions, An^{2+} (An = Th, U, Np, Pu, Am) in the Gas Phase: Synthesis and Characterization of the Isolated Uranyl, Neptunyl and Plutonyl Ions UO_2^{2+}(g), NpO_2^{2+}(g) and PuO_2^{2+}(g)," *J. Phys. Chem. A*, web-published March 03, 2005.
3. J. K. Gibson, R. G. Haire (2005), "Activation of Pentamethylcyclopentadiene by Bk^+, Cf^+ and Es^+ Ions in the Gas Phase: A Probe of the Electronic Structures of Heavy Actinides," *Organometallics*, **24**, 119-26.
4. G. P. Jackson, J. K. Gibson, D. C. Duckworth (2004), "Gas-Phase Reactions of Bare and Ligated Uranium Ions with Sulfur Hexafluoride," *J. Phys. Chem. A*, **108**, 1042-51.
5. J. K. Gibson, R. G. Haire (2004), "Ternary Gas-Phase Plutonium Oxide Cluster Ions, $Pu_xM_yO_z^+$: Exploring the Oxidation Behavior of Pu," *J. Alloys Cmpds.*, **363**, 112- 21.
6. J. K. Gibson (2003), "The Role of Atomic Electronics in f-Element Bond Formation: Bond Energies of Lanthanide and Actinide Oxide Molecules," *J. Phys. Chem. A*, **107**, 7891-99.
7. J. K. Gibson, R. G. Haire (2003), "Einsteinium Ion Chemistry in the Gas Phase: Divalent Character of the Heavy Actinides," *Radiochimica Acta*, **91**, 441-48.
8. M. Santos, J. Marçalo, J. P. Leal, A. Pires de Matos, J. K. Gibson, R. G. Haire (2003), "FTICR-MS Study of the Gas-Phase Thermochemistry of Americium Oxides," *Int. J. Mass Spectrom.*, **228**, 457-65.

Other references

9. J. Han, L. A. Kaledin, V. Goncharov, A. V. Komissarov, M. C. Heaven (2003), "Accurate Ionization Potentials for UO and UO_2: A Rigorous Test of Relativistic Quantum Chemistry Calculations," *J. Am. Chem. Soc.*, **125**, 7176-77.
10. D. L. Hildenbrand, L. V. Gurvich, V. S. Yungman (1985), "The Chemical Thermodynamics of Actinide Elements and Compounds. The Gaseous Actinide Ions," IAEA: Vienna.
11. L. V. Moskaleva, S. Krüger, A. Spörl, N. Rösch (2004), "Role of Solvation in the Reduction of the Uranyl Dication by Water: A Density Functional Study," *Inorg. Chem.*, **43**, 4080-90.
12. L. Gagliardi, P. Pyykkö (2004), "Theoretical Search for Very Short Metal-Actinide Bonds: NUIr and Isoelectronic Systems," *Angew. Chem. Int. Ed.*, **43**, 1573-76.

Oral Session 5:

Surfaces and Interfaces

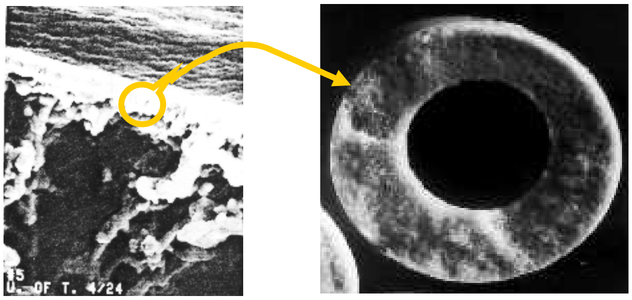
Thickness & History Dependent Effects on Crosslinked Polyimide Membrane Materials for Natural Gas Separation

William J. Koros
Adam Kratochvil
Georgia Institute of Technology
wjk@chbe.gatech.edu and http://www.chbe.gatech.edu/faculty_staff/faculty/koros.htm

Donald R. Paul
Jooheon Kim
University of Texas at Austin
drp@chbe.gatech.edu

Overall research goals: The goal of this project is to establish a fundamental framework to enable maintaining the desirable intrinsic separation properties of solution-processable polyimides under aggressive separation conditions. Polyimides are being studied due to their robust natures and ability to be formed into asymmetric membrane structures. Excessive swelling of a membrane causes large amplitude segmental motions, which reduces ability to selectively pass penetrants on the basis of size and shape. To prevent excessive swelling, carboxylic acid groups are incorporated into the polymer and covalently crosslinked to stabilize the matrix. During crosslinking and subsequent storage, the polymer undergoes physical aging. This aging causes removal of excess free volume within the polymer matrix by diffusion of free volume and lattice contraction, thus allowing the polymer chains to become more tightly packed.

We have shown the ability to stabilize these materials for both dense thick films (25-50 μm) and for asymmetric hollow fibers with ultrathin selective layers (0.10 μm) (Figure 1). Prior work has shown that physical aging can provide stabilization even in the absence of chemical crosslinking; however, in this case, the permeability of the membrane is also reduced. The chemical crosslinking approach being studied here offers the ability to use various diol crosslinkers as a “prop” that actually increases free volume and penetrant permeability. The added free volume, coupled with stabilization against swelling, enables maintaining or even increasing intrinsic material selectivity.



0.1-0.2 μm skin

200 μm OD hollow fiber

Figure 1: Typical asymmetric hollow fiber membrane with ultrathin selective layer supported on an open cell porous support, which also has ultrafine submicron features.

The above issues becomes even more significant when one realizes that glassy polymers undergo physical aging, which is more accelerated when the physical dimensions of the system shrink to submicron sizes (like the features in asymmetric membranes). It appears that an additional mechanism (diffusive loss of free volume) becomes important in these cases, while it is not significant over normal time scales for thick film samples. The “time scale” for this diffusive process is controlled by the *square* of the characteristic dimension of the sample. For example, the amount of free volume diffusive aging in a 0.1 μm selective layer is $(50/0.1)^2$ = 250,000 times faster than in a corresponding 50 μm standard film. In principle, aging due to free volume diffusion from a 0.1 μm dense selective layer of an asymmetric membrane or a thin dense film over a single month (~730 hours) could equal that observed in a 50 μm film over 20,800 years.

Our DOE-supported work focuses on dense films to eliminate ambiguities due to a distribution of effective length scales. Nevertheless, we believe the work is relevant to practical asymmetric fibers like that in Fig. 1, since these also have morphologies with submicron length scales.

Studies are being performed to consider the basic issue of aging of thin (i) noncrosslinkable, (ii) crosslinkable (but still not crosslinked) and (iii) actual crosslinked glass films. Some preliminary results are shown in Figure 2 below for a thin sample (~0.37 μm) from the first class of materials (noncrosslinkable, i.e., without carboxylic acid groups present). The two sets of data correspond to a sample that was never exposed to CO_2 and only probed with CH_4 at 50 psia (triangles) and another sample (solid dots) that was periodically exposed to CO_2 as well as CH_4 to enable characterization of the CO_2/CH_4 selectivity. The CO_2 pressure was only 50 psia in this latter case, but sorbed CO_2 affects aging compared to the sample only exposed to aging under periodically probed with CH_4. After these control cases are completed, (ii)noncrosslinkable samples (with carboxylic acids but <u>no diol crosslinkers present</u>) and also (iii) actual crosslinked samples using different diol crosslinkers will be pursued. The dotted line shown at a permeability of 1.63 Barrers for thick (50 μm films) illustrates that thin film samples actually start with a significantly higher intrinsic permeability and can age to values either above or below the thick bulk film permeability value depending upon test conditions. Even these early data show the complex nature of the effects being probed and help understand why aging phenomena often confuse the interpretation of membrane data.

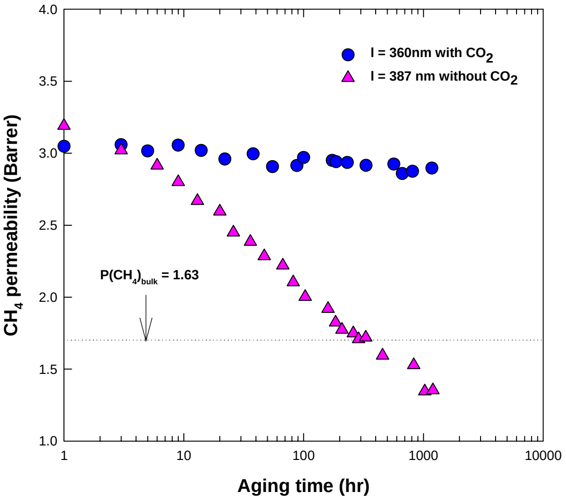


Figure 2: CH_4 permeability in a 0. 37 μm film of 6FDA-6FpDA polyimide aged without exposure to CO_2 vs. a film exposed to <u>both</u> CO_2 and CH_4 for periodic permeability evaluation of both gases.

<u>Significant achievements in 2003-2005:</u> Demonstration of the ability of covalent crosslinks to significantly affect permeability of glassy materials exposed to aggressive gas separations feeds.

<u>Specific objectives for 2005-2006:</u> Expand the investigation of aging effects to the other two classes of materials noted above, (ii)crosslinkable and (iii) crosslinked glassy polyimides.

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

1. Wind, J., C. Staudt-Bickel, D. Paul, & W. Koros, (2003) “Solid-State Covalent Crosslinking of Polyimide Membranes for CO_2 Plasticization Reduction”, *Macromol.*, **36**, 1882-1888.
2. W. Xu, D. Paul, and W. Koros, (2003) “Carboxylic acid containing polyimides for pervaporation separations of toluene/*iso*-octane mixtures”, *J. Membr. Sci.,* **219**, 89-102.
3. J. Wind, S. Sirard, D. Paul, P. Green, K. Johnson & W. Koros,(2003) “CO2-induced Plasticization of Polyimide Membranes: Pseudo-equilibrium relationships of diffusion, sorption and swelling”, *Macromol.*, **36**, 6433-6441.
4. J. Wind, S. Sirard, D. Paul, P. Green, K. Johnson & W. Koros, (2003) “CO2-induced Plasticization of Polyimide Membranes: Relaxation Dynamics of Diffusion, Sorption, and Swelling”, *Macromol.*, **36**, 6442-6448 (2003).
5. A. Taubert, J. Wind, D. Paul, W. Koros & K. Winey, (2003) ”Novel polyimide ionomers: CO_2 plasticization, morphology, and ion distribution”, *Polymer*, **44**, 1881-1892.
6. J. Wind, D. Paul & W. J. Koros, “Natural gas permeation in polyimide membranes”, (2004) *J. Membr. Sci.,* **228**(2), 227-236.
7. W. Koros, “Evolving beyond the thermal age of separation processes: membranes can lead the way”, (2004) *AIChE Journal.,* **50**(10), 2326-2334.

Motion of Single DNA Molecules at a Liquid-Solid Interface as Revealed by Variable-Angle Evanescent-Field Microscopy

Edward S. Yeung
Yan He, Hung-Wing Li, Marc D. Porter, S. Robert Houk
Ames Laboratory, Iowa State University, Ames, IA
yeung@ameslab.gov

Overall research goals: Scientific and technological advancements in the new millennium will be fueled by our ability to manipulate processes at nanometer length scales. Indeed, it is the local structure and environment in nanodomains that dictate the efficiency and selectivity of catalysts, the performance of electronic devices and computers, the response of the immune system, and the resolution of complex samples by liquid chromatography. To address key characterization issues in the next decade, the Ames team will focus on the development of new concepts for chemical analysis and the evaluation of structure-function relationships at nanometer length scales and in microenvironments. These projects range from characterizing reactions at solid/gas and solid/liquid interfaces to probing details of homogeneous chemical reactions. By drawing on the unique expertise of the individual groups through collaboration on these and other projects, the team is well positioned to play a major role in the National Nanotechnology Initiative. The results of these studies are expected to impact other areas of interest to DOE as well, such as catalysis, energy conversion, and environmental monitoring.

Significant achievements in 2004-2005: A variable-angle total internal-reflection fluorescence microscope (VATIRFM) capable of providing a large range of incident angles was constructed for imaging single DNA molecule dynamics at a solid/liquid interface. An algorithm using a public-domain image processing program, ImageJ, was developed for single-molecule counting. The experimental counts at various incident angles with different evanescent field layer (EFL) thickness are affected by molecular diffusion. The dynamics of molecules near the surface and the observed counts in VATIRFM are elucidated using a limited one-dimensional random walk diffusion model. The simulation fits well with the experimental counting results. Further analysis using the simulation reveals the details of single-molecule motion. One implication is that the measured intensities cannot be used directly to determine the distances of molecules from the surface, though the majority of fluorescence does come from the EFL. Another implication is that rather than providing molecular concentrations within EFL, the experimental counting results depict the distance-dependent dynamics of molecules near the surface. Thus VATIRFM could be a powerful technique to study the surface repulsion/attraction of molecules within a few hundred nanometers of the surface. Further studies show that molecules at low ionic strengths experience electrostatic repulsion at distances much further away from the surface than the calculated thickness of the electrical double layer.

References of work that were supported by this project

1. E. S. Yeung (2004), “Dynamics of Single Biomolecules in Free Solution,” *Annu. Rev. Phys. Chem.*, **55**, 97.
2. J. Zheng, H. Li and E. S. Yeung (2004), “Manipulation of Single DNA Molecules via Lateral Focusing in a PDMS/Glass Microchannel,” *J. Phys. Chem. B*, **108**, 10357.
3. S. H. Kang, S. Lee and E. S. Yeung (2004), “Direct Observation of Single Native DNA

Molecules in a Microchannel by Differential Interference Contrast Microscopy," *Anal. Chem.*, **76**, 4459.

4. C. A. Aspinwall and E. S. Yeung (2004), "Screening Populations of Individual Cells for Secretory Heterogeneity," *Anal. Bioanal. Chem.*, **380**, xxx.
5. J. Gruenhagen and E. S. Yeung (2004), "Investigation of G-protein Initiated Ca^{2+}-Dependent Release of ATP from Endothelial Cells," *Biochim. Biophys. Acta*, **1693**, 135.
6. J. Gruenhagen, P. Lovell, L. L. Moroz and E. S. Yeung (2004), "Monitoring Real-Time Release of ATP from the Molluscan Central Nervous System," *J. Neurosci. Methods*, **139**, 145.
7. C. Sluszny and E. S. Yeung (2004), "One- and Two-Dimensional Miniaturized Electrophoresis of Proteins with Native Fluorescence Detection," *Anal. Chem.*, **76**, 1359.
8. A. D. Pris and M. D. Porter (2004), "Nanoparticle Bar-Codes: Size-Based Assays using Atomic Force Microscopy," *Langmuir*, **20**, 6969.
9. D. B. Gazda, J. S. Fritz, and M. D. Porter (2004), "Determination of Nickel(II) as the Nickel Dimethylglyoxime Complex Using Colorimetric Solid Phase Extraction," *Anal. Chim. Acta*, **508**, 53.
10. D. B. Gazda, R. J. Lipert, J. S. Fritz, and M. D. Porter (2004), "Investigation of the Iodine-PVP Interaction Employed in the Determination of Biocidal Iodine by Colorimetric Solid-Phase Extraction," *Anal. Chim. Acta*, **510**, 241.
11. D. B. Gazda, J. S. Fritz, and M. D. Porter (2004), "Multiplexed Colorimetric Solid Phase Extraction (MC-SPE): Determination of Silver(I), Nickel(II), and Sample pH," *Anal. Chem.*, **76**, 4881.
12. L. M. Ponton and M. D. Porter (2004), "High Speed Electrochemically Modulated Liquid Chromatography," *Anal. Chem.*, **76**, 5823.
13. N. Pekas, M. D. Porter, M. Tondra, A. Popple, and A. Jander (2004), "Giant Magnetoresistance Monitoring of Magnetic Picodroplets in an Integrated Microfluidic System," *J. Appl. Phys.*, **85**, 4783.
14. L. M. Ponton and M. D. Porter (2004), "Electrochemically Modulated Liquid Chromatographic Separations of Inorganic Anions," *J. Chromatogr. A*, **11059**, 103.
15. H.-Y. Park, R. J. Lipert, and M. D. Porter (2004), "Single Particle Raman Measurements of Gold Nanoparticles Used in Surface-Enhanced Raman Scattering (SERS)-Based Sandwich Immunoassays," *SPIE*, in press.
16. F. Li and R. S. Houk (2004), "Controlled Dissolution for Elemental Analysis of Sample Layers by ICP-MS: A Feasibility Study," *Appl. Spectrosc.*, **58**, 776.
17. N. C. Dias, D. B. Gazda, J. S. Fritz, M. D. Porter, J. Rutz, P. Mudgett, and J. Schultz (2004), "Application of Colorimetric Solid Phase Extraction (C-SPE) to Monitoring Nickel(II) and Lead(II) in Spacecraft Water Supplies," *SAE International*.
18. J. S. Fritz (2004), "Early Milestones in the Development of Ion-Exchange Chromatography: A Personal Account," *J. Chromatogr. A*, **1039,** 3.
19. S. A. Steiner, J. Hooker, J. Dederich, B. Scott, and J. S. Fritz (2004), "Capillary Electrophoresis of Organic Cations at High Salt Concentrations," *J. Chromatogr. A*, **1039**, 227.

Chemical Selectivity and Reactivity within Ultrathin Layered Polymer Structures

Gary J. Blanchard
Stephen B. Bakiamoh (PhD, PD), Jaycoda S. Major (PhD), Richard M. Bell (MS), Alayna M. Goetsch (MS), Alexis A. Blevins (MS, current student), Janelle D. S. Newman (current student).
Michigan State University, Department of Chemistry, East Lansing, MI 48824
http://curley.cem.msu.edu/blanchard.htm

Overall Research Goals: The primary goal of the work supported during this Grant cycle has been to gain selective control over analyte adsorption and desorption at gas-solid and liquid-solid interfaces. To create and control chemically selective interfaces, we adsorb discrete molecular layers (ca. 30 Å/layer) of maleimide-vinyl ether alternating copolymers onto optically- or electrochemically addressable substrates. The properties under our experimental control are the substrate identity, polymer adlayer density, side group identity and interlayer cross-linking chemistry. We have focused on three issues for these interfaces: (1) Creation of structural gradients, where each layer in a polymer multilayer stack contains different polymer side groups, (2) demonstration of kinetic and thermodynamic control over chemically selective interactions at these interfaces, and (3) the development of ways to probe the local environments created by these polymer adlayers.

Significant Achievements in 2003 – 2005:
Controlling the selectivity of interfacial adsorption. We can control interfacial adsorption phenomena by modifying solid substrates with stacked polymer layers.[10-13] We create multiple interfaces between the polymer layers, and the equilibrium constant for each of these new interfaces is unique for a given analyte. We constructed several step-wise (~30 Å/step) structural gradients normal to the substrate surface, and measured their adsorption isotherms for methanol and hexane uptake to evaluate overall equilibrium constants for these systems.[1] The identity and order of the polymer adlayers determines the chemical selectivity of these interfaces.
Covalent adlayer growth on gold. The synthesis of functional interfaces on metallic and semiconducting substrates is important if the interfaces are to be probed electrochemically. Bonding adlayers to metal surfaces covalently, however, represents a significant challenge. We have devised a means to react an electrochemically generated gold oxide surface layer with an acid chloride to form a stable interface capable of participating in subsequent covalent adlayer growth reactions.[2,3] To this point, the chemistry applicable to metals has been limited to silanization of oxidized metallic surfaces, precluding many interfacial structures from being applied to electrochemically-active surfaces. Our method provides a direct, simple means to circumvent this limitation.
Gold nanoparticle synthesis and surface modification. We have been active in developing synthesis and modification strategies for gold nanoparticles.[7,8] We will use functionalized nanoparticles to measure equilibrium constants in polymer thin films. Both size control and surface modification of gold nanoparticles are required for this purpose, and we have made gold nanoparticles in the size range of ~14 nm. We have also formed an ω-hydroxyalkanethiol monolayer on the surface of the gold nanoparticles,[8] resulting in a spectral red-shift of the gold plasmon band. The presence of the terminal hydroxyl moiety allows for subsequent surface modification, which will allow us to make polar or non-polar coated nanoparticles.

Photochemical stability of surface-bound chromophores. We need to understand the photo- and electrochemical degradation mechanism(s) of surface-bound polycyclic aromatic hydrocarbons (PAHs). PAHs find extensive use in the characterization of local organization at interfaces, but these compounds tend to degrade with use. We have studied three surface-bound PAHs both electrochemically and spectroscopically to determine the mechanism of photobleaching.[4,5] UV light or electrochemical oxidation in the presence of ambient O_2 leads to the formation of mono- and dihydroxy/dione PAH derivatives. Because the structures and spectroscopic properties of the three PAHs we studied differ significantly, the similarity of their degradation products points to the general applicability of our findings.

Ternary polymer synthesis and characterization. We use maleimide-vinyl ether (MVE) alternating copolymers in the construction of polymer multilayers.[10-13] To understand the molecular-scale interactions between adsorbate molecules and the polymer layers, we incorporate chromophore-containing monomers into the MVE polymers. A critical issue in making these polymers is controlling the density and distribution of the chromophores along the polymer chain. We have synthesized MVE polymers containing pyrene side groups because pyrene has a propensity for forming excimers. Emission data for these polymers show pyrene excimer formation in polymer-containing solutions, with the amount of excimer varying with pyrenyl side group density and solvent. We can thus control morphology of polymer-modified interfaces by choice of solvent used during adlayer deposition.

Specific Objectives for 2005 – 2006: We will focus on two issues this year: (1) The molecular origin of chemical selectivity in ultrathin polymer multilayers, and (2) how the viscoelastic properties of the polymer layers are influenced by exposure to solvents and analytes. We will measure the equilibrium constants for nanoparticle interactions with chromophores imbedded in selected polymer layers. We will measure the viscoelastic properties of the polymer adlayers as a function of solvent overlayer identity using quartz crystal microbalance and time-resolved fluorescence measurements. Collectively, these studies will provide insight into the chemical and physical properties that determine the chemical selectivity of these interfaces.

References of work supported by this project:
1. Major, J. S.; Blanchard, G. J., *Langmuir*, **2003**, *19*, 2267.
2. Blanchard, G. J.; Krysinski, P., *Bioelectrochem.*, **2005**, *66*, xxxx.
3. Krysinski, P.; Blanchard, G. J., *Bioelectrochem.*, **2005**, *66*, xxxx.
4. Mazur, M.; Blanchard, G. J., *Langmuir*, **2005**, *21*, 1441.
5. Mazur, M.; Blanchard, G. J., *J. Phys. Chem. B*, **2005**, *109*, 4076.
6. Goetsch, A. M.; Blanchard, G. J., *J. Phys. Chem. B*, **2005**, *in revision*.
7. Newman, J. D. S.; Blanchard, G. J., *Langmuir*, **2005**, *in review*.
8. Newman, J. D. S.; Blanchard, G. J., *Langmuir*, **2005**, *in preparation.*

Other References (also supported by under this Grant):
9. Jessop, J. L. P.; Goldie, S. N.; Scranton, A. B.; Blanchard, G. J., *J. Vac. Sci. Technol. B*, **2002**, *20*, 219.
10. Major, J. S.; Blanchard, G. J., *Chem. Mater.*, **2002**, *14*, 2567.
11. Major, J. S.; Blanchard, G. J., *Chem. Mater.*, **2002**, *14*, 2574.
12. Major, J. S.; Blanchard, G. J., *Chem. Mater.*, **2002**, *14*, 4320.
13. Major, J. S.; Blanchard, G. J., *Langmuir*, **2002**, *18*, 6548.

f-Ion–Polyoxometalate Interactions

Mark R. Antonio, Mark L. Dietz, L. Soderholm, Mark P. Jensen, S. Skanthakumar, Paul G. Rickert, Guokui K. Liu, Julie A. Dzielawa, and Ming-Hsi Chiang
Chemistry Division, Argonne National Laboratory
Mantonio@anl.gov, Mdietz@anl.gov, LS@anl.gov, MJensen@anl.gov, Skantha@anl.gov, Rickert@anl.gov, GLiu@anl.gov

Overall research goals: The molecular clusters known as polyoxometalates (POMs) possess nanometer-size metal-oxygen framework structures that are soluble and redox active in conventional—both aqueous and organic—and neoteric (novel) solvents. These pivotal features distinguish POMs from the more common extended metal-oxide network solids of, for example, Nb^{5+}, Mo^{6+}, and W^{6+}. Our interest centers of the preparation and characterization of hybrid POMs wherein the incorporation of f-block ions into M-O structures drive unusual electrochemical phenomena that result from bonding interactions between d and f states. These responses are very different from those exhibited by the individual centers on their own. Because such hybrid POMs are rare, there are few metrical details and even fewer electrochemical insights, particularly for those complexes with multivalent actinide (An) ions. Moreover, there is no molecular-level understanding of the major factors that influence the orbital energetics of An-POM clusters, and particularly little knowledge about how the redox activity of the M-O framework influences the bonding and redox behavior of the f-ions and *vice versa*. Such information would be invaluable with regard to the design of targeted behaviors for studies of longstanding issues in correlated electron interactions and the participation of f-electrons in bonding. Although theoretical calculations would be useful in understanding the energy levels of frontier molecular orbitals of An-POM complexes, the large numbers of metal ions and their high negative charges combine to result in significant computational limitations.

Significant achievements in 2003-2005: We are taking a multifaceted experimental approach to provide a fundamental perspective of the electronic state structures of POM complexes. Through use of a combination of synthetic, electroanalytical, spectroscopic, and physical methods, we are directing programmatic efforts at the deliberate manipulation and molecular tuning of orbital energies, including the HOMO-LUMO gap and, in so doing, creating new prospects in electrochemistry. The novelty and success of our approach is illustrated by the results of experiments with the Keggin anion, $[PW_{12}O_{40}]^{3-}$, in ionic liquids as well as with f-ion clusters of the Preyssler, $[P_5W_{30}O_{110}]^{15-}$ and the Wells-Dawson, $[P_2W_{17}O_{61}]^{10-}$, anions in aqueous solutions. We have found evidence for redox activities that may have impact on reactions catalyzed by POMs and have discovered correlated electronic behavior that is the result of energetically-degenerate f-states and W-O d-bands. We have determined the exact manner in which cations of varying charge and size are coordinated by the Preyssler and Wells-Dawson anions. This work demonstrates the application of a new tactic to understanding the electronic structure and the influence of f-ions on the chemical properties of Ln/An-POM clusters.

Specific objectives for 2005-2006: Programmatic research activities will continue to focus on the design and synthesis of new molecular materials, including redox active ionic liquids with POM anions. In addition, through use of small angle X-ray scattering and electrochemistry methods, both alone and in combination, studies are underway to obtain direct structural information about the nature of short-range associations, i.e., anion-cation, anion-solvent, anion-anion, that are now proving to be pivotal to the electrochemistry and aggregation of POMs in aqueous media. Such investigations of molecular hierarchy in solution are anticipated to lead to new avenues of research.

References of work supported by this project:

1. Actinyl peroxide nanospheres
   P. C. Burns, K.-A. H. Kubatko, G. Sigmon, B. J. Fryer, J. Gagnon, M. R. Antonio, and L. Soderholm
   Angew. Chem., Int. Ed. 44(12), in press (2005).

2. X-ray absorption spectroscopy of the actinides
   M. R. Antonio and L. Soderholm
   In *The Chemistry of the Actinide and Transactinide Elements*, edited by J. J. Katz, L. R. Morss, J. Fuger, and N. Edelstein, 3rd Edition (Kluwer, Amsterdam: in press) Ch. 28.

3. Energetics of the Preyssler anion's molecular orbitals: Quantifying the effect of the encapsulated-cation's charge
   M.-H. Chiang, M. R. Antonio, and L. Soderholm
   Dalton Trans. 3562-3567 (2004)

4. A unique coordination environment for an ion: EXAFS studies and bond valence model approach of the encapsulated cation in the Preyssler anion
   M.-H. Chiang, M. R. Antonio, C. W. Williams, and L. Soderholm
   Dalton. Trans. 801-806 (2004)

5. In situ actinide X-ray absorption spectroelectrochemistry
   M. R. Antonio, M.-H. Chiang, C. W. Williams, and L. Soderholm
   Mater. Res. Soc. Symp. Proc. 802 (Actinides - Basic Science, Applications and Technology), 157-168 (2004)

6. Redox chemistry of the Keggin heteropolyoxotungstate anion in ionic liquids
   M.-H. Chiang, J. A. Dzielawa, M. L. Dietz, and M. R. Antonio
   J. Electroanal. Chem. 567 (1), 77-84 (2004)

7. Redox chemistry of actinide ions in Wells-Dawson heteropolyoxoanion complexes
   M.-H. Chiang, L. Soderholm, and M. R. Antonio
   Eur. J. Inorg. Chem. 2929-2936 (2003)

8. Coordination of actinide ions in Wells-Dawson heteropolyoxoanion complexes
   M.-H. Chiang, C. W. Williams, L. Soderholm, and M. R. Antonio
   Eur. J. Inorg. Chem. 2663-2669 (2003)

X-Ray Studies of Actinide-Ion Speciation

L. Soderholm, S. Skanthakumar, M.R. Antonio, M.P. Jensen, J.V. Beitz
Argonne National Laboratory

ls@anl.gov

Collaborators: J. Neuefeind, Spallation Neutron Source, ORNL; Peter Burns, University of Notre Dame

Students: Karrie-Ann Hughes Kubatko and Tori Ziemann, University of Notre Dame

Overall research goals: Actinide ions have complex solution chemistries. Often ambiguities in oxidation state and coordination environments are difficult to assess, particularly in amorphous solids and solutions. Synchrotron experiments are providing this valuable information and thereby allowing a deeper understanding of the impact of actinide speciation on observed behaviors and properties. The Actinide Facility is developing, demonstrating and using synchrotron techniques to assist the actinide community with a predictive understanding of this complex chemistry.

Significant achievements in 2003-2005: Efforts have focused on the development of x-ray scattering as a probe of actinide-ion coordination environments in non-crystalline solids and in solution. The majority of work has focused on the use of high-energy x-rays (115 keV) to probe actinide ions in solution. This has been a two-pronged effort. In studies on uranyl and curium solutions, the coordination environment about the metal ion was determined. Metal-solvent correlations were quantified out to distances of about 9 Å. A comparison of uranyl-sulfate and uranyl-selenate solutions reveals that they exhibit very different correlations, which are consistent with solid-state structural behavior. The second prong of this effort has used precise electron densities determined from scattering data to obtain a non-integral number of coordinating waters about a uranyl ion in a perchlorate solution. In addition, specific projects have used our recently developed expertise in small-angle x-ray scattering to probe the growth and ripening of actinyl-peroxide nanospheres in solution prior to their precipitation. The data clearly show the evolution of actinyl peroxide speciation with time and the eventual presence in solution of a relatively monodisperse species that is consistent with a 28-uranium cluster.

Specific objectives for 2005-2006: The high-energy scattering efforts will continue with a more detailed study on uranyl speciation as a function of solution pH. The work on coordination environment of the uranyl ion will be extended to neptunyl ions which will be probed in order to understand cation-cation interactions and their origins. Small-angle scattering studies will continue on our actinyl peroxide project.

Reference of work supported by this project:

1. THE INCORPORATION OF Am INTO THE SUPERCONDUCTOR-RELATED PHASE Pr_2CuO_4
S. Skanthakumar, C.W. Williams, L. Soderholm; Phys. Rev. B 68 (2003) 064510 (8 pages).

2. COORDINATION OF ACTINIDE IONS IN WELLS-DAWSON HETEROPOLYOXOANION COMPLEXES
   Ming-Hsi Chiang, C.W. Williams, L. Soderholm and M.R. Antonio; Eur. J. Inorg. Chem. (2003) 2663-2669.

3. REDOX CHEMISTRY OF ACTINIDE IONS IN WELLS-DAWSON HETEROPOLYANION COMPLEXES
   M.H. Chiang, L. Soderholm, M.R. Antonio; Eur. J. Inorg. Chem (2003) 2929-2936.

4. COVER PICTURE: REDOX CHEMISTRY OF ACTINIDE IONS IN WELLS-DAWSON HETERPOLY-OXOANION COMPLEXES
   M.-H. Chiang, L. Soderholm, M.R. Antonio; Eur. J. Inorg. Chem. (2003) Vol 16 2003

5. MECHANISM FOR METAL ION TRANSFER INTO ROOM-TEMPERATURE IONIC LIQUIDS: THE ROLE OF ANION EXCHANGE
   M.P. Jensen, J. Neuefeind, J.V. Beitz, S. Skanthakumar, L. Soderholm; J. Amer. Chem. Soc. 125 (2003) 15466-15473.

6. EXPERIMENTAL ELECTRON DENSITIES OF AQUEOUS URANYL (VI) SOLUTIONS
   J. Neuefeind, L. Soderholm, S. Skanthakumar; J. Phys. Chem A 108 (2004) 2733-2739.

7. THE STRUCTURE OF THE UO_2SO_4 ION PAIR IN AQUEOUS SOLUTION
   J. Neuefeind, S. Skanthakumar, L. Soderholm; Inorg. Chem. 43 (2004) 2422-2426.

8. SYNTHESES, STRUCTURES, MAGNETIC PROPERTIES, AND X-RAY ABSORPTION SPECTRA OF CARNOTITE-TYPE URANYL CHROMIUM(V) OXIDES: $A[(UO_2)_2Cr_2O_8](H_2O)_n$ ($A=K_2$, Rb_2 Cs_2, Mg; n=0,4)
   A.J. Locock, S. Skanthakumar, P.C. Burns; L. Soderholm, Chem. Mater. 16 (2004) 1384-1390.

9. A UNIQUE COORDINATION ENVIRONMENT FOR AN ION: EXAFS STUDIES AND BOND VALENCE MODEL APPROACH OF THE ENCAPSULATED CATION IN THE PREYSSLER ANION
   M.-H. Chiang, M.R. Antonio, C.W. Williams, L. Soderholm; Dalton Trans. 2004 (2004) 801-806.

10. Am DOPING IN COPPER-OXIDE SUPERCONDUCTING SYSTEMS
    S. Skanthakumar, L. Soderholm; Mater. Res. Soc. Proc. 802 (2004) 175-180.

11. CHANGING Np REDOX SPECIATION IN THE SYNCHROTRON BEAM
    S. Skanthakumar, D. Gorman-Lewis, A. Locock, M.-H. Chiang, M.P. Jensen, P.C. Burns, J. Fein, C.D. Jonah, K. Attenkofer, L. Soderholm; Mater. Res. Soc. Proc. 802 (2004) 151-156.

12. IN SITU ACTINIDE X-RAY ABSORPTION SPECTROELECTROCHEMISTRY
    M.R. Antonio, M.-H. Chiang, C.W. Williams, L. Soderholm; Mater. Res. Soc. Proc. 802 (2004) 157-168.

13. ADVANCING ACTINIDE CHEMISTRY
    L. Soderholm; Synchrotron Radiation News 17 (2004) 11-12.

14. ACTINYL PEROXIDE NANOSPHERES
    P.C. Burns, K.-A. Hughes Kubatko, G. Sigmon, B.J. Fryer, J. Gagnon, M.R. Antonio, L. Soderholm; Angew. Chem. Inter. Ed. (in the press).

15. X-RAY ABSORPTION STUDIES OF THE ACTINIDES
    M.R. Antonio and L. Soderholm, Chapter 29 in *“Chemistry of the Actinides and Transactinides”* Editors: J.J. Katz, L.R. Morss, J. Fuger and N.M. Edelstein, Kluwer, (in the press).

Molecular Aspects of Transport in Thin Films of Controlled Architecture

Paul W. Bohn
Keqing Fa, Enid N. Gatimu, Carla B. Swearingen, Jing Yang, 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.*, the nanoscale channels of a nanocapillary array (NCA) membrane. 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 2003-2005. Our specific objectives are listed here: (1) Quantitative characterization of differential transport rates in injection and sampling through nanocapillary array membranes; (2) Characterize the use of nanocapillary array membranes to achieve reactive mixing between molecular adsorbates and supermolecular carriers, *e.g.* Au nanoparticles. (3) Develop single pore fabrication capabilities and implement transport measurements in single pores.

Significant Achievements

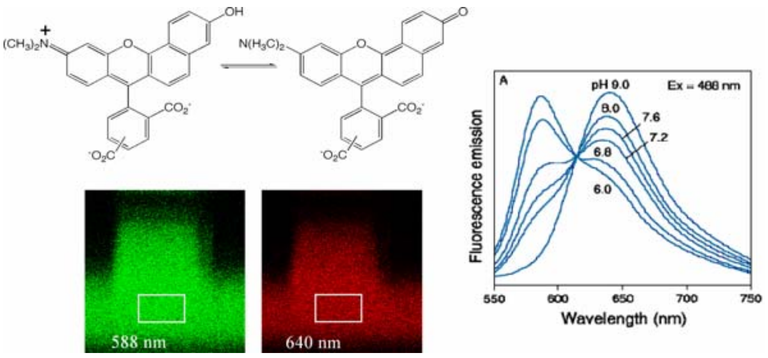


Figure 1. The dye SNARF, which produces pH-sensitive fluorescence emission, is used in conjunction with scanning confocal fluorescence microscopy to generate *in situ* measurements of pH gradients across NCA membranes.

Differential Transport. A key capability is the ability to establish and maintain chemical gradients across the NCA. We investigated the possibility of sustaining unique chemical environments across spatially distinct microfluidic channels that are coupled via nanofluidic interconnects. These novel interconnects provide fluidic communication between microfluidic channels such that mass transport between channels is possible while maintaining unique chemical environments in each channels. Figure 1 shows results from an experiment investigating gradients of H^+, which, due to its large mobility, constitutes the most difficult isolation problem.

Quantitative confocal fluorescence microscopy of the intersection region of two microfluidic channels coupled by an NCA membrane permit the exploration of the dynamic behavior of NCA membranes to proton transport. The pH gradient magnitude was studied as a function of the wettability of the nanocapillary wall, nanopore size, surface charge density, and solution ionic strength. In all cases it was possible to maintain pH gradients of significant magnitude, up to ΔpH = 4, over times long enough to effect quantitative transfer of microfluidic voxels.

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.

Specific Objectives for 2005-06. Our efforts in the coming period will extend and explore in greater detail the results presented here. In particular our goals are:

(1) Characterize reactive mixing for different analytes and for readouts without fluorescent tags. To characterize the use of Au nanoparticles as carriers for mass-limited analytes, we will study analyte-carrier reactivity in microfluidic streams following injection through NCA membranes. *(2) Continue 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 – 2003-5

(1) I.S. Lokuge and P.W. Bohn, “Voltage-Tunable Volume Transitions in Nanoscale Films of Poly(hydroxyethylmethacrylate) Surface Grafted onto Gold,” *Langmuir*, **2005**, ASAP.

(2) D.M. Cannon, Jr., B.R. Flachsbart, M.A. Shannon, J.V. Sweedler and P.W. Bohn, “Fabrication of single nanofluidic channels in poly(methylmethacrylate) films via focused-ion beam milling for use as molecular gates,” *Appl. Phys. Lett.*, **2004**, 85, 1241-1243.

(3) J.S. Kirk and P.W. Bohn, “Surface Adsorption and Transfer of Organomercaptans to Colloidal Gold and Direct Identification by Matrix Assisted Laser Desorption/Ionization Mass Spectrometry, *J. Am. Chem. Soc.* **2004**, 126, 5920-5926.

(4) 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.* **2004**, 43, 1862-1865.

(5) 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.

(6) 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.

(7) 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.

Intermediate-valence Ground States in Cerocene and Selected Ytterbocenes

Corwin H. Booth and Richard A. Andersen
Wayne W. Lukens
Marc Walter
Million Daniel
Lawrence Berkeley National Laboratory
chbooth@lbl.gov

Overall research goals: In many cerium and ytterbium-based intermetallics, a magnetic singlet ground state develops that is a quantum mechanical mixture of both localized and delocalized f-electrons, as well as a corresponding partial localization of the conduction electrons. Our group is exploring this mechanism of f-electron bonding, commonly known as the “Kondo effect”, in both cerium and ytterbium organometallic molecules where the “conduction” electrons come from the delocalized π-orbitals in carbon-based rings, such as in the cyclooctatetraene rings in cerocene $Ce(C_8H_8)_2$. The ensuing intermediate rare-earth valence state is directly measured using L_{III}-edge x-ray absorption near-edge spectroscopy (XANES). A close correspondence between this bonding mechanism and the Kondo effect in metals and semiconductors also allows for predictions of certain magnetic properties. In particular, we utilize magnetic susceptibility measurements to test these predictions. Our goals are to establish the presence of intermediate-valence and the Kondo effect as the mechanism for this state, and to obtain a better understanding of manipulating the important variables. Finally, in addition to establishing the analogy with the intermetallics, we use these data to better understand the differences between such behavior in bulk material and predictions for this phenomenon in the nanoscale.

Significant achievements in 2003-2005: We measured the magnetic susceptibility, $\chi(T)$, and f-occupancy, n_f, for cerocene and several pentamethylcylcopentadienyl ytterbocenes, several of which have been synthesized for the first time. The L_{III}-edge XANES measurements firmly establish fractional f-occupancy in several of these materials. In particular, we measure $n_f=0.89\pm0.03$, consistent with a very high Kondo temperature scale, T_K, in this system. Measurements of $\chi(T)$ have also been obtained that show the cerium f-contribution exhibits temperature-independent paramagnetism (TIP), with $\chi(0)=(1.5\pm0.2)\times10^{-5}$ emu/mol. Using conventional Kondo concepts relating $\chi(0)$ and T_K, we estimate $T_K\sim5000$ K, consistent with TIP and the estimate of n_f and in rough agreement with predictions made by quasirelativistic pseudopotential configuration interaction calculations.[12]

The ytterbocenes offer the hope of weaker coupling and lower T_K's, and therefore of observing temperature dependences in the magnetic susceptibilities. Indeed, a peak is often observed in $\chi(T)$ between 250 K and 400 K, indicating T_K's in the 800-1500 K range. The position of these peaks tracks the estimated f-occupancy obtained from Yb L_{III}-edge XANES. Some differences are observed in $\chi(T)$ between that expected from a conventional Kondo state in a bulk metal that may be explained by the HOMO/LUMO gap, in analogy to behavior predicted in quantum dots.

Taken together, these results establish intermediate valence ground states and relationships to magnetism in these molecules that are consistent with the formation of the Kondo singlet.

Specific objectives for 2005-2006: The most important objective for the coming years is to synthesize compounds with different ligand character in order to probe the effect of changes in T_K and in the HOMO/LUMO gap. Furthermore, it may be possible to find molecules that undergo a valence transition, such as occurs in cerium metal. Finally, this route to local moment behavior may allow probing Kondo coupling in uranium compounds in ways that have proven difficult in the intermetallics. In the future, plutonium organometallics should be even more promising in this regard.

In addition, the nature of the mixed valence state will be probed by L_{III}-edge XANES under applied pressure. In particular, it has been shown in CeO_2 and related early rare-earth oxides, that f-weight increases with increasing O 2p covalency. In contrast, f-weight decreases within the conventional Kondo scheme under pressure, since the exchange coupling typically goes as $1/r^n$, where n is an integer that depends on the angular momentum. Lastly, other techniques for probing the nature of the intermediate valence state will be explored, such as heat capacity.

References of work that were supported by this project

1. E. J. Nelson, K.J.M. Blobaum, M.A. Wall, P.G. Allen, A.J. Schwartz, and C.H. Booth, Local structure and vibrational properties of α'-Pu martensite in Ga-stabilized δ-Pu, Phys. Rev. B **67**, 224206 (2003).
2. C. H. Booth, S.-W. Han, S. Suellow, and J.A. Mydosh, Local lattice symmetry of spin-glass and antiferromagnetic URh_2Ge_2, In International Conference on Magnetism (ICM 2003), Rome, Italy; July 27 - August 1, 2003. 2003, J. Magn. Magn. Mater. **272-276**, 941 (2004).
3. C. H. Booth, L. Shlyk, K. Nenkov, J.G. Huber, and L.E. De Long, X-ray absorption fine structure and field-dependent specific heat measurements of non-Fermi liquid $U_3Ni_3Sn_4$, Phys. Rev. B **69**, 104430 (2004).
4. C. H. Booth, and F. Bridges, Improved self-absorption correction for extended X-ray absorption fine-structure measurements, In The 12th International Conference on X-ray Absorption Fine Structure (XAFS XII), Malmo, Sweden; June 22-27, 2003, Physica Scripta, in press.
5. E. D. Bauer, C. H. Booth, J. M. Lawrence, M. F. Hundley, J. L. Sarrao, J. D. Thompson, P. S. Riseborough, and T. Ebihara, Investigations of Anderson lattice behavior in $Yb_{1-x}Lu_xAl_3$, Phys. Rev. B **69**, 125102 (2004).
6. N. Mannella, A. Rosenhahn, C. H. Booth, S. Marchesini, B. S. Mun, S.-H. Yang, K. Ibrahim, Y. Tomioka, and C. S. Fadley, Direct observation of high-temperature polaronic behavior in colossal magnetoresistive manganites, Phys. Rev. Lett. **92**, 166401 (2004).
7. M. Daniel, S.-W. Han, C. H. Booth, A. L. Cornelius, P. G. Pagliuso, J. L. Sarrao, and J. D. Thompson, X-ray absorption studies of the local structure and *f*-level occupancy in $CeIr_{1-x}Rh_xIn_5$, Phys. Rev. B **71**, 054417 (2005).
8. C. H. Booth, S.-W. Han, S. Skanthakumar, and J. L. Sarrao, Lattice disorder and magnetism in *f*-electron intermetallics, Physica B **354**, 313 (2004).
9. E. J. Nelson, P. G. Allen, K. J. M. Blobaum, M. A. Wall, and C. H. Booth, Local structure and vibrational properties of α-Pu, and the α-U charge density wave," Phys. Rev. B, in press.
10. L. Perrin, L. Maron, O. Eisenstein, D. J. Schwartz, C. J. Burns, and R. A. Andersen, Organometallics **22**, 5447 (2003).
11. D. J. Berg and R. A. Andersen, "Reaction of $(C_5Me_5)_2Yb(ER)(NH_3)$ with Me_3Al: formation of $(C_5Me_5)_2Yb(AlMe_4)$ and $[(C_5Me_5)_2Yb(ER)(AlMe_3)_2]_2$," Organometallics **22**, 627 (2003).

Other references

12. M. Dolg, P. Fulde, H. Stoll, H. Preuss, A. Chang, and R. M. Pitzer, Chem. Phys. **195**, 71 (1995).

Investigation of Transport Mechanisms in Surface Modified Inorganic Membranes

J. Douglas Way, Principal Investigator
Rajinder Pal Singh, Graduate Student
Dept. of Chemical Engineering, Colorado School of Mines, Golden, CO 8040-1887
Email: dway@mines.edu; Web: http://www.mines.edu/Academic/chemeng/faculty/dway

Collaborators: Dr. Kent Abney, LANL, NMT-2, MS-E511, Los Alamos, NM 87545
Dr. Glen E. Fryxell, Pacific Northwest National Laboratory, Materials Synthesis and Modification Group, Richland, WA 99352

Overall research goals: The objective of this project is to synthesize, characterize, and investigate the transport mechanisms in surface modified inorganic membranes for a variety of separations.

Significant achievements in 2003-2005: In the modification of porous inorganic substrates, octadecyltrichlorosilane (ODS) could form a number of structures depending on the amount of water present either in the solution or on the surface. As shown in Figure 1, examples of possible structures include a thin dense polymer layer on the surface or a covalently attached monolayer with or without crosslinking among adjacent silane molecules or a mixture of these two structures.

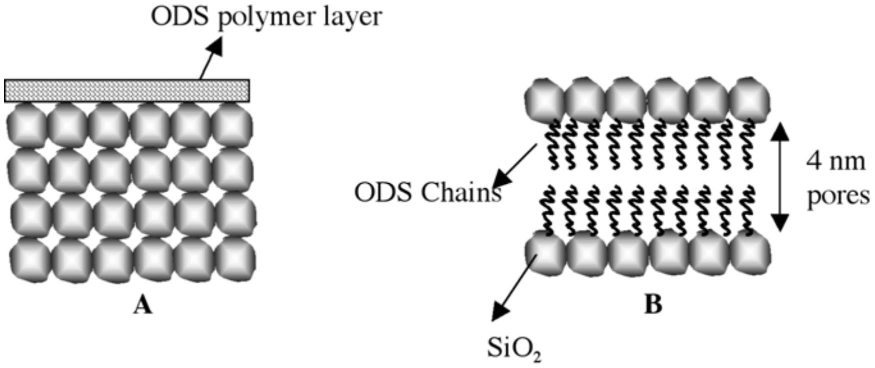


Figure 1. Hypothetical structures of the silane modified Vycor porous glass. A. Polymer layer on the surface of the membrane. B. Polymer brush in the pores, decreasing the pore size.

Vycor glass membranes were also modified with the monochlorosilane, dimethyl octadecylchlorosilane (OCS) to study the structure of silane treated membranes. OCS cannot polymerize and can only form a polymer brush on the pore surface. The comparison of OCS membranes with similar ODS and HDFS (heptadecafluoro-tetrahydrodecyl-trichlorosilane) treated membranes suggests that a polymer layer is required to produce a hydrocarbon selective membrane with “reverse selectivity” for pure gases. As shown in Tables 1 and 2, the OCS membrane has poor selectivity for pure gases but **higher** selectivity for gas mixtures. This is consistent with the pore blocking mechanism previously reported for a variety of porous membranes.

Simultaneously with the membrane synthesis, silica gel was modified as a control to study the reaction of the silanes with surface silanols using ^{29}Si CP-MAS NMR spectroscopy. The surface chemistry and pore size of silica gel and porous Vycor glass are similar; therefore, silica gel is a suitable surrogate material to simulate the Vycor glass. As shown in Figures 2 and 3, the NMR data support our hypotheses about the structure of the silane layers in the modified materials. A polymer layer is present in the ODS modified Vycor, while the OCS membrane has only surface silanes presumably in a polymer brush orientation.

Specific objectives for 2005-2006:

- In collaboration with Dr. Fryxell of PNNL, modify mesoporous membrane materials, such as Vycor glass with silane complexation agents selective for metal cations in an aqueous phase and test them for adsorption and transport of metal cations.
- Develop a synthetic route to produce both polymerized ODS and polymer brush structures in the same mesoporous support and characterize this membrane using transport experiments, adsorption, FTIR, and ^{29}Si CP-MAS NMR.

Table 1. Comparison of the ODS and OCS pure gas selectivities. Table reports the data for the OCS membrane with the highest n-C_4H_{10}/N_2 pure gas selectivity.

Gas pair	ODS Membrane	OCS Membrane
n-C_4H_{10}/He	29.7	9.96
n-C_4H_{10}/CO_2	6.69	6.51
n-C_4H_{10}/N_2	52.4	13.7
n-C_4H_{10}/C_2H_6	7.03	4.07
n-C_4H_{10}/i-C_4H_{10}	2.16	1.72

Table 2. Comparison of the mixed gas separation factors for the OCS and ODS modified Vycor glass membranes. *Lower values than the pure gas selectivities could be due to driving force limitations.

n-C_4H_{10}-N_2	ODS Membrane	OCS Membrane
50 – 50 mixture	20.1*	56.1
80 – 20 mixture	49.7	218

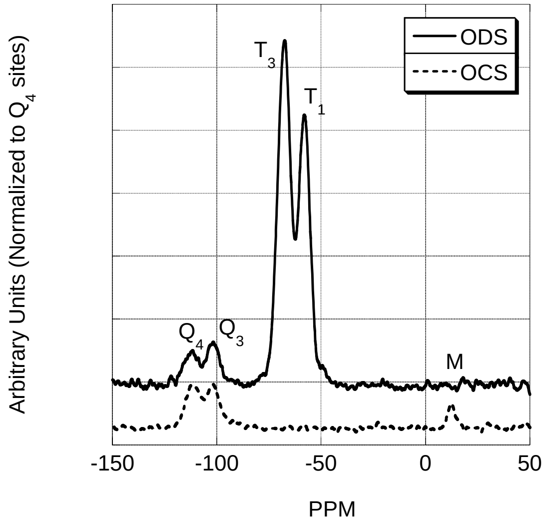


Figure 2. NMR spectra obtained on silica gel modified with the ODS and OCS. Peak assignments are shown in Figure 3.

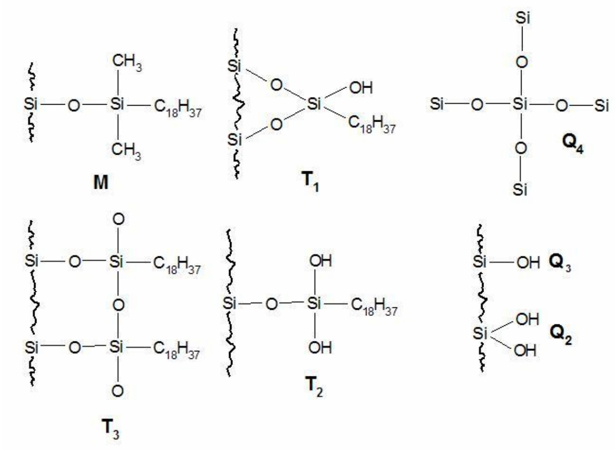


Figure 3. Assignment of silicon moieties present on the surface of silica gel.

References of work that were supported by this project

1. Takaba, H. and J. D. Way, "Separation of Isomeric Xylenes Using Cyclodextrin Modified Ceramic Membranes," *I&EC Res.*, **42**(6), 1243–1252(2003).
2. Ames, R. L., Bluhm, E. A., Bunge, A. L., Abney, K. D., Way, J. D., and S. B. Schreiber, “Aqueous Ion Transport Studies in Stainless Steel Membranes,” *I&EC Res.*, **42**(12), 2853–2860(2003).
3. Roa, F. Way, J. D., McCormick, R. L. and S. N. Paglieri, “Preparation and Characterization of Pd-Cu Composite Membranes for Hydrogen Separation,” *The Chem. Engineering Journal*, **93**(1), 11(2003).
4. Roa, F. and J. D. Way, “The influence of alloy composition and membrane fabrication on the pressure dependence of the hydrogen flux of palladium-copper membranes,” *I&EC Res.*, **42**(23), 5827(2003).
5. Singh, R. P., Way, J. D., and K. C. McCarley, “Development of a Model Surface Flow Membrane by Modification of Porous Vycor Glass with a Fluorosilane, *I&EC Res.*, **43**, 3033-3040(2004).

6. Plummer, M. A., Kim, M., Way, J. D. and R. M. Baldwin, “Determination Of Mechanisms Via Computational Chemistry For Xylene And Hydroxynaphthalene Separations On Beta-Cyclodextrin, *Molecular Physics*, **102**(2), 183-189(2004).
7. Roa, F. and J. D. Way, “The Effect of Air Exposure on Palladium-Copper Composite Membranes,” *Applied Surface Science*, **240**(1-4), 85-104(2005).

Chemistry of Novel Separation

Principal Investigator: Sheng Dai
Co-PI: Costa Tsouris and Valmor F. de Almeida,
Student: Chengdu Liang, Patricia Taboada-Serrano, Chia-Hung Hou
Institution: Oak Ridge National Laboratory
e-mail address: dais@ornl.gov

Collaborators: K. L. Hong (ORNL), Georges A. Guiochon (ORNL), and J. W. Mays (ORNL)

Overall research goals: The overall goal of this project is to investigate fundamental issues in designing chemical architectures that selectively bind target species through tailored and organized interactions. The current systems of study include novel nanoporous materials and ionic liquids. One aim is to develop hierarchically structured porous materials for novel separation based on molecular recognitions and interfacial structures through the controlled chemical synthesis employing self-assembly and different length-scale molecular imprinting. A second aim is to explore the fundamental aspects of ionic liquids in novel separation. A third aim is to develop fundamental understanding of the separation behaviors within confined nanopores, organized hosts, and ionic liquids through the synergistic applications of spectroscopic characterization and computer modeling.

Significant achievements in 2003-2005:

(1) ***Ion Imprinting for Synthesis of Adsorption Sites***. We have continued the investigation of the ion-imprinting methodology for synthesizing adsorption sites for tailored recognition. Our ion-imprinting synthesis technique have been extended to the generation of recognition sites in crystalline matrices, resulting in a simplified procedure for functionalizing layered crystalline silicate materials with good control of both distributions of functional ligands and chemical interactions [1]. The essence of this template-synthesis methodology is to make use of the unique charge requirements associated with the ion-template synthesis to control both location and stereochemistry of adsorption sites. In addition, we have initiated research to tailor the adsorption sites for anions via organic-inorganic hybrid materials. The controlled secondary environment has been demonstrated to play a key role in enhancing anion recognition for bulky anions [2].

(2) ***Complex Separation Media with Tailored Secondary Environments for Adsorption Sites***. The development of monolithic silica separation media is one of the key recent advances in separation science. In monolithic separation media, adsorption sites and pore architectures are structurally integrated. Accordingly, new hierarchical synthesis methods are required, which allow the control of the chemical interactions of both adsorption sites and their secondary environments to generate hierarchical structures. Although the silica-based monolithic separation media can be utilized under various environments, the major obstacle to a wider use of the silica-based separation media is their limited resistance to hydrolysis, which restricts their uses to a relatively narrow pH range. This deficiency prompted us to develop carbon-based monolithic materials for separation applications. We have recently developed two hierarchical synthesis methods using silica beads and phase segregations as templates for generation of hierarchical pores in monolithic carbon materials [3].

(3) ***Synthesis of Nanoporous Materials with Orientation Control***. [4] The orientation of channels in ordered mesoporous films is of technological importance for the development of new nanostructured materials for novel separation processes. Although numerous methods have been developed for the fabrication of carbon films, no ordered nanoporous carbon films have been obtained. Accordingly, the large-scale alignment of the carbon nanostructural films is still a big challenge. In this research period, we have demonstrated a stepwise self-assembly approach to the preparation of large scale, highly ordered carbon nanoporous films. The carbon precursor molecules are spatially arranged into well defined nanostructures via the self-assembly of block copolymers. The hexagonally packed carbon channel array whose orientation is normal to the carbon film surface has been successfully synthesized.

(4) ***High-Yield Functionalization of Nanoporous Carbon Materials***. [5] A new fluorinated carbon with an ordered mesoporous structure was synthesized by reacting ordered carbon with fluorine at room temperature or moderately elevated temperature. The structure was confirmed with XRD, microscopy, FTIR, and nitrogen adsorption. Compared to fluorinated carbon nanotubes, the pore structure of the fluorinated ordered carbons can be well controlled by selecting proper silica templates or precursors. Furthermore, these fluorinated carbons can be synthesized on a much larger scale than the fluorinated carbon nanotubes. These fluorinated carbons with ordered pore structure could have great potential applications in separation, electrochemistry, or batteries.

(5) ***Ionic Distribution at Charged Interfaces***. Monte Carlo techniques have been developed to investigate the distribution of ions near charged interfaces in confined geometries. Results showed that a layer of water molecules strongly adsorbs on the charged surface. As the width of a pore becomes smaller, the maximum ion concentration appears in the middle of the pore, which contradicts the Poisson-Boltzmann equation. The reason for this discrepancy is that the Monte Carlo method allows accounting for the effects of water molecules, while the Poisson-Boltzmann equation does not. In this regard, the Monte Carlo method is more accurate. Through coupled experimental and computational studies employing atomic-force microscopy and molecular simulations of ions in aqueous solutions, it was determined that charge heterogeneity and charge asymmetry lead to local heterogeneities in the distribution of ions near solid surfaces and the resulting surface forces. This observation indicates that molecular-scale interactions must be taken into account in understanding macroscopic surface forces and phenomena occurring under unfavorable chemical conditions.

Specific objectives for 2005-2006: Novel methodologies to tailor the secondary environments of adsorption sites through self-assembly methods will be continuously explored. The separation properties of monolithic carbon materials with tailored nanostructures will be investigated. Computer modeling will be conducted to develop fundamental understanding of the separation behaviors within confined nanopores and organized hosts. The key fundamental issues we seek to address are (1) synergistic effect of hierarchical structures on separation, (2) effect of interfacial and host properties on liquid/solid and gas/solid partitions, and (3) effect of space confinement induced by nanopores on separation mechanisms (e.g. recognition capabilities).

Selected References of work that were supported by this project (selected publications from > 40)

1. Zhang, Z. T.; Saengkerdsub, S.; Dai, S. "Intersurface ion-imprinting synthesis on layered mazadifte hosts" *Chem. Mater.* **2003**, *15*, 2921-2925.
2. 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.
3. Liang, C. D.; Dai, S.; Guiochon, G. "A graphitized-carbon monolithic column" *Anal. Chem.* **2003**, *75*, 4904-4912.
4. Liang, C. D.; Hong, K. L.; Guiochon, G. A.; Mays, J. W.; Dai, S. "Synthesis of a large-scale highly ordered porous carbon film by self-assembly of block copolymers" *Angew. Chem.-Int. Edit.* **2004**, *43*, 5785-5789
5. Li, Z. J.; Del Cul, G. D.; Yan, W. F.; Liang, C. D.; Dai, S. "Fluorinated carbon with ordered mesoporous structure" *J. Am. Chem. Soc.* **2004**, *126*, 12782-12783.
6. Yan, W. F.; Hagaman, E.; Dai, S. "Functionalization of aluminophosphate AlPO4-H1 (VPI-5) with phenylphosphonic acid" *Chem. Mat.* **2004**, *16*, 5182-5186.

Poster Session 2

The Electronic Structure of Heavy Element Complexes

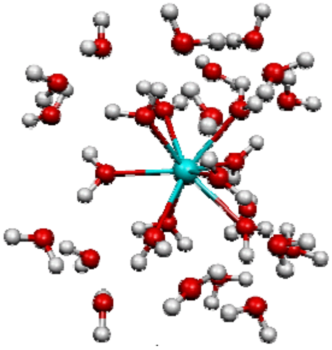
Bruce E. Bursten, PI, Dept. of Chemistry, The Ohio State University, bursten.1@osu.edu
Tianxiao Yang, postdoctoral; Jason Sonnenberg, graduate student; Kurt Frey, undergraduate student (currently graduate student in Chemical Engineering at MIT)
Collaborators: Lester Andrews (University of Virginia), Mary Neu, Jeff Hay, Rich Martin (LANL), Jean-Phillipe Blaudeau (Wright-Patterson Air Force Base), Jun Li (PNNL), Lynne Soderholm (ANL)

Overall research goals: The overarching goal of our research is to use quantum chemical calculations to increase the understanding of the electronic structure of heavy-element systems. Our group has strengths in inorganic chemistry, electronic structure theory, and applications of supercomputing, and we believe that our most important function in the heavy element community is to provide theoretical results and explanations that are significant to experimentalists in the field. Therefore, our highest priority has been to obtain experimentally relevant theoretical results for the heavy-element community. The focus of the research in the past year has been on obtaining an increased understanding of the structure and bonding in small- and medium-sized actinide complexes.

Significant achievements in 2003-2005: The most significant progress in 2003-2005 derived from our collaborative efforts with the group of Professor Lester Andrews of the University of Virginia. Andrews and his group are experts in studying the reactions and spectroscopy of products of laser-ablated metal atoms with small substrate molecules. In 2002, we reported evidence for the first uranium-to-noble-gas (Ng) bonding, which occurred when the CUO molecule was formed in solid argon matrices (*Science* **2002**, *295*, 2242). Since then, we have used computational chemistry in concert with new experimental studies at Virginia to expand the motif of actinide-Ng bonding. We have now demonstrated that CUO can bind multiple Ar, Kr, and Xe atoms, leading to unprecedented detail about subtle electronic state changes induced by the U-Ng bonds. We have also proposed that the Lewis acid-base interactions between high-valent actinide complexes and the noble gases extends beyond the CUO molecule. We have provided evidence for the existence of actinide-Ng bonding in f^1 UO_2^+ and f^2 UO_2; the latter molecule has been a particularly controversial one owing to new spectroscopic studies of its electronic structure by Heaven and coworkers at Emory. We have also proposed that U-Ng bonding is significant in some of the new products we have reported from the reaction of laser-ablated U atoms with H_2O. These products include the H_2UO_2 molecule, which is the smallest possible neutral complex of the uranyl ion.

We have also had a successful collaborations with Mary Neu, Jeff Hay, and Rich Martin of Los Alamos National Laboratory. These University-National Lab activities were facilitated in part by the fact that one of the PI's graduate students, Jason Sonnenberg, was a multi-year participant in the Summer Research Program sponsored by the Seaborg Institute at LANL. Our collaborative efforts with Neu have focussed on fundamental coordination chemistry of trivalent actinide complexes, either in aqueous solution or in the presence of potential complexing agents such as siderophores. With Hay and Martin, we have been exploring the fundamental bonding of different ligands to high-valent actinyl complexes, such as the uranyl ion, UO_2^{2+}.

One more area in which we are starting to have an impact is in combining quantum chemical electronic structure calculations with molecular dynamics calculations to explore the bonding and dynamics of actinide ions in aqueous solution. These studies include complete quantum chemical calculation of the first and second coordination spheres of H_2O around the actinide ion, such as the



$[Cm(H_2O)_9(H_2O)_{18}]^{3+}$ complex shown to the right. The conclusions of these studies will be tested experimentally by x-ray scattering experiments at ANL by Soderholm and coworkers.

Specific objectives for 2005-2006: In this coming year, we plan to continue our research in actinide electronic structure along several different thrust lines: (1) We continue to collaborate with our colleagues at Virginia on the structure and bonding of small actinide-containing molecules. That group has started reactions of laser-ablated actinide atoms with methane, which should lead to remarkable new small organometallic species. (2) We will continue to develop our modeling of the aqueous chemistry of actinide ions (and other actinide speciation) using our combined quantum chemical/molecular dynamics approach. (3) We want to initiate new studies of large actinide-containing systems that employ combined quantum mechanics/molecular mechanics (QM/MM) approaches. In addition to continuing such studies on actinide-siderophore complexes, we also want to look at strongly bonded large organometallic systems, such as those with multiple C_5Me_5 ligands.

References of work supported by this project (2003-2005):

L. Andrews, B. Liang, J. Li, and B. E. Bursten, "Noble Gas-Actinide Complexes of the CUO Molecule with Multiple Ar, Kr, and Xe Atoms in Noble-Gas Matrices," *JACS* **2003**, *125*, 3126-39.

B. Liang, L. Andrews, J. Li, and B. E. Bursten, "Bonding of Multiple Noble-Gas Atoms to CUO in Solid Neon: $CUO(Ng)_n$ (Ng = Ar, Kr, Xe; n = 1, 2, 3, 4) Complexes and the Singlet-Triplet Crossover Point," *Chem. European J.* **2003**, *9*, 4781-4788.

B. E. Bursten, M. L. Drummond, and J. Li, "Spiers Memorial Lecture: The Quantum Chemistry of d- and f-Element Complexes: From an Approximate Existence to Functional Happiness," *Faraday Disc. Chem. Soc.* **2003**, *124*, 1-24.

L. Andrews, B. Liang, J. Li, and B. E. Bursten, "Noble Gas-Uranium Coordination and Intersystem Crossing for the $CUO(Ne)_x(Ng)_n$ (Ng = Ar,Kr,Xe) Complexes in Solid Ne," *New J. Chem.* **2004**, *28*, 289-94.

B. Liang, L. Andrews, J. Li, and B. E. Bursten, "On the Noble-Gas Induced Intersystem Crossing for the CUO Molecule: Experimental and Theoretical Investigations of $CUO(Ng)_n$ (Ng = Ar, Kr, Xe; n = 1, 2, 3, 4) Complexes in Solid Neon," *Inorg. Chem.* **2004**, *43*, 882-94.

J. Li, B. E. Bursten, L. Andrews, and C. J. Marsden, On The Electronic Structure of Molecular UO_2 in the Presence of Ar Atoms: Evidence for Direct U-Ar Bonding," *JACS* **2004**, *126*, 3424-5.

W. Wang, L. Andrews, J. Li, and B. E. Bursten, "Robust Bonds between Uranium and Noble-Gas Atoms: Coordination of the UO_2^+ Cation by Ne, Ar, Kr, and Xe Atoms," *Angew. Chem. IE* **2004**, *43*, 2554-7.

M. P. Neu, J. L. Sonnenberg, and B. E. Bursten, "Homoleptic Nine-Coordinate An(III) and Ln(III) Complexes: Classic High-Symmetry Species that Advance our Understanding of f-Element Structure, Bonding, and Dynamics," *LANL-Actinide Research Quarterly* **2004**, 1st Quarter, LALP-04-060, 7-10.

B. Liang, R. D. Hunt, G. P. Kushko, L. Andrews, J. Li, and B. E. Bursten, "Reactions of Laser-Ablated Uranium Atoms with H_2O in Excess Argon: A Matrix Infrared and Relativistic DFT Investigation of Novel Uranium Oxyhydrides,"*Inorg. Chem.* **2005**, *44*, 2159-68.

J. L. Sonnenberg, P. J. Hay, R. L. Martin, and B. E. Bursten, "Theoretical Investigations of Uranyl-Ligand Bonding: Four- and Five-Coodinate Uranyl Cyanide, Isocyanide, Carbonyl, and Hydroxide Complexes,"*Inorg. Chem.* **2005**, *44*, 2255-62.

N. Kaltsoyannis, P. J. Hay, J. Li, J.-P. Blaudeau, and B. E. Bursten, "Theoretical Studies of the Electronic Structure of Compounds of the Actinide Elements," in *Chemistry of the Actinide and Transactinide Elements, 3rd Ed.*, J. J. Katz, L. R. Morss, N. Edelstein, and J. Fuger, Editors, Kluwer: Dordrecht, The Netherlands, to be published in 2005.

Electrochemically-Modulated Separation of Uranium and Plutonium

Douglas C. Duckworth
Sea Hoon Park
Oak Ridge National Laboratory
duckworthdc@ornl.gov

Overall research goals:

An electrochemically modulated separation (EMS) process for uranium and plutonium is being investigated.[1-3] In this process, accumulation and release of U and Pu occurs at an anodized glassy carbon (AGC) surface at significantly different potentials for accumulation and release. The separation is effected by changes in target electrode potential in a flow-by electrochemical cell that is used on-line with inductively coupled plasma mass spectrometry to improve the speed, sensitivity, and selectivity of plutonium and uranium separations. Applying positive/negative potentials to the anodized glassy carbon electrode controls accumulation/release of plutonium or uranium, resulting in separation from other species in solution, including those that cause chemical interferences in mass spectrometry.

The goal of this research is to understand better the process of U and Pu accumulation and release at anodized carbon surfaces. Our research has initially focused on parametric investigations affecting deposition and release of plutonium — pH, redox potentials, accumulation time, and concentration. Additionally, studies have been performed to evaluate the elemental selectivity of the separation. Future studies will seek to answer the question of surface functional groups and their role in analyte accumulation, colloid size dependencies on accumulation, and surface redox chemistry.

Significant achievements in 2003-2005:

Parametric studies focused primarily on understanding the accumulation and release of Pu at the AGC electrode. Initial investigations support the hypothesis that Pu accumulation occurs as the hydrolysis product under oxidation potentials. For plutonium, it was demonstrated that accumulation was occurring at the AGC under oxidative potentials. This potential affects the accumulation efficiency, which increases as the potential shifts to more positive potentials until it reaches a threshold potential (~0.7 V vs. Ag/AgCl). Any potential greater than 0.7 V shows minimal improvement over the efficiencies. Varying the accumulation time has a negligible effect on the accumulation efficiency; however, the extensive accumulation time results in saturation of electro-active sites on the anodized glassy carbon and lowers the effectiveness of plutonium accumulation. Results from the electrochemical potential studies also show that release rate of plutonium strongly depends on the reduction potential applied, and the stripping peak intensity increases as the reduction potential shifts in the negative direction.

It was also shown that solution pH significantly effects plutonium accumulation. Studies show that dilute nitric acid (~0.3 M) provides a better condition for plutonium accumulation. This suggests that a local acidity change at the surface-solution interface of the AGC promotes plutonium accumulation, and applying an oxidation potential for the accumulation catalyzes the change in acidity that is not possible at lower pH. Pu is known to disproportionate between Pu (III) and Pu (IV) oxidation states. Dual electrode studies were performed, using the first electrode to adjust redox states and the second for accumulation. The results indicate that both Pu (III) and Pu (IV) are accumulated and subsequent released was obtained.

Specific objectives for 2005-2006:

The identity of oxygen-containing moieties on the AGC surface is also of interest. Raman surface analyses were performed to determine local coordination and bonding information, but were inconclusive due to sensitivity issues. Alternative approaches will be investigated.

Uranium accumulation has been performed on highly porous reticulated vitreous carbon to increase the mass available for spectroscopic studies. These studies were performed in anticipation of x-ray absorption fine structure measurements, where larger U loadings will be required. XAFS studies are being planned to explore the coordination and redox chemistry of uranium accumulated on anodized glassy carbon.

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

References of work that were supported by this project

Other references

1. J.R. Pretty, D.C. Duckworth, G.J. Van Berkel, (1998) “Adsorptive Stripping Voltammetry as a Sample Pretreatment Method for Trace Uranium Determinations by Inductively Coupled Plasma Mass Spectrometry,” *Int. J. Mass Spectrom. Ion Processes*, **178**, 51.

2. J.R. Pretty, D.C. Duckworth, G.J. Van Berkel, (1998) “Electrochemical Sample Pretreatment Coupled On-line with ICP-MS: Analysis of Uranium Using and Anodically Conditioned Glassy Carbon Working Electrode,” *Anal. Chem.*, **70(6)**, 1141.

3. J.R. Pretty, D.C. Duckworth, G.J. Van Berkel, (1997) “Anodic Stripping Voltammetry Coupled On-Line with Inductively Coupled Plasma Mass Spectrometry: Optimization of a Thin-Layer Flow Cell System for Analyte Signal Enhancement,” *Anal. Chem.*, **69**, 3544.

Radiation Effects and Thermal Stability of Muratiate Ceramics as Candidate Nuclear Waste Forms

Rodney C. Ewing
Jie Lian
University of Michigan
rodewing@umich.edu
http://www.geo.lsa.umich.edu/relw/

S. V. Yudintsev
Institute of Geology of Ore Deposits RAS, Russia
S. V. Stefanovsky
SIA Radon, Russia

Overall research goals

Synthetic murataite is an isometric derivative of the fluorite structure with the general formula $A_3B_6C_2O_{22-x/2}$ ($0 \leq x \leq 1$). The interest in murataite as a candidate waste form is due to its four distinct cation sites as well as cation vacancies. By a variety of coupled substitutions, murataite can accommodate a wide range of complex nuclear waste stream compositions, particularly those with high iron concentrations and actinides. Radiation damage-induced crystalline-to-amorphous transformation and thermal instability may result in the macroscopic swelling, crack and phase decomposition, leading to a significant change in the chemical durability and an increase in the release of incorporated radionuclide. The research goal is to determine the radiation stability and thermal stability of murataite polytypes as candidate waste forms for the immobilization of actinides, particularly Pu.

Significant achievements in 2003-2005

1) Murataite ceramics were synthesized in the system of Ca-Ti-U-Mn-Al-Fe-Zr-Ce-O by sintering at 1400-1600 °C followed by crystallization under slightly oxidizing conditions (in air). Different murataite polytypes were synthesized depending on the conditions of synthesis as a result of cation ordering on the four specific sites, leading to an ordered murataite superstructure (Fig. 1). Murataite can occur as a superstructure of 3-multiples (Mu-3x3x3), 5-multiples (Mu-5x5x5) and 8-multiples (Mu-8x8x8) of the fluorite unit cells, and a disordered murataite was also synthesized. The phase composition and crystal structure were well characterized.

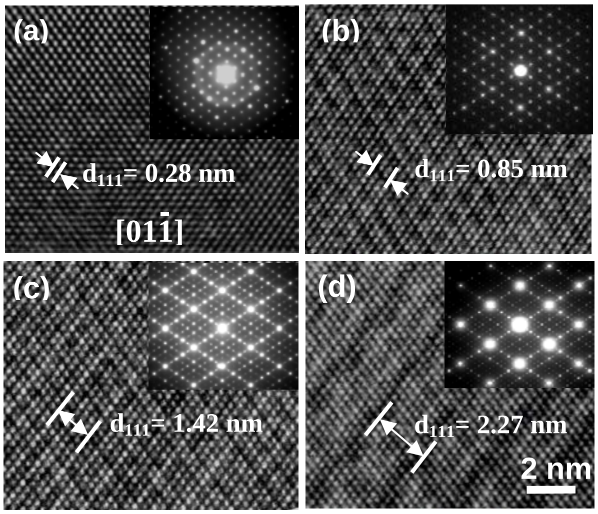


Fig. 1. HRTEM images and selected area electron diffraction (SAED) patterns of murataite polytypes: (a) a disordered murataite; (b) 3-multiples; (c) 5-multiples; and (d) 8-multiples of the fluorite unit cells (see Ref. 1).

2) The radiation resistance and structural transformation of murataite polytypes were studied by 1 MeV Kr^{2+} ion irradiation and in-situ TEM observation using IVEM-Tandem facility at Argonne National Laboratory. The critical amorphization dose was determined as a function of temperature and the degree of structural

disordering. Generally, murataite ceramics are sensitive to ion beam-induce amorphization. An ion beam-induced ordered-murataite to a disordered-fluorite transition occurred in the murataite superstructure, similar to that observed in the closely-related pyrochlore structure-type, $A_2B_2O_7$. The critical amorphization temperature of murataites was determined in the range of 860 K to 1060 K upon 1 MeV Kr^{2+} ion irradiation. A decreased susceptibility to ion beam irradiation-induced amorphization was observed for the disordered murataite, suggesting that the amorphization susceptibility for fluorite-related compounds depends, in part, on the initial degree of intrinsic disorder prior to irradiation.

3) The thermal stability of murataite polytypes was studied by *in-situ* heat treatment under TEM observation. A Fe-rich phase decomposition with the precipitation of nanocrystals (Fig. 2) was induced by thermal treatment in the murataite structure, probably due to the reduction of Fe^{3+} to Fe^{2+}. Ce^{3+} is closely associated with the Fe-rich phase in the Ce-incorporated murataite phase. The phase decomposition and nanocrystal formation have no significant effects on the radiation resistance of murataite ceramics used as potential host phases for the immobilization of actinides.

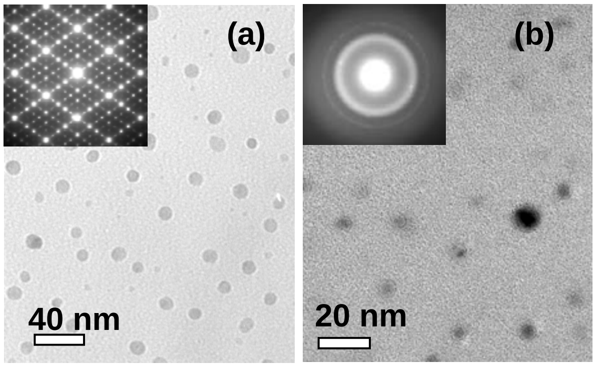


Fig. 2. Bright-field TEM images showing thermally-induced phase decomposition occurred in murataite ceramics: (a) before irradiation and (b) after 1 MeV Kr^{2+} ion irradiations (see Ref. 2).

Specific objectives for 2005-2006

Further research will be conducted on murataite-type ceramics, particularly in understanding the formation of different polytypes varying with the synthetic conditions and the radiation-induced order-disorder structural transition. The effect of intrinsic structural disordering will be further investigated emphasizing the correlation between the long range ordering (the periodic fluorite unit cells) and the radiation susceptibility. The radiation stability of murataites doped with actinides, specifically ^{239}Pu or $^{239}Pu/^{241}Am$ will be studied. The results will be compared with other candidate waste forms such as pyrochlore or garnet-type samples.

References of work that were supported by this project (2003-2005)

1) J. Lian, L.M. Wang, R. C. Ewing, S. V. Yudintsev, and S. V. Stefanovsky (2005), Ion Beam-induced Amorphization and Order-disorder Transition in the Murataite Structure, *Journal of Applied Physics*, submitted.
2) J. Lian, L. M. Wang, R. C. Ewing, S. V. Yudintsev, S. V. Stefanovsky (2005), “Nanocrystal Formation and Phase Decomposition in Murataite Ceramics”, *Journal of Materials Chemistry*, **15**, 709-714.
3) S. Utsunomiya, S. Yudintsev, R.C. Ewing (2005), Radiation Effects in Ferrate Garnet, *Journal of Nuclear Materials*, **336**, 251-260.
4) J. Lian, L. M. Wang, R. C. Ewing, S. V. Yudintsev, S. V. Stefanovsky (2004), “Radiation effects in murataite ceramics”, *Mater. Res. Soc. Symp. Proc.*, **807**, 225-230.
5) N. P. Laverov, S. V. Yudintsev, T. S. Ioudintseva, S. V. Stefanovsky, R. C. Ewing, J. Lian, S. Utsunomiya, L. M. Wang (2003), “Influence of Radioactive Decay on Properties of Confinement Matrices of Actinide-containing Waste”, *Geology of Ore Deposits*, **45**, 6-35.

Joint NMR and Diffraction Studies of Catalyst Structure and Binding

Clare P. Grey
Santanu Chaudhuri, Leslie Holmes, Luming Peng
Chemistry Department, SUNY Stony Brook, Stony Brook, NY 11794-3400
cgrey@mail.chem.sunysb.edu
http://www.sunysb.edu/chemistry/faculty/cgrey.htm

Overall research goals: Research carried out under DOE support has focused on two areas. In the first project, we aim to develop and apply new NMR methods to study structure and gas binding in molecular sieves and catalysts. In the second project we use a variety of different structural probes to characterize fluorinated aluminum oxides for use as acid catalysts or for F/Cl exchange reactions. We aim to establish the nature of the active sites involved in catalysis and how the structures of the catalytic sites change during the reaction.

Significant achievements in 2003-2005:
Sorption of diphosphines combined with ^{31}P NMR has been employed to study proximity between different acid sites inside the zeolite pores. By using molecules with two basic groups separated by variable lengths, $Ph_2P(CH_2)_nPPh_2$, (n = 1- 6) probes were designed that can probe distances between acid sites. Double quantum, two-dimensional NMR methods were applied to connect one end of the molecule/protonated phosphine with the other, to determine whether the phosphines were mono- or di-protonated and to help assign the resonances. The method was first applied to characterize strength and proximity between sites in zeolite HY.[11] The method has now been extended to investigate clustering in steamed, low Al-content zeolites. The results show the acidic sites are uniformly distributed throughout the zeolite.

In a parallel project, we have observed the ^{17}O signal from the Brønsted acid site in zeolite HY for the first time, by using a series of ^{17}O MAS NMR methods, allowing the effect of gas sorption on local structure to be monitored.[12] ^{17}O-^{1}H double resonance (REDOR) experiments were used to prove unambiguously that the ^{17}O signal arises from O directly bound to H (Figure 1). A quadrupolar coupling constant, the measure of the local distortion surrounding this site, of 6.6 MHz is determined, which is similar to that obtained by ab-initio calculations of zeolite HY-like clusters; this value drops to 5 MHz on acetone binding, as determined by ^{1}H/^{17}O TRAPDOR NMR. Finally, ^{1}H-^{17}O cross-polarization NMR spectroscopy is used to select the much weaker Brønsted acid site signal and remove the large ^{17}O background signal from the framework oxygen anions. These results open up new methods for characterizing acidity in zeolites and investigating H^{+}-sorbent interactions.

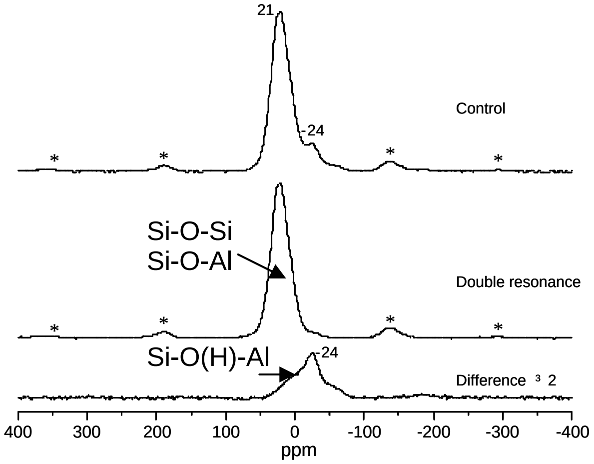


Figure 1. ^{17}O-^{1}H REDOR NMR spectra of zeolite HY (14.1 T), with a REDOR dephasing time of 308 μs. The difference spectrum, obtained by subtracting the double resonance spectrum from the control spectrum, shows the signal due to the Brønsted acid site.

Solid state NMR[1,5,6,7,8] and diffraction methods along with molecular dynamics (MD) simulations have been used to characterize catalytic surfaces and how they change during halogen exchange reactions. MD simulations were performed on nano-particles of the catalyst α-AlF_3. These calculations helped to rationalize structural differences seen (by NMR and diffraction), between the catalytically active form of α-AlF_3 that grows on γ-Al_2O_3 during Cl/F exchange reactions involving hydrofluorochlorocarbons and bulk α-AlF_3. Reconstruction of the edges and corners of the particles is seen in the MD simulations, resulting in structures that resemble those present in other polymorphs of AlF_3. Lewis acid sites are formed on the surfaces of the nano-particles, although some surface reconstruction occurs, involving the movement of a terminal fluorine atom to bridge more than one aluminum atom. The surface fluoride ions are extremely mobile, even at moderately low temperatures, Lewis acid sites forming and disappearing as the ions move across the surface even in the timescale of a typical MD run (10 ps).

Specific objectives for 2005-2006:

(i) Design and test new probe molecules for studying proximity between sites in bifunctional catalysts

(ii) Obtain ^{17}O spectra of a wider range of zeolites, so as to establish correlations between the quadrupole-coupling constant (QCC) of the Brønsted acid site and zeolite structure.

(iii) Investigate the effect of gas binding on the QCC of the Brønsted acid site.

References of work that were supported by this project

1. "A Combined Solid State NMR and Diffraction Study of the Structure and Acidity of Fluorinated Aluminas: Implications for Catalysis," P.J. Chupas, David R. Corbin, V. N. M. Rao, J.C. Hanson, C.P. Grey, *J. Phys. Chem. B.*, 107, (33), 8327-8336, (2003).
2. "Sorptive Reconstruction of the $CuAlCl_4$ Framework upon Reversible Ethylene Binding", R.M. Sullivan, H. Liu, D.S. Smith, J.C. Hanson, D. Osterhout, M. Ciraolo, C.P. Grey, and J.D. Martin, *J. Am. Chem. Soc.*, 125 (36), 11065-11079, (2003).
3. "Hydrothermal Synthesis and Structural Characterization of Four Scandium Phosphate Frameworks", I. Bull, V. Young, S. J. Teat, L. Peng, C.P. Grey, J.B. Parise, *Chem. Mater.*, 15, (20), 3818-3825, (2003).
4. "Nuclear Magnetic Resonance Studies of Zeolites", C. P. Grey, Chapter 6 in Handbook of Zeolite Science and Technology, S. M Auerbach, K. A. Carrado, P. K. Dutta, ed., *Marcel Dekker, Inc., New York* (2003).
5. "Rapid Acquisition Pair Distribution Function (RA-PDF) Analysis," P. J. Chupas, X. Qiu, J. C. Hanson, P. L. Lee, C. P. Grey, S. J. L. Billinge, *J. Applied Cryst.* 36, 1342-1347 (2003).
6. "Study of the nature and mechanism of the rhombohedral to cubic phase transition in α-AlF_3 with molecular dynamics simulations", S. Chaudhuri, P. Chupas, M. Wilson, P.A. Madden, C.P. Grey, *J. Phys. Chem. B.*, 108, 3437-3445 (2004).
7. "Probing Local and Long Range Structure Simultaneously: An In-Situ Study of the High Temperature Phase Transition of α-AlF_3," P. J. Chupas, S. Chaudhuri, J. C. Hanson, Xiangyun Qiu, P. L. Lee, S. D. Shastri, S. J. L. Billinge and C. P. Grey, *J. Am. Chem. Soc.*, 126, 4756-4757, (2004).
8. "Surface Modification of Fluorinated Aluminas; Application of Solid State NMR Spectroscopy to the Study of Acidity and Surface Structure", P. J. Chupas and C. P. Grey, *J. Catal.*, 224, (1), 69-79 (2004).
9. "[Li-Si-O]-MFI: A New Microporous Lithosilicate with the MFI Topology", S.-H. Park, H. Liu, M. Kleinsorge, C. P. Grey, B. H. Toby, J. B. Parise, *Chem. Mater.*, 16, 2605-2614 (2004).
10. "Comparison of the ^{17}O NMR spectra of zeolites LTA and LSX", J. E. Readman, C. P. Grey, M. Ziliox, L. M. Bull, *Solid State NMR*, 26, 153-159 (2004).
11. "Measuring Brønsted Acid Densites in Zeolite HY with Diphosphine Molecules and Solid State NMR Spectroscopy", L. Peng, P. J. Chupas, C. P. Grey, *J. Am. Chem. Soc.*, 126, 12254-12255, (2004).
12. "Detection of Brønsted acid sites in zeolite HY with high field ^{17}O MAS NMR techniques", L. Peng, Y. Liu, N. Kim, J. E. Readman and C. P. Grey, *Nature Materials*, 4, 215-216 (2005).

Spectroscopic Methods to Characterize Adsorption and Binding to Surface-Immobilized Ligands

Joel M. Harris, P.I.
Rory H. Uibel, Postdoctoral Associate
Vanessa Oklejas, Josh Wayment, Yiyong Tan, and Eric Peterson, Graduate Students
Department of Chemistry, University of Utah
harrisj@chem.utah.edu
http://www.chem.utah.edu/faculty/harrisj/index.html

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

A major theme of the current DOE project has been to develop *in situ* Raman spectroscopy for monitoring metal-ion binding to ligands immobilized on porous silica surfaces. To understand the effects of surface-immobilization on these reactions, a water-soluble form of 8HQ is needed that is analogous in structure to the phenylazo-linked ligand employed in most of the surface chemistry studies. We synthesized a water-soluble 8HQ, 5-(p-sulfophenylazo)-8-hydroxy-quinoline (SPAHQ) and investigated the proton-transfer and stepwise metal-ion complex formation reactions of the water-soluble model SPAHQ ligand [1]. We have also developed a templating approach to generating higher-order metal-ion complexes with immobilized 8HQ whereby the silica-framework built around a preformed metal-complex during a silica sol-gel synthesis [2]. The metal-ion concentration responses of sol-gels prepared with varying amounts of metal ion during the syntheses were tested, and the results indicate control over the fraction of imprinted binding sites in these sol-gel structures [2]. A related project in collaboration with the Eyring research group involved multivariate least squares methods were applied to the Raman and ultrasound spectroscopic analysis of the complexation kinetics of zinc with thiocyanate [3].

A second area of spectroscopic research has been to adapt surface-enhanced Raman scattering (SERS) to characterize active-sites on metals, the self-assembly process for immobilizing ligands on the metal surface, the effects of electric fields at chemically modified-metal surfaces, and adsorption of aromatic molecules to n-alkane ligands. The underlying metal substrate provides the means of controlling and varying the interfacial potential at which this chemistry occurs. A first study addressed SERS-active sites on silver to determine the role of surface pretreatment on the generation and properties of these sites [4]. SERS-based spectroelectrochemistry was used to characterize the potential dependence and chemical heterogeneity of adsorption sites found on both highly-polished and electrochemically-roughened polycrystalline silver electrodes. For the preparation of well-ordered, self-assembled monolayers on metal surfaces, it is critical to understand the chemistry of the self-assembly process. By collecting surface-enhanced Raman spectra versus applied potential to control the free energy for binding, multivariate statistical methods can resolve the component concentration profiles along with their corresponding Raman spectra [5]. SERS-based spectroelectrochemistry was also used to investigate structural properties of mixed self-assembled monolayers (SAMs) as a function of their composition [6]. Mixed monolayers were formed from ethanol solutions containing 12-mercaptododecanenitrile and n-hepanethiol. Stark-tuning rates of the nitrile group served as a localized probe of the interfacial environment and exhibited a dependence on monolayer composition. A major breakthrough in the application of vibrational Stark-tuning measurements to probe interfacial electric fields was to map the field distribution near a SAM/solution interface by using a nitrile-terminated n-alkanethiol probe diluted into a series of shorter n-alkanethiols. Interfacial electric fields derived from the Stark-tuning rates were examined to map the structure of the diffuse double-layer region versus distance from the SAM/solution interface. The results demonstrate the ability of this spectroelectrochemical experiment to characterize the diffuse double-layer at dielectric interfaces on a subnanometer distance scale [7]. In an analytical application of chemically-modified metal surfaces for SERS detection, metal colloids immobilized on a glass support substrate were modified with a self-assembled alkylsilane (C18) layer to preconcentrate polycyclic aromatic hydrocarbons (PAH) from aqueous solutions onto a SERS-active surface [8]. Selective adsorption and SERS detection of PAH compounds from low (ppb) concentration solutions onto C18-modified gold colloid substrates was reported.

References:

1. “Spectroscopic studies of proton-transfer and metal-ion binding of a solution-phase model for silica-immobilized 8-hydroxyquinoline”, Rory H. Uibel and Joel M. Harris, ***Analytica Chimica Acta***, 494 105 (2003).
2. “Templating of Multiple Ligand Metal-ion Complexation Sites in 8-Hydroxyquinoline-Modified Silica Sol-gel Materials Investigated by In Situ Raman Spectroscopy", Rory H. Uibel and Joel M. Harris, ***Analytical Chemistry***, 77, 991 (2005).
3. “Ultrasonic and Raman Scattering Spectroscopy of Zinc Thiocyanate Complexes in Water at 25^{o}C. Kinetics of Complex Formation Determined by Multivariate Analysis”, Rory H. Uibel, Emily Heider, Jennifer Gasser, Joel M. Harris, Edward M. Eyring and Sergio Petrucci, ***Journal of Solution Chemistry*** (in press).
4. “Potential-Dependent Surface-Enhanced Raman Scattering from Adsorbed Thiocyanate for Characterizing Silver Surfaces with Improved Reproducibility”, Vanessa Oklejas and Joel M. Harris, ***Applied Spectroscopy***, 58, 945 (2004).
5. “Resolution of Intermediate Adsorbate Structures in the Potential-dependent Self Assembly of n-Hexanethiolate on Silver by *In-Situ* Surface-Enhanced Raman Spectroscopy”, Rory H. Uibel and Joel M. Harris, ***Applied Spectroscopy***, 58, 934 (2004).
6. "In-Situ Investigation of Binary-Component Self-Assembled Monolayers: A SERS-Based Spectroelectrochemical Study of the Effects of Monolayer Composition on Interfacial Structure", Vanessa Oklejas and Joel M. Harris, ***Langmuir***, 19 5794 (2003).
7. “SERS-Based Vibrational Stark Effect as a Spatial Probe of Interfacial Electric Fields in the Diffuse Double-Layer”, Vanessa Oklejas, Christopher Sjostrom, Joel M. Harris, ***Journal of Physical Chemistry B***, 107 7788 (2003).
8. “C18-Modified Metal-Colloid Substrates for Surface-Enhanced Raman Detection of Trace-level Polycyclic Aromatic Hydrocarbons in Aqueous Solution”, Lydia G. Olson, Rory H. Uibel and Joel M. Harris, ***Applied Spectroscopy***, 58, 1394 (2004).

Chemical Analysis at Nanodomains:
Inorganic Mass Spectrometry with ICP and Electrospray Ionization Sources

R. S. Houk, PI
Fumin Li, Cory Gross and Nicholas Lentz, 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. BES research in analytical chemistry at the Ames Laboratory is now directed into a common theme: chemical analysis at nanodomains. Several projects involving ICP and electrospray ionization mass spectrometry pertinent to this theme are under investigation.

Specific achievements in 2003-2005.

Electrospray of Counter Ion Complexes and Clusters. 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. Collision-induced dissociation has been used to investigate the structure and properties of these ions. Recent work has investigated counter ion clusters of amines of general formula $[(RNH_3)_xCl_{x+1}]^-$. A typical spectrum is shown below. 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. The key point is whether the matrix and analytes are removed at the same rates. For steel, some elements like Mn are removed consistently with the Fe matrix, while other elements like Nb are underrepresented in the solutions.

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. A number of metals can be removed at a single applied potential and a carbon cathode. A new, metal-free column specifically for these experiments has been evaluated.

Specific Objectives for 2005-2006

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 – 2003-05

1. 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.

2. 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.

3. 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.

4. B. Zhang, F. Li, R. S. Houk and D. W. Armstrong, “Pore Exclusion Chromatography ICP-MS for Monitoring Elements in Bacteria: A Study of Microbial Removal of Uranium from Aqueous Solution,” Anal. Chem 2003, 75, 6901-6905.

5. F. Li and R. S. Houk, Controlled Dissolution for Analysis of Sample Layers by ICP-MS: A Feasibility Study,” *Appl. Spectrosc.*, 2004, 58, 776-783.

6. F. Li, D. W. Armstrong and R. S. Houk, “The Behavior of Bacteria in the ICP: Atomization and Production of Atomic Ions for Mass Spectrometry,” Anal. Chem 2005, 77, 1407-1413.

7. T. Hasan, D. Gazda, M. D. Porter and R. S. Houk, “On-Line Cleanup of Blanks for ICP-MS by EMLC,” *Anal. Chim. Acta*, 2005, in press.

The Impact of Ion-Phonon Interaction on f-Element Chemistry

Guokui Liu, James V. Beitz, and Mark P. Jensen
Xueyuan Chen, Postdoc. Associate
Chemistry Division, Argonne National Laboratory
gkliu@anl.gov

Collaborators: Norman Edelstein and Linfeng Rao, Lawrence Berkeley National Laboratory, Mike Reid, University of Canterbury, New Zealand, Valentin Vikhnin, A.F. Ioffe Physical Technical Institute, Russia, Donglu Shi, University of Cincinnati

Overall research goals: We seek to provide a fundamental understanding of the electronic interactions of actinides and lanthanides in solution and solid phases. In order to elucidate the consequences of the synergistic interplay between f-ions and their vibronic environments, which include primarily energy and charge transfer, non-radiative relaxation, and coordination, we use laser spectroscopic methods to obtain the electronic energy level structure and excited-state dynamics of the f-element ions, and analyze the experimental results with theoretical models of crystal-field interactions and electron-phonon coupling. Whereas our research addresses the fundamental characteristics of electron-phonon coupling [1, the results from our research benefit efforts centered on understanding chemical bonding and more technical issues such as actinide separation and speciation.

Significant achievements in 2003-2005: We have performed theoretical analyses and modeling of vibronic coupling and charge transfer transitions [2,4,10]. We have developed a theoretical model, based on a fundamental theory of electron-phonon interaction, to determine the interaction parameters that characterize the local structure of uranyl $(UO_2)^{2+}$ ions in solution and compounds [2,9,12]. Application of our model to fit experimental data provides detailed information about the spectra and luminescence dynamics of uranyl ions that have long been used to study solution speciation and as a fingerprint probe of structure variation. We have extended our work to quantitatively analyze the intense vibronic spectra of actinide- and lanthanide-ion f-d transitions in crystals. The frequencies and Huang-Rhys parameter of the vibrational modes that couple to electronic transitions have been evaluated in fitting the experimental results from Ce^{3+} and Pa^{4+} in various crystalline materials [4,10].

The electronic properties of f ions may be strongly influenced by confined ion-lattice vibronic interactions when lanthanides and actinides are incorporated into nanophases. As observed in our experiments on Eu^{3+} and Er^{3+} in nanocrystals, the nonradiative relaxation of selected excited states exhibits an abrupt decrease as a function of temperature. This novel phenomenon has been interpreted based on quantum confinement of phonon relaxation in nanoparticles [1,3,5]. Based on a detailed and predictive understanding of electronic energy level structure, our studies have shown the feasibility of using time- and wavelength-resolved laser-induced fluorescence techniques to fundamentally investigate radiation damage in glassy silica when that damage is due to alpha decay that occurs in heavy metal phosphate nanophases embedded in the silica [11,15].

Specific objectives for 2005-2006: The nano-effects of ion-phonon interactions on electronic transition and luminescence efficiency will be further investigated. New efforts will focus primarily on understanding the impact of charge transfer on the crystal-field spectra and excited state dynamics of actinide and lanthanide ions in soft-donor complexes in which covalence and charge transfer impose significant influence [8,16]. Our work also includes evaluation of ligand-induced orbital hybridization of f-element ions in solids [13,14,17].

References of work that were supported by this project

1. G. K. Liu, X. Y. Chen, and H. Z. Zhuang (2003), Confinement of electron-phonon interaction on luminescence dynamics in nanophosphors of Er^{3+}:Y_2O_2S, *J. Solid State Chem.* **171**,123-132.
2. G. K. Liu, X. Y. Chen, and J. Huang (2003), Intensity and Bandwidth of Multiphon Vibronic Transitions of Rare Earth Ions in Crystals, *Molecular Physics* **101**, 1029-1036.
3. X. Y. Chen, H. Z. Zhuang, and G. K. Liu, S. Li and R. S. Niedbala (2003), Confinement on the energy transfer between luminescent centers in nanocrystals, *J. Appl. Phys*. **94**, 5559-65.
4. P. A. Tanner, C. S. K. Mak, N. M. Edelstein, K. M. Murdoch, G. K. Liu, J. Huang, L. Seijo, Z. Barandiarán (2003), Absorption and Emission Spectra of Ce^{3+} in Elpasolite Lattices. *JACS* **125**, 13225-33.
5. X. Y. Chen, L. Yang, E. E. Cook, S. Skanthakumar, D. Shi, and G. K. Liu (2003), Crystallization, phase transition and optical properties of the rare-earth-doped manophosphors synthesized by chemical deposition, *Nanotechnology* **14**, 670-674.
6. H. Liu, S. T. Li, F. E. Fernandez, G. K. Liu (2003), Optical property of Eu in strontium barium niobate thin film grown by pulsed laser deposition, *Thin Solid Films* **424**, 161-65.
7. K. Horchani, J.C. Gâcon, M. Ferid, M. Trabelsi-Ayedi, O. Krachni and G. K. Liu (2003), Energy Levels of Pr^{3+} in $CsPrP_4O_{12}$ and $RbPrP_4O_{12}$ Cyclotetra Phosphates, *Optical Materials* **24**, 169-174.
8. X. Y. Chen, W. Zhao, R. E. Cook, and G. K. Liu (2004), Anomalous luminescence dynamics of Eu^{3+} in BaFCl microcrystals, *Phys. Rev. B* **70**, 205122-9.
9. P. L. Zanonato, P. Di Bernardo, A. Bismondo, G. K. Liu, X. Y. Chen, L. F. Rao (2004), Hydrolysis of uranium(VI) at variable temperatures (10 – 85 °C), *JACS* **126**, 5515-5522.
10. G. K. Liu, X. Y. Chen, N. Edelstein, M. F. Reid, and J. Huang (2004), Analysis of f-element multiphonon vibronic spectra, *J. Alloys and Comp*. **374**, 240-244.
11. J. V. Beitz, S. Skanthakumar, S. Seifert, and P. Thiyagarajan (2004), f-element influence on the size of nanophase phosphate inclusions in silica, *MRS Proceedings* **802**, 125-130.
12. X. Y. Chen, L. F. Rao, and G. K. Liu (2004), On the physical nature of uranyl charge transfer vibronic interactions, *MRS Proceedings* **802**, 169-174
13. G. K. Liu (2005), Electronic Energy Level Structure of Rare Earth Ions in Crystals, Chapter 1 in "*Spectroscopic Properties of Rare Earths in Optical Materials*",(Springer-Verlag), 1-92.
14. G. K. Liu (2005), Systematics of f-element crystal-field interaction, *J. Solid State Chem*.**178**, 489-498.
15. J. V. Beitz, C. W. Williams, K. –S. Hong, G. K. Liu (2005), Heavy metal phosphate nanophases in silica: influence of radiolysis probed via f-electron state properties, *J. Solid State Chem*.**178**, 511-520.
16. X. Y. Chen and G. K. Liu (2005), The standard and anomalous crystal-field spectra of Eu^{3+}, *J. Solid State Chem*.**178**,419-428.
17. G. K. Liu and J. V. Beitz (2005), Optical spectra and electronic structure of actinides in condensed phases, Chapter 18 in "*The Chemistry of the Actinide and Transactinide Elements*", (Kluwer, in press).

Multinuclear Magnetic Resonance Study of Silica and Modified Silica (Derivatization of Silica by PCl_5)

Gary E. Maciel
I-Ssuer Chuang , Shaokuan Zheng and Joseph A. DiVerdi
Department of Chemistry, Colorado State University, Ft. 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 suggested by our previous research and 2) a study of the reactivity of the silica surface with certain reactive agents (e.g., ‘simple’ organometallic agents like methyl-metal compounds (a) and PCl_n reagents (b)). The first topic is important and timely because silica surface structure is at the heart of most important silica-based chemistry, including separations, catalysis, composite materials, soils chemistry and geochemistry. The second topic is aimed at i) providing a fundamental chemical foundation for the largely empirical practice of ‘immobilizing’ an organometallic center on a silica surface (e.g., to transform a homogeneous catalyst system into a heterogeneous catalyst system) and ii) providing new avenues for derivatizing a silica surface, an ability that is key to optimizing a wide variety of basic chemical and technological strategies. Work on the 1) and on 2a) continued during the past year along the lines described in last year’s abstract. Substantial progress was made in both directions. The present abstract focuses on an area (2b) that was not covered last year, i.e., derivatization of the silica surface with PCl_5.

Significant achievements in 2004. Solid-state ^{31}P NMR experiments were carried out with magic-angle spinning (MAS) and with $^{1}H \rightarrow ^{31}P$ cross polarization (CP) or with direct polarization (DP, no CP, just ^{31}P spin-lattice relaxation) on samples prepared by treating dried silica with a CCl_4 solution of PCl_5 at 25 ^{o}C. The molar ratio of PCl_5 to SiOH (silanol) groups on the surface was for most experiments either 1:10 or 1:1. While the corresponding ^{29}Si NMR experiments yielded little primary information, the corresponding ^{31}P MAS spectra show a variety of species on the surface immediately after the reaction period or after periods of storage in the MAS rotor or after periods of exposure to moisture. Fig. 1 shows a representative set of ^{31}P NMR spectra, based on a 1:1 sample. In Fig. 1 one sees that immediately after the prescribed reaction period (lowest spectra) the only species observed is a species (at roughly 14 ppm) in which the silanol hydrogen is replaced by a PCl_4 group , i.e., with a $SiOPCl_4$ moiety (II) at the silica surface (Also observed, if the PCl_5 is not removed from the sample by evacuation, is physisorbed PCl_5 (I) (at about –80 ppm), which does not appear in any of the spectra shown in Fig. 1). The bottom five spectra (*a* – *e*) shown in Fig. 1 correspond to samples that were never exposed intentionally to moisture (stored in the rotor for increasing times indicated in h); moving up in the figure, the next five spectra (*f* – *k*) correspond to samples that had been exposed to humidity for increasing periods (indicated in h). The top spectra (*l*) correspond to sample *k* that had been evacuated (10^{-3} torr) for 12 h at room temperature. One sees a variety of species represented in the spectra of Fig. 1, including species formed during storage (*a* – *e*) in the MAS rotor – i.e., $(Si\text{-}O\text{-})_2PCl_3$ (III) and/or

$(Si\text{-}O\text{-}PCl_3)_2O$ (IV) at –4 ppm and, to a small degree for the longest storage period (*e*), $POCl_3$(ads) (V) at about 6 ppm, Si-O-P(O)$(OH)_2$ (VI) at –12 ppm and $(Si\text{-}O\text{-})_2P(O)OH$ (VII) and/or $[Si\text{-}O\text{-}P(O)OH]_2O$ (VIII) at –24 ppm. These latter species are more heavily represented upon exposure to moisture (*f* – *k*), along with H_3PO_4(ads). Dramatic differences in relative intensities observed for a given sample by DP-MAS (left) and CP-MAS (right) reflect the known dependences on different details of spin dynamics and the expected dependences of these details on local, atomic-level dynamics.

For the case of the broad peak centered at – 4 ppm, an echo train of the Carr-Purcell-Meiboom-Gill type was used to distinguish between nominally ‘isolated’ ^{31}P nuclei (structure III) and ^{31}P nuclei in more closely spaced (and hence dipolar-coupled) pairs (structure IV). Preliminary results indicate that about 2/3 of this peak is due to IV and about 1/3 to III.

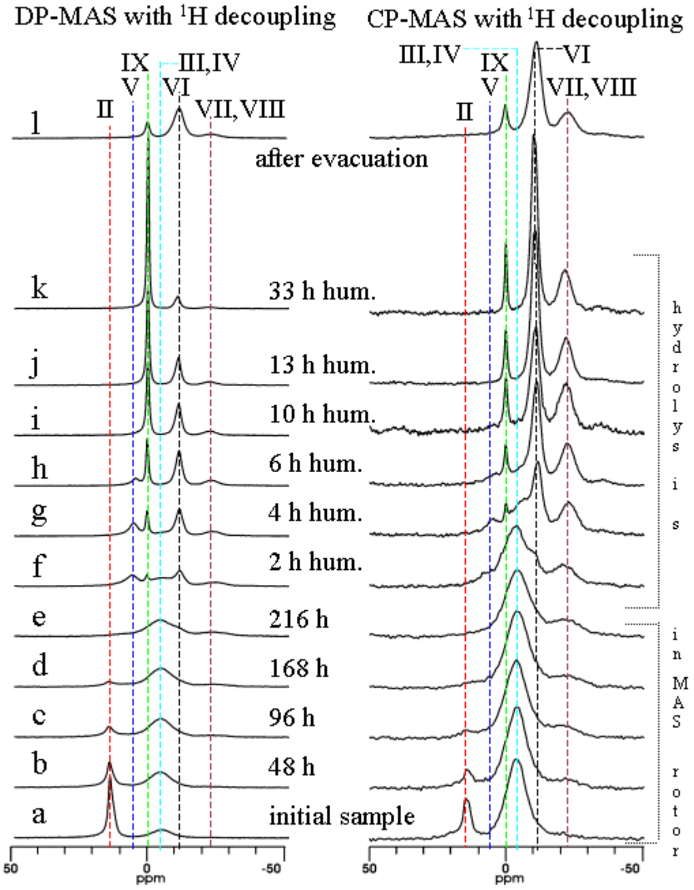


Fig. 1. ^{31}P MAS NMR spectra obtained with direct polarization (left) and cross polarization (right) on a 1:1 (PCl_5:silanol) sample of PCl_5 on dry silica. Sample stored in MAS rotor for specified hours (a – e). Samples exposed to humidity for specified hours (f – k).

<u>Specific objectives for 2005-2006</u>: Complete studies already initiated. Examine silica treated with SCF CO_2 (with Carl Tripp, U. Maine). Examine mesoporous silicas.

<u>Publications of this project for 2004</u>:

Camille Keeler, Eugene Kelly and Gary E. Maciel, “Chemical-Structural Information from Solid-State ^{13}C NMR Studies of a Suite of Humic Materials from a Lower Montane Forest Soil, Colorado, USA”, *Geoderma*, in press.

Principles of Chemical Recognition and Transport in Extractive Separations: Selectivity in Liquid-Liquid Extraction of Anions

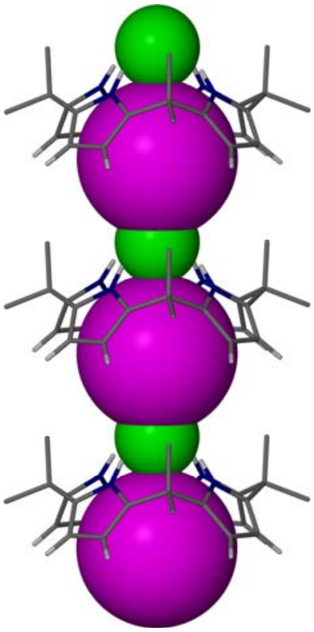
Bruce A. Moyer, Principal Investigator
Hyun-Ah Kang and Maryna Gorbunova, Postdoctoral
Chemical Sciences Division, Oak Ridge National Laboratory
moyerba@ornl.gov
http://www.ornl.gov/sci/casd/csg/

Collaborators, Peter V. Bonnesen, Laetitia H. Delmau, Nancy L. Engle, Tamara J. Keever, and Radu Custelcean, Oak Ridge National Laboratory; Benjamin P. Hay, Pacific Northwest National Laboratory; Kristin Bowman-James, Univ. of Kansas; Jonathan L. Sessler and Eric V. Anslyn, Univ. of Texas, Austin; Philip A. Gale, Univ. of Southampton.

Overall research goals: The means to control and enhance selectivity, the most important generic issue in extractive separations, is attacked in this program via a holistic theory-based experimental effort. A major focus on anions has supplanted previous emphasis on cation issues in the context of understanding both the basis of controlling anion selectivity and the role of anions in extraction generally. Systems of interest concern anion receptors containing organized hydrogen-bond donor groups. A key success criterion lay in finding systems exhibiting anion selectivity other than the ubiquitous Hofmeister bias, which monotonically favors anions with decreasing charge density. Molecular-design calculations performed at PNNL are being used to identify candidate anion receptors with complementary and preorganized architectures for specific anion binding. Experimental quantities of candidate receptors are obtained through synthesis at ORNL, the Univ. of Texas, Austin, and the Univ. of Kansas. Extractive behavior and structural characterization data then permit evaluation of binding and transport properties in the light of receptor conformation and coordination geometries.

Significant achievements in 2003–2005: Results on theory and molecular-design of anion receptors (B. P. Hay) and anion recognition in solid-state materials (R. Custelcean) are summarized in separate abstracts. Below are key results from synthesis and binding studies by ORNL investigators and external collaborators:

- Demonstrated for the first time that calix[4]pyrrole can act as an ion-pair receptor by binding simultaneously the Cs^+ cation and F^-, Cl^-, Br^-, CO_3^{2-}, or $EtOCO_2^-$ anions (see figure); in collaboration with J. L. Sessler and P. A. Gale.
- Showed that a set of bis-urea and bis-thiourea tweezers possessing linking groups generated by HostDesigner enhance the extraction of cesium salts of oxo-anions.
- Synthesized fluorinated α-diols and demonstrated their potential as a new class of dual H-bond donors for oxo-anion extraction.
- Found that the synergistic effect of neutral anion receptors on anion exchange may be quantitatively related to competitive anion binding; in collaboration with J. L. Sessler and K. Bowman-James.


X-ray structure showing calix[4]pyrrole as ditopic host for CsF.

Specific objectives for 2005–2006: The unprecedented behavior of calix[4]pyrroles as anion and ion-pair receptors will be examined in greater detail, both in extraction and structural studies, in collaboration with J. L. Sessler and P. A. Gale. Speciation, solution structure, and selectivity will be important issues, as we seek to draw parallels between solution and solid-state behavior. The selectivity of urea-based tweezers will be determined and correlated with conformational energies to test and refine molecular-design computations. Higher levels of organization and complementarity (e.g., tripods) in this class of anion receptor will be sought toward more selective anion binding. Other classes of H-bond donors, such as α-diols, will be incorporated into multi-functional anion receptors with the aid of molecular-design computations. Synergism in anion-exchange employing neutral anion receptors will be explored toward imparting high selectivity and understanding binding and speciation, in collaboration with J. L. Sessler and K. Bowman James. New charged anion receptors will be examined toward increased control of charge-charge complementarity in ditopic receptors, in collaboration with K. Bowman-James and E. V. Anslyn.

<u>References of work that was supported by this project in 2003–2005:</u>

(1) R. Custelcean, L. H. Delmau, B. A. Moyer, J. L. Sessler, W.-S. Cho, D. Gross, G. W. Bates, S. J. Brooks, M. E. Light, and P. A. Gale (2005), "Calix[4]pyrrole: An old yet new ion-pair receptor." *Angew. Chem. Int. Ed.*, in press.

(2) B. A. Moyer, J. F. Birdwell, Jr., P. V. Bonnesen, and L. H. Delmau (2005), "Use of Macrocycles in Nuclear-Waste Cleanup: A Real-World Application of a Calixcrown in Technology for the Separation of Cesium." In *Macrocyclic Chemistry—Current Trends and Future*, Kluwer Academic Publishers: London, in press.

(3) B. A. Moyer, P. V. Bonnesen, R. Custelcean, L. H. Delmau, and B. P. Hay (2005), "Strategies for Using Host-Guest Chemistry in the Extractive Separation of Ionic Guests." *Kem. Ind.*, **54** (2), 65–87.

(4) B. P. Hay, T. K. Firman, and B. A. Moyer (2005), "Achieving Anion Shape Recognition through the Complementary Placement of Urea Donor Groups." *J. Am. Chem. Soc.*, **127**, 1810–1819.

(5) L. H. Delmau, T. J. Lefranc, P. V. Bonnesen, J. C. Bryan, D. J. Presley, B. A. Moyer (2005), "Fundamental Studies Regarding Synergism Between Calix[4]arene-bis(*tert*-octylbenzo-crown-6) and Alcohol Modifiers in the Solvent Extraction of Cesium Nitrate." *Solvent Extr. Ion Exch.*, **23**, 23–57.

(6) B. A. Moyer and R. Singh, Eds. (2004), *Fundamentals and Applications of Anion Separations*, Kluwer Academic/Plenum: New York.

(7) K. Kavallieratos, J. C. Bryan, R. A. Sachleben, G. J. Van Berkel, O. D. Espetia, M. Kelly, A. Danby, K. Bowman-James, and B. A. Moyer (2004), "Dual-Host Combinations: Using Tripodal Amides to Enhance Cesium Nitrate Extraction by Crown Ethers." In *Fundamentals and Applications of Anion Separations*, B. A. Moyer and R. P. Singh, Eds., Kluwer Academic/Plenum: New York, pp 125–150.

(8) B. P. Hay, M. Gutowski, D. A. Dixon, J. Garza, R. Vargas, and B. A. Moyer (2004), "Structural Criteria for the Rational Design of Selective Ligands. Convergent Hydrogen Bonding Sites for the Nitrate Anion." *J. Am. Chem. Soc.* **126**, 7925–7934.

(9) T. J. Haverlock, S. Mirzadeh, and B. A. Moyer (2003), "Selectivity of calix[4]arene-bis(benzocrown-6) in the complexation and transport of francium ion." *J. Am. Chem. Soc.* **125** (5), 1126–1127.

(10) T. G. Levitskaia, M. Marquez, J. L. Sessler, J. A. Shriver, T. Vercouter, and B. A. Moyer (2003), "Fluorinated calixpyrroles: anion-binding extractants that reduce the Hofmeister bias." *Chem. Commun.* (17), 2248–2249.

(11) L. H. Delmau, C. F. Baes, Jr., D. A. Bostick, T. J. Haverlock, and B. A. Moyer (2003), "Solvent Extraction System Modeling Using the Program SXFIT." In *Leaching and Solution Purification*, C. A. Young, A. M. Alfantazi, C. G. Anderson, D. B. Dreisinger, B. Harris, A. James, Eds., TMS (The Minerals, Metals, and Materials Society): Warrendale, PA, 2003; pp. 969–981.

f-shell Calculations: Er^{3+}:GaN and CUO

Russell M. Pitzer
Yang Yang, Rajni Tyagi, Tianxiao Yang
Department of Chemistry
Ohio State University
pitzer.3@osu.edu

Overall research goals:

We are working to make significant improvements in relativistic quantum chemistry capabilities, particularly for studying lanthanide and actinide molecules and complexes. We are cooperating with other research groups to make this possible. Our recent applications to molecules of these types are described below.

Significant achievements in 2003-2005:

The ground state of Er^{3+} is $4f^{11}\ {}^4I_{15/2}$. The spin-orbit transition ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ is at 1.54 μm. When Er^{3+} is doped into GaN, this transition can be used for optical-fiber signaling due to the low temperature dependence of its intensity. The 13/2 and 15/2 states are both split by the crystalline environment. The resulting spectrum has not been assigned in detail. We have modeled this system using clusters centered on Er^{3+}. This is complicated by the existence of two GaN crystal forms: zinc blende and wurzite. We use the method of multireference configuration interaction with relativistic effective core potentials and corresponding spin-orbit operators. The fact that this spectrum consists of spin-orbit transitions means that single excitations have a primary role in determining the the energy levels, in contrast to the usual dominance of double excitations in electronic transitions. Reasonable agreement is obtained with line postions and intensities, but the latter are dependent on assumptions about initial populations of levels. More needs to be done with respect to convergence of cluster sizes.

A number of workers[1-3] have attempted to compute whether the lowest-energy state of CUO is $\sigma^2\ {}^1\Sigma^+_0$ or $\sigma^1\varphi^1\ {}^3\Phi_2$ and whether there is a global ground state or whether different states are lower at different geometries (principally variation in the C–U distance). With our methods as already described, and using a triple-valence basis set, the global minimum is for ${}^1\Sigma^+_0$ but ${}^3\Phi_2$ has lower energy for larger C–U distances.

Specific objectives for 2005-2006:

Finish ongoing parallel programming and basis-set development work to enable final higher-accuracy calculations on a number of projects, including the above.

References of work that were supported by this project

1. R. M. Pitzer (Book review) Relativistic Electronic Structure Theory; Ed. P. Schwerdtfeger; Part 1 J. Am. Chem. Soc., 125, 13304 (2003); Part 2 J. Am. Chem. Soc. 126, 13875 (2004).

Other references

1. B. E. Bursten, J. Li, B. Y. Liang, and L. Andrews, Abstr. Pap. – Am. Chem. Soc. 226, U721 (2003).
2. B. O. Roos, P. O. Widmark, and L. Gagliardi, Faraday Discuss. 124, 57 (2004).
3. I. Infante and L. Visscher, J. Chem. Phys. 121, 5783 (2004).

Advancing the Capabilities of SERS in Chemical Analysis

Michael Sepaniak, PI; Robert Hinde, UTK Chemistry colloborator; Pampa Dutta, postdoctoral associate; Maggie Connatser, Marco Dejesus, Kathleen Giesfeldt, and Kasey Hill, students
The University of Tennessee, Knoxville, Department of Chemistry; **msepaniak@utk.edu**

Overall Research Goals

Despite the impressive recording of distinctive spectra for single molecules of a few highly Raman active molecules, positioned at “hot spots” on random morphology substrates, certain persistent fundamental limitations of SERS have significantly lessened the general impact of the technique in chemical analysis. Specifically, SERS has not seen general use for more traditional trace analysis largely because of limitations in qualitative and quantitative reproducibility and dynamic range. The overall objective of our project is the fundamental and practical development of novel nanocomposite materials as SERS substrates and unique measurement approaches to address these limitations in the analytical figures of merit of SERS. Our principle application is in the area of detection for μ-fluidic separations, initially capillary electrophoresis (CE), although other methods of analysis are also benefiting from these new multi-functional nano-materials.

Significant Achievements During 2003-2005

Random Morphology Metal-Polymer Nanocomposites. In pursuit of improved SERS substrates, we developed an interesting new class of nanostructured materials based on the creation of dielectric material-metallic nanocomposites. Our initial efforts involved physical vapor deposition of silver and gold onto the elastomer (poly)dimethylsiloxane (PDMS). We have published the first reports characterizing these novel materials in terms of morphology, optical properties, and, in particular, their SERS capabilities.[1-6] As the deposition proceeds, the metal atoms or very small clusters penetrate into the phase-separated layer of the polymer, diffuse, and agglomerate until a particle size is reached for which diffusion is negligible. Among the advantages that the nanocomposites exhibit as SERS substrates are the following: (i) The particles are suspended in a polymer, therefore all of the effective metal surface is accessible to analyte. (ii) The suspended particles are somewhat protected from the local environment, therefore oxidation and other deleterious effects are reduced. (iii) The polymer can be molded in practical shapes (e.g., titer plates or μ-fluidic channels) prior to metal deposition. (iv) PDMS is an excellent solid phase extractor for organics and can concentrate analyte near the metal surface. (v) The pliable polymer can be physically manipulated to alter inter-particle distances to influence optical properties including SERS activity.[2,7]

Sample Translation Technique. Despite the attributes cited above for noble metal-PDMS materials, problems with reproducibility and authenticity to literature spectra were encountered when these (and other) substrates were initially used. We came to the realization that photolytic alteration of both substrate and sample was the cause. It is possible to reduce photon density to reduce or eliminate these effects, but not without serious loss in signal. The solution was the development of a sample translation technique (STT) so that neither photon or analyte density is compromised in the measurement.[1] More authentic and reproducible spectra are observed with the STT, which is accomplished by rapidly spinning the sample, off-center, under the focused laser beam.[1-6] Under these conditions, the effective residence time of analyte/substrate within the irradiated zone is dramatically decreased without reducing spectral acquisition time or the density of analyte in the zone at any given time. Moreover, the translation tends to average out irregularities in the substrate.[1]

SERS in μ-Fluidics. With the discovery that Ag-PDMS is a viable, high performing SERS substrate, the next logical step was to move from the conventional capillary format[8] to chip-based μ-fluidic separations, since PDMS is one of the most common polymer-based chip materials. We recently reported the first combination of these emerging technologies.[9] Early CE-SERS work touted the lessening of some of the disadvantages of CE.[8] Specifically, the sensitive fingerprint nature of SERS spectra can serve to reduce problems with electroosmotic flow variations and co-elution of bands. Those limitations are even more pronounced for separations performed on polymer chips with short (hence small theoretical plate height count) channels. Figure 1 provides information from our first publication in this area.[9]

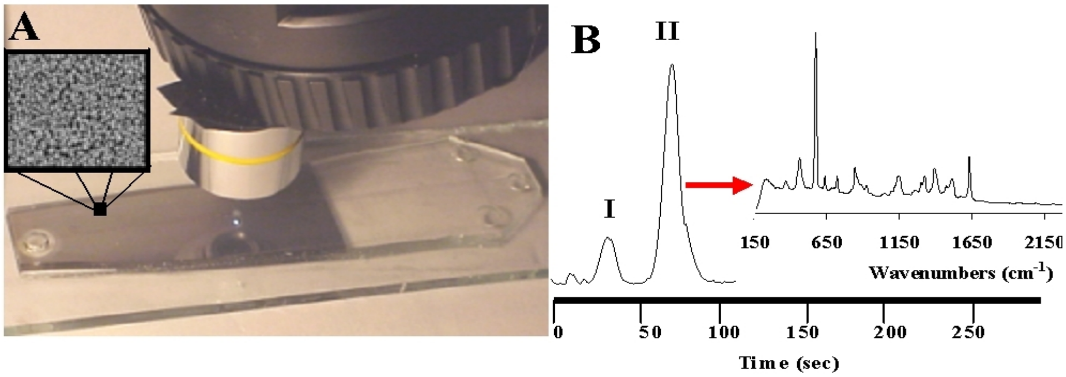


Figure 1. **(A)** - Photograph of PDMS μ-fluidic separation chip under the microscope objective of Raman spectrometer. The channel configuration is a simple 4-reservoir system with offset injection zone. Approximately 60% of the conformally sealed PDMS cover plate is actually Ag-PDMS nanocomposite. **(B)** - Real time LIF detection of a separation of Riboflavin (I) and Resorufin (II) at less than 1 μM injected. Post separation, the platform was interrogated using the spectrometer and the SERS spectrum of II is shown.

Specific Objectives for 2005-2006

Among our near term goals are two key specific objectives next year. *First*, we will employ e-beam lithography to create positive photoresist reliefs (~ 200 nm high nano-pillars) of various geometries (rectangles, ellipses, triangles, etc.) and with different inter-pillar morphologies (spacings). Silver and gold will be deposited onto the pillars as metallic pillows and the optical properties (including SERS activity) evaluated. The more promising nanostructures will be nano-imprinted (metal transferred) onto pliable polymer surfaces. The optimization of random morphology nanocomposites by physical manipulation of the underlying polymer has been demonstrated.[2,7] Determining the degree to which optimization can be improved when the structures are regular, geometrically-optimized, periodic lattices of metal nanoparticles is a key outcome of the first objective. *Second*, the channel architectures employed in initial μ-fluidic work will be optimized in terms of the materials and channel dimensions and STT implemented in some form.

Cited 2003-05 BES References

1. M.A. De Jesus, K. S. Giesfeldt, and M.J. Sepaniak, "The Development of a Substrate Translation Technique to minimize the Adverse Effect of Laser Irradiation Effects on Surface Enhanced Raman Scattering Spectra," *Appl. Spectrosc.*, **57**, 428-438 (**2003)**.

2. K.S. Giesfeldt, R.M. Connatser, N.V. Lavrik, P. Dutta, and M.J. Sepaniak, "Studies of the Optical Properties of Metal-Pliable Polymer Composite Materials," *Appl. Spectrosc*., **57,** 1346-1352 (**2003**).

3. M.A. De Jesus, K. S. Geisfeldt, and M.J. Sepaniak, "Improving the Analytical Figures of Merit of SERS in the Analysis of Model Environmental Pollutants," *J. Raman Spectro*., **35,** 895-904 (**2004**).

4. M.J. Sepaniak, M.A. DeJesus, and K.S. Giesfeldt, "Advances in Surface Enhanced Raman Spectroscopy for Phamaceutical Analysis," *Amer. Pharmaceutical Rev*., **Issue 3,** 90-97 **(2004)**.

5. M.A. DeJesus, K.S. Giesfeldt, and M.J. Sepaniak, "Factors Affecting the Sorption of Model Environmental Pollutants onto Silver-Polydimethylsiloxane nanocomposite Raman Substrates," *Appl. Spectrosc*., **58,** 1157-1164 **(2004)**.

6. K.S. Giesfeldt, R.M. Connatser, P. Dutta, and M.J. Sepaniak, "Studies of of Gold-Polydimethylsiloxane Nanocomposite as SERS Substrates for Biologically Relevant Analytes," *J. Raman Spectrsc*.., **submitted**.

7. R..J. Hinde, M.J. Sepaniak. R.N. Compton, N.V. Lavrik, and J. Nordling, "Surface Enhanced Raman Scattering Under Liquid Nitrogen," *Chem. Phys. Lett.*, **339**, 167 -173 (**2001**).

8. G.L. Devault and M.J. Sepaniak, "Spatially Focused Deposition of Electrophoresis Effluent Onto SERS Substrates for Off-Column Spectroscopy," *Electrophoresis*, **22**, 2303 -2311 **(2001)**.

9. R.M. Connatser, L.A. Riddle, and M.J. Sepaniak, "Metal-Polymer Nanocompsites for Integrated μFluidic Separations and SERS detection," *J. Sep. Sci***., 27,** 1545-1550 **(2004)**.

Soft X-ray Synchrotron Radiation Investigations of Actinide Materials

David K. Shuh

Actinide Chemistry Group, Chemical Sciences Division
The Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA
DKShuh@lbl.gov, www.lbl.gov/LBL-Programs/CSD/directory/

H. J. Nilsson (Postdoctoral Fellow), SKB, Stockholm, Sweden
P. Nachimuthu (Postdoctoral Fellow), D. Lindle, Dept. of Chemistry, UNLV, Las Vegas, NV
S. M. Butorin, L. Werme, J. A. Nordgren, Dept. of Physics, Uppsala University, Sweden
S. Thevuthasan, W. J. Weber, Pacific Northwest National Laboratory, Richland, WA
A. E. V. Gorden (Seaborg Postdoctoral Fellow), K. N. Raymond UCB/LBNL, Berkeley, CA

Overall research goals: Microspectroscopic and fluorescence-based techniques have been exploited for the initial investigations of actinide materials at sources of soft X-ray synchrotron radiation (SR) because of improved radiological safety infrastructure and the capability to perform experiments with small amounts of actinide materials. The research objectives are to elucidate and understand the roles of the 5f electrons in the chemical bonding of the actinides; characterization of the electronic structures of actinide materials; surface chemistry of actinide materials; and the optimization of soft X-ray SR techniques for actinide investigations. The fundamental knowledge gained from the investigations will have impact in areas of actinide science related to f-electron bonding, aging, corrosion, gas-solid interactions, actinide transport, and the development of nanoscale actinide materials characterization techniques.

Significant achievements in 2003-2005: The first soft X-ray SR resonant inelastic X-ray scattering (RIXS) investigations of a transuranic material, NpO_2, have been performed at the 5d edge. The chemical reaction of Np with Fe surfaces was characterized under the same conditions as in previous studies of U interactions with Fe surfaces. The oxidation state of the surface Np species was Np(V) since the RIXS loss features differed from those of NpO_2. These first Np measurements have been followed by recent measurements on PuO_2.

The Advanced Light Source Molecular Environmental Science (ALS-MES) Beamline 11.0.2 at LBNL has moved into full user operations. The ALS-MES scanning transmission X-ray microscope (STXM) has recently been developed as a tool for actinide investigations under ambient conditions. The ALS-MES STXM permits spectromicroscopy with a spatial resolution of 25 nm and NEXAFS with high energy resolution with an effective energy range of 130 eV to 2160 eV. Investigations of the common U oxides, Np, and Pu materials have yielded excellent images and reproducible NEXAFS charge state shifts at the actinide 4d $_{5/2}$ edge.

Disorder in $Gd_2Ti_2O_7$ pyrochlore has been investigated by near-edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy. NEXAFS shows Ti^{4+} ions occupy octahedral sites with a tetragonal distortion induced by vacant oxygen sites. O 1s XPS spectra obtained from $Gd_2Ti_2O_7$(100) yielded a single peak. There is no evidence for an anisotropic distribution of Ti and O. Thus, an earlier result confirming the direct observation of simultaneous cation–anion antisite disordering and lending credence to the split vacancy model has been clarified. Similarly, disorder in $Gd_2(Ti_{1-y}Zr_y)_2O_7$, for y=0.0-1.0, has been investigated As Zr substitutes for Ti, the tetragonal distortion decreases and Zr coordination increases from 6 to 8. This is evidence for simultaneous cation disorder with anion migration.

Specific objectives for 2005-2006: The RIXS studies will investigate the electronic structures of a PuO_2 single crystal, several Pu oxides, and Cm materials. The energy range of the ALS-MES STXM will be modified to encompass the actinide 5d edges (~100 eV). STXM experiments will examine the electronic structure of transuranic reference materials prior to initiating chemical reaction studies with actinide particulates. A comprehensive soft X-ray polarized x-ray emission/RIXS experiment will be initiated on a plutonyl molecule. The actinide structural and coordination collaboration with Raymond will be expanded and will begin to utilize hard X-ray absorption fine structure (XAFS). A new transuranic glove box for the preparation of actinide materials will be implemented in the main radiochemical laboratory to support the aforementioned programs.

References (2003-2005):

1. K. T. Moore, M. A. Wall, A. J. Schwartz, B. W. Chung, D. K. Shuh, R. K. Schulze, and J. G. Tobin, "The Failure of Russell-Saunders Coupling in the 5f States of Plutonium," Phys. Rev. Lett. **90**, 196064 (2003).
2. J. G. Tobin, B. W. Chung, G. D. Wadddill, R. K. Schulze, J. Terry, J. D. Farr, T. Zocco, D. K. Shuh, K. Heinzelman, E. Rotenberg, and G. Van der Laan, "Resonant Photoemission in f Electron Systems: Pu and Gd," Phys. Rev. B **68**, 155109 (2003).
3. J.-H. Guo, Y. Luo, A. Augustsson, S. Kashtanov, J.-E. Rubensson, D. Shuh, Hans Ågren, and J. Nordgren, "Molecular Structure of Alcohol-Water Mixtures," Phys. Rev. Lett. **91**, 157401 (2003).
4. K. E. Roberts, T. J. Wolery, C. E. A. Palmer, T. Prussin, P. G. Allen, J. J. Bucher, D. K. Shuh, R. Finch, and S. G. Prussin, "Precipitation of Crystalline Neptunium Dioxide from Near-neutral Aqueous Solution," Radiochim. Acta **91**, 87-92 (2003).
5. D. K. Shuh, S. M. Butorin, J.-H. Guo, and J. Nordgren, (2004), "Soft X-ray Synchrotron Radiation Investigations of Actinide Materials Systems Utilizing X-ray Emission Spectroscopy and Resonant Inelastic X-ray Scattering," Mater. Res. Soc. Symp. Proc. **802**, 131-136 (2004).
6. K. T. Moore, M. A. Wall, A. J. Schwartz, B. W. Chung, J. G. Tobin, D. K. Shuh, and R. K. Schulze, "Experimental Verification of the Need for Either *jj* or Intermediate Coupling in the 5*f* States of Plutonium," Mater. Res. Soc. Symp. Proc. **802**, 71-80 (2004).
7. P. Nachimuthu, S. Thevuthasan, M. H. Engelhard, W. J. Weber, D. K. Shuh, N. M. Hamdan, B. S. Mun, E. M. Adams, D. E. McCready, V. Shutthanandan, D. W. Lindle, G. Balakrishnan, D. M. Paul, E. M. Gullikson, R. C. C. Perera, J. Lian, L. M. Wang, and R. C. Ewing, (2004), "Probing Cation Antisite Disorder in $Gd_2Ti_2O_7$ Pyrochlore by Site-specific Near-edge X-ray Absorption Fine Structure and X-ray Photoelectron Spectroscopy," Phys. Rev. B **70**, 100101 (2004).
8. S. M. Butorin, D. K. Shuh, K. Kvashnina, I. Soroka, K. Ollila, J.-H. Guo, K. E. Roberts, L. Werme, and J. Nordgren, "Resonant Inelastic Soft X-ray Scattering Studies of U(VI) Reduction on Iron Surfaces," Mater. Res. Soc. Symp. Proc. **807**, 166-171 (2004).
9. T. Tyliszczak, T. Warwick, A. L. D. Kilcoyne, S. Fakra, D. K. Shuh, T. H. Yoon, G. E. Brown, Jr., S. Andrews, V. Chembrolu, J. Strachan, and Y. Acremann, "Soft X-ray Scanning Transmission Microscope Working in an Extended Energy Range at the Advanced Light Source," Synchrotron Radiation Instrumentation 2003, AIP Conference Proceedings **705**, 1356-1359 (2004).
10. T. Warwick, N. Andresen, J. Comins, P. J. McKean, D. K. Shuh, T. Stevens, and T. Tyliszczak, "New Implementation of an SX700 Undulator Beamline at the Advanced Light Source," Synchrotron Radiation Instrumentation 2003, AIP Conference Proceedings **705**, 458-461 (2004).
11. Z. Assefa, R. G. Haire, D. L. Caulder, and D. K. Shuh, "Correlation of the Oxidation state of Cerium in Sol-gel Glasses as a Function of Thermal Treatment via Optical Spectroscopy and XANES Studies," Spectrochimica Acta Part A **60**, 1873-1881 (2004).
12. P. Nachimuthu, S. Thevuthasan, V. Shutthanandan, E. M. Adams, W. J. Weber, B. D. Begg, D. K. Shuh, D. W. Lindle, E. M. Gullikson, and R. C. C. Perera, "The Impact of Au^{2+} Ion Beam Irradiation on the Structural and Electronic Properties of $Gd_2(Ti_{1-y}Zr_y)_2O_7$ Pyrochlores: Ti 2p and O 1s NEXAFS Study," J. Appl. Phys. **97**, 033518 (2005).
13. P. Nachimuthu, S. Thevuthasan, E. M. Adams, B. S. Mun, W. J. Weber, B. D. Begg, D. K. Shuh, D. W. Lindle, E. M. Gullikson, and R. C. C. Perera, "Effect of Zr Substitution for Ti in $Gd_2Ti_2O_7$ Pyrochlore: Ti 2p and O 1s NEXAFS Study," J. Phys. Chem. *B* **109**, 1337-1339 (2005).
14. A. E. V. Gorden, D. K. Shuh, B. E. Tiedeman, R. E. Wilson, A. G. Oliver, J. Xu, and K. N. Raymond, "Sequestered Plutonium: $[Pu^{IV}\{5LIO(Me\text{-}3,2\text{-}HOPO)\}_2]$ -The First Structurally Characterized Plutonium Hydroxipyridonate Complex," Chem. Eur. J. **11**, 1-8 (2005).

Oral Session 6:

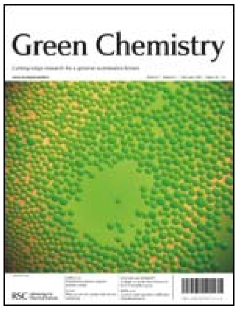
Polymers, Solutions, Thermodynamics

DE-FG02-96ER14673 - Alternative (Potentially Green) Separations Media: Aqueous Biphasic and Related Systems - Extending the Frontier

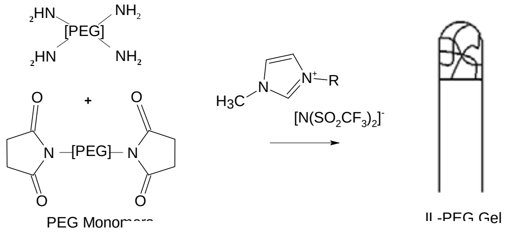
Prof. Robin D. Rogers, Dr. Jonathan G. Huddleston, Dr. Scott K. Spear, Dr. Ji Chen, Dr. Scott T. Griffin, Marc A. Klingshirn, Melanie L. Moody, Nicholas J. Bridges, and Meghna Dilip
Center for Green Manufacturing and Department of Chemistry
The University of Alabama, Tuscaloosa, AL 35401
[RDRogers@bama.ua.edu; http://bama.ua.edu/~rdrogers; http://bama.ua.edu/~cgm]

Overall Research Goals: The goals of this research are to gain a fundamental, molecular level understanding of the critical phase separation of aqueous polymer solutions, and to develop a similar understanding of their application as novel solvent systems. The wholly aqueous nature of these systems represents an opportunity to develop liquid-liquid systems for separations and as novel reaction media representing both a safer and a "greener" approach to technologies that typically rely heavily on the use of organic solvents.

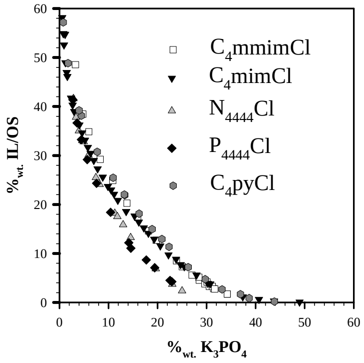
Significant Achievements in 2003-2005: *ABS as Solvents and ABRE:* Our review of this field was recently featured on the cover of *Green Chemistry*.[1] We have developed aqueous biphasic systems (ABS) as novel reaction media for Aqueous Biphasic Reactive Extraction (ABRE) as demonstrated for the synthesis of adipic acid from cyclohexene,[2] as well as, glutaric acid from cyclopentene.[3] Other oxidations of this type have relied on the use of phase transfer catalysts, which are costly and difficult to recover, however, polyethylene glycol (PEG)-rich phases can serve as phase transfer catalyst, reaction solvent, and provide the reaction driving force all at the same time.



PEG Gels: The solution properties of a free-standing PEG hydrogels constructed from the reaction of functionalized PEG monomers has been studied with[4] and without[5] inclusion of conductive ionic liquids (ILs). This is the first time that a cross-linked PEG matrix, like this, has been used to gel non-aqueous solvents.



Salt-Salt ABS: We are continuing our study of ABS produced by salting out numerous classes of ILs[6] and exploiting these new ABS for separations.[7] The mutual coexistence curves for the several ionic liquids/salt ABS show biphasic systems can be formed for almost all ILs with a variety of simple salts.



Specific Objectives for 2005-2006: *Understanding Solvent Properties of Salt-Salt ABS:* We will further our understanding of the salt/salt systems and characterize their solvent properties and linear free energy relationships.

Temperature Effects on Distribution in ABS and ABEC: We will probe the differences between ABS based on PEG and ABEC® resins having PEG attached to a polystyrene divinylbenzene backbone. We will further explore the affects of PEG support by direct comparison of liquid/liquid ABS, ABEC resins, and PEG gels. Specifically we will determine why the affect of temperature on uptake to these systems is opposite for unsupported vs. supported PEG.

Effect of Organics on Distribution of Environmentally-Relevant Ions: The effect of environmental parameters on partitioning to ABS, ABEC, and PEG gels will be examined, including studies of ground water. The specific interferences (e.g., humic acids) present in the environment will be studied.

<u>*Uptake of Dyes using ABS, ABEC resins, and PEG Gels:*</u> The uptake of several classes of dye molecules will be studied to differentiate the specific contributions of molecular size and shape, intermolecular interactions, and charge effects to observed partitioning behavior, allowing a molecular level understanding of dye purification, delivery, and removal.

<u>References to Work Supported by This Project (2003-2005):</u>

1. Chen, J.; Spear, S. K.; Huddleston, J. G.; Rogers, R. D. "Polyethylene Glycol and Solutions of Polyethylene Glycol as Green Reaction Media," *Green Chem.* **2005**, *7*, 64-82. [Cover Article]
2. Chen, J.; Spear, S.K.; Huddleston, J.G.; Holbrey, J.D.; Swatloski, R.P.; Rogers, R.D. "The application of polyethylene glycol-based aqueous biphasic systems as reaction and reactive extraction media," *Ind. Eng. Chem. Res.* **2004**, *43*, 5358-5364.
3. Chen, J.; Spear, S.K.; Huddleston, J.G.; Holbrey, J.D.; Rogers, R.D. " Application of polyethylene glycol-based aqueous biphasic reactive extraction to the catalytic oxidation of cyclic olefins," *J. Chromatography B.* **2004**, *807*, 145-149.
4. Huddleston, J. G.; Looney, T. K.; Broker, G. A.; Griffin, S. T.; Spear, S. K.; Rogers, R.D. "Comparative Behavior of Poly(ethylene glycol) Hydrogels and Poly(ethylene glycol) Aqueous Biphasic Systems," *Ind. Eng. Chem. Res.* **2003**, 42, 6088-6095.
5. Klingshirn, M. A.; Spear, S. K.; Subramanian, R.; Holbrey, J. D.; Huddleston, J. G.; Rogers, R. D. "Gellation of ionic liquids using a cross-linked poly(ethylene) glycol gel matrix," *Chem. Mater.* **2004**, *16*, 3091-3097.
6. Gutowski, K. E.; Broker, G. A.; Willauer, H. D.; Huddleston, J. G.; Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. "Controlling the Aqueous Miscibility of Ionic Liquids: Aqueous Biphasic Systems of Water-Miscible Ionic Liquids and Water-Structuring Salts for Recycle, Metathesis, and Separations," *J. Am. Chem. Soc.* **2003,** 125, 6632-6633.
7. Rogers, R. D.; Gutowski, K. E.; Griffin, S. T.; Holbrey, J. D. "Aqueous biphasic systems based on salting-out polyethylene glycol or ionic liquid solutions: strategies for actinide or fission product separations," Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry **2004**, *44*, 403-407.
8. Abraham, M.H.; Zissimos, A.M.; Huddleston, J. G.; Willauer, H. D.; Rogers, R. D.; Acree, W. E. Jr. "Some Novel Liquid Partitioning Systems: Water-Ionic Liquids and Aqueous Biphasic Systems," *Ind. Eng. Chem. Res.* **2003**, 42, 413-418.
9. Huddleston, J. G.; Willauer, H.D.; Rogers, R.D. "Phase Diagram Data for Several PEG+Salt Aqueous Biphasic Systems at 25°C," *J. Chem. Eng. Data,* **2003**, 48, 1230-1236.
10. Griffin, S. T. (Ph.D.-UA, 2003), "The Development and Applications of ABEC Resins."
11. Griffin, S. T.; Spear, S. K.; Rogers, R.D. "Effects of Speciation on Partitioning of Iodine in Aqueous Biphasic Systems and onto ABEC® Resins," *J. Chromatography B.* **2004**, *807*, 151-156.
12. Katritzky, A. R.; Tämm, Kaido, Kuanar, M.; Fara, D. C.; Oliferenko, A.; Oliferenko, P.; Huddleston, J. G.; Rogers, R. D. "Aqueous Biphasic Systems. Partitioning of Organic Molecules: A QSPR Treatment," *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 136-142.
13. Huddleston, J. G.; Willauer, H. D.; Burney, M. T.; Tate, L. J.; Carruth, A. D.; Rogers, R. D. "Comparison of an empirical and a theoretical linear salvation energy relationship applied to the characterization of solute distribution in a poly(ethylene) glycol-salt aqueous biphasic system," *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 549-558.
14. Holbrey, J. D.; Chen, J.; Turner, M. B.; Swatloski, R. P.; Spear, S. K.; Rogers, R. D. "Applying ionic liquid solvent characteristics for controlled processing of polymer materials," *Polymer Preprints* (American Chemical Society, Division of Polymer Chemistry) **2004**, *45*, 297-298.
15. Klingshirn, M. A.; Spear, S. K.; Subramanian, R.; Holbrey, J. D.; Rogers, R. D. "Synthesis, characterization, and application of ionic liquid-poly(ethylene) glycol gel matrices," *Polymer Preprints* (American Chemical Society, Division of Polymer Chemistry) **2004**, *45*, 307-308.
16. Oliferenko, A. A.; Oliferenko, P. V.; Huddleston, J. G.; Rogers, R. D.; Palyulin, V. A.; Zefirov, N. S.; Katritzky, A. R. "Theoretical Scales of Hydrogen Bond Acidity and Basicity for Application in QSAR/QSPR Studies and Drug Design. Partitioning of Aliphatic Compounds," *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 1042-1055
17. Moody, M. L.; Willauer, H. D.; Griffin, S. T.; Huddleston, J. G.; Rogers, R. D. "Solvent property characterization of polyethylene glycol and dextran aqueous biphasic systems using the free energy of transfer of a methylene group and a linear solvation energy relationship," *Ind. Eng. Chem. Res.* **2005**, In Press.

Fundamentals of Electric Field-Enhanced Multiphase Separations and Analysis

Osman A. Basaran
School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907-2100
obasaran@ecn.purdue.edu

Overall research goals: Drop breakup, which is a phenomenon of everyday occurrence as in dripping of faucets and shattering of rain drops upon impact with a solid surface, has unparalleled beauty and richness and is of immense technological importance. Indeed, in the absence as well as the presence of electric fields, drop breakup plays a central role in applications as diverse as separations, ink jet printing, DNA and protein microarraying, and manufacture of micro- and nano-particles and capsules. It is not an exaggeration to say that the formation of drops from nozzles lies at the heart of many emerging MEMS and NEMS applications. Theoretical, computational, and experimental analysis of drop formation is challenging because the phenomenon entails occurrence of finite time singularities. Therefore, a major objective of this research program is to study through theoretical, computational, and experimental means the physics of interface rupture in single-fluid, e.g. a drop forming in air, and two-fluid, e.g. a drop forming in another liquid, systems in the absence and presence of electric fields. A long-term goal of this research is to exploit the fundamental understanding gained through the aforementioned studies to improve the efficiency of electroseparations and advance the science of microencapsulation processes among others.

Significant achievements in 2003-2005: We have made a number of significant discoveries in this period on pinch-off and scaling behavior during interface rupture. Perhaps the most exciting of these discoveries concerns the pinch-off of a low-viscosity drop inside a more viscous fluid, as when air bubbles entrained in syrup or honey rise and breakup. We have shown (Doshi et al. 2003) through experiment, computation, and theory that the breakup under conditions in which the interior viscosity can be neglected gives rise to an exceptional form of singularity. In contrast to previous studies of drop breakup, universality is violated in this case so that the drop shape at breakup retains a memory of the initial and boundary conditions. We have further shown that a finite interior viscosity, no matter how small, cuts off this form of singularity and produces an unexpectedly long and slender thread. If the exterior viscosity is large enough, however, the cutoff does not occur because the minimum radius of the drop reaches subatomic dimensions before the effect of the interior viscosity is felt. For example, a 1-cm drop of 0.2-poise in a surrounding fluid of 2×10^5 poise can break to create a thread of radius less than 100 nm. Thus, it should be possible to manufacture thin solid threads by exploiting this scientific discovery.

Fascinating dynamics results when the flow rate Q at which water drips from a faucet is varied. Starting with simple (period-1) dripping, the system transitions as Q increases to complex dripping, where it exhibits period-n (n=2, 4, …) and chaotic responses, and then jets once Q exceeds a threshold. We have shown by new experiments and simulations (Ambravaneswaran et al. 2004) that high viscosity (μ) liquids, e.g. syrup, transition directly from simple dripping to jetting as Q increases. We have developed phase diagrams showing transitions between simple and complex dripping and jetting in (Q,μ)-space. Values of Q for transition from dripping to jetting are estimated from scaling arguments and shown to accord well with simulations.

We have discovered a new method for making microcapsules that consists of colliding two microscopic drops in air and causing one drop to surround completely the other drop (Yeo et al. 2003). Various extensions of this discovery are now underway.

Specific objectives for 2005-2006: We are continuing our fundamental studies of interface pinch-off to improve the understanding of surfactant, polymer, and electric field effects. As further evidence of the impact of our work in this area, it is noteworthy to mention that the PI, O. A. Basaran, has been invited to give a plenary lecture on electroseparations at the upcoming meeting of the ESA (Electrostatics Society of America). We also plan on performing computational and experimental studies to gain insights into the fluid physics of two-fluid breakup. We expect that such studies will have broad impact in the science of micro- and nano-encapsulation.

(Selected) References

1. Doshi, P., Cohen, I., Zhang, W. W., Siegel, M., Howell, P., Basaran, O. A., and Nagel, S. R. 2003 Persistence of memory in drop breakup: the breakdown of universality. *Science* **302**, 1185-1189.
2. Yeo, Y., Chen, A. U., Basaran, O. A., and Park, K. 2003 Microencapsulation of drugs by solvent exchange. U.S. Patent No. 6,599,627 B2, July 29, 2003.
3. Liao, Y. C., Franses, E. I, and Basaran, O. A. 2003 Computation of dynamic adsorption with adaptive integral, finite difference, and finite element methods. *J. Colloid Interface Sci.* **258**, 310-321.
4. Doshi, P., Suryo, R., Yildirim, O. E., McKinley, G. H., and Basaran, O. A. 2003 Scaling in pinch-off of generalized Newtonian fluids. *J. Non-Newtonian Fluid Mech.* **113**, 1-27.
5. Liao, Y. C., Basaran, O. A., and Franses, E. I. 2003 Micellar dissolution and diffusion effects on adsorption dynamics of surfactants. *AIChE J.* **49**, 3229-3240.
6. Doshi, P. and Basaran, O. A. 2004 Self-similar pinch-off of power law fluids. *Phys. Fluids.* **16**, 585-593.
7. Ambravaneswaran, B., Subramani, H. J., Phillips, S. D., and Basaran, O. A. 2004 Dripping-jetting transitions in a dripping faucet. *Phys. Rev. Lett.* **93**, 034501.
8. Notz, P. K. and Basaran, O. A. 2004 Dynamics and breakup of a contracting liquid filament. *J. Fluid Mech.* **512**, 223-256.
9. Yeo, Y., Chen, A. U., Basaran, O. A., and Park, K. 2004 Solvent exchange method: a novel microencapsulation technique using dual microdispensers. *Phar. Res.* **21**, 1419-1427.
10. Suryo, R., Doshi, P., and Basaran, O. A. 2004 Non-self-similar, linear dynamics during pinch-off of a hollow annular jet. *Phys. Fluids.* **16**, 4177-4184.
11. Liao, Y.-C., Subramani, H., Franses, E. I., and Basaran, O. A. 2004 Effects of soluble surfactants on the deformation and breakup of stretching liquid bridges. *Langmuir.* **20**, 9926-9930.
12. Liao, Y.-C., Basaran, O. A., and Franses, E. I. 2004 Hydrodynamic effects on the oscillations of supported bubbles: implications for accurate measurements of surface properties. *Colloids Surf. A* **250**, 367-384.
13. Yildirim, O. E., Xu, Q., and Basaran, O. A. Analysis of the drop weight method. Submitted to *Phys. Fluids*.
14. Suryo, R., Doshi, P., and Basaran, O. A. Nonlinear dynamics and breakup of compound jets. Submitted to *Phys. Fluids.*

O6-3

Actinide Solution Chemistry:
Chemical Thermodynamics and Structure of Actinide Complexes in Solution

Linfeng Rao
Guoxin Tian, Thandankorai G. Srinivasan
Lawrence Berkeley National Laboratory
lrao@lbl.gov

Collaborators: PierLuigi Zanonato and Plinio Di Bernardo, University of Padova, Italy

Overall research goals: To measure the thermodynamic properties of actinide complexes in solution and improve the fundamental understanding of the thermodynamic principles governing the chemical behavior of actinides in solution.

Significant achievements in 2003-2005

Hydrolysis of U(VI) and Np(V) at 10 – 85 ^oC. Studies on the hydrolysis of U(VI) and Np(V) at 10 - 85 ^oC have been completed and the results published. In general, the hydrolysis constants of U(VI) and Np(V) increase by up to a few orders of magnitude as the temperature was increased from 10 to 85 ^oC (Fig.1 and Fig.2). The enhancement of hydrolysis at elevated temperatures is mainly due to the significant increase of the degree of ionization of water as the temperature is increased. Approximation approaches to predict the effect of temperature were tested with these data.

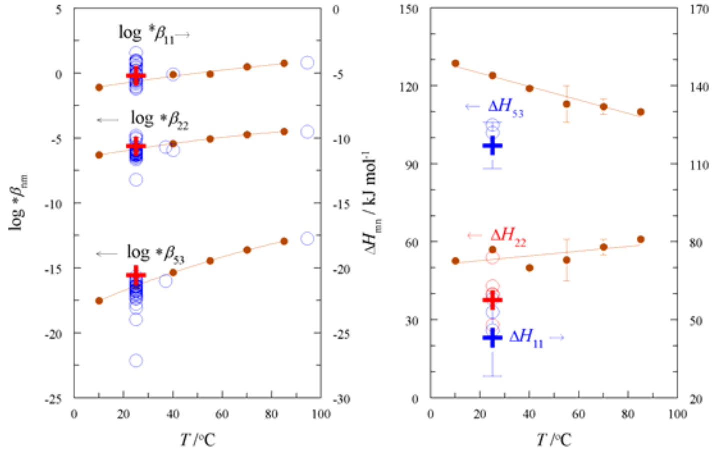


Fig. 1. Hydrolysis of U(VI). (●) Our data, I = 0.10 mol dm^{-3} $(C_2H_5)_4NClO_4$. Experimental (O) and recommended (+) data in the literature.

Complexation of actinides with carboxylates at elevated temperatures. Several systems have been studied from 10 to 85 ^oC, covering four oxidation states of actinides (III, IV, V and VI) and ligands with different denticity and donor atoms. In general, the results indicate that the complexes become stronger by 1-2 orders of magnitude when the temperature is increased from 10 to 85 ^oC. The enhancement in the stability is mainly due to the increasingly larger entropy of complexation that exceeds the increase in the unfavorable enthalpy of complexation when the temperature is elevated. The trends in the enthalpy and entropy are related to the change

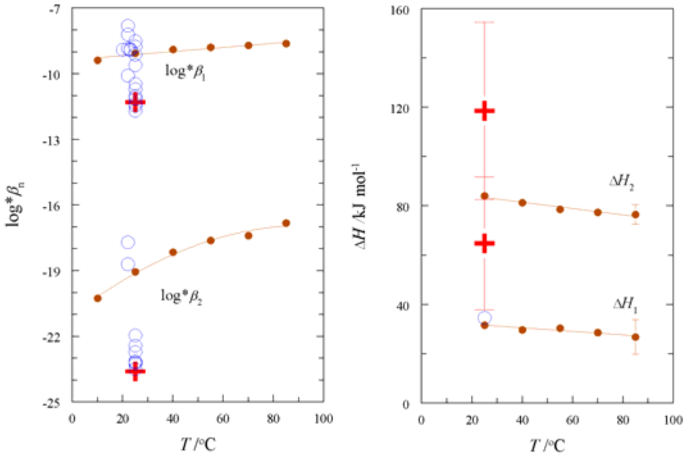


Fig. 2. Hydrolysis of Np(V). (●) Our data, I = 1.0 mol dm^{-3} $(C_2H_5)_4NCl$. Experimental (O) and recommended (+) data in the literature.

in the structure of water as the temperature is elevated.

Actinide complexation with dithiophosphinic acids (DTP) and amides. Complexes of actinides and lanthanides with DTP were characterized by EXAFS and IR. Thermodynamic, spectroscopic and structural properties of the amide complexes were studied. A single crystal structure of the 1:2 Np(V)/tetramethyl-3-oxa-glutaramide (TMOGA) complex (Fig.3) was determined by using the Beam Line for Small-Molecule X-Ray Crystallography at the Advanced Light Source at LBNL. The center-symmetric structure supports the observation by Near-IR absorption spectroscopy that the *f-f* transition of Np(V) in this complex is forbidden probably because it is highly symmetric with an inversion center.

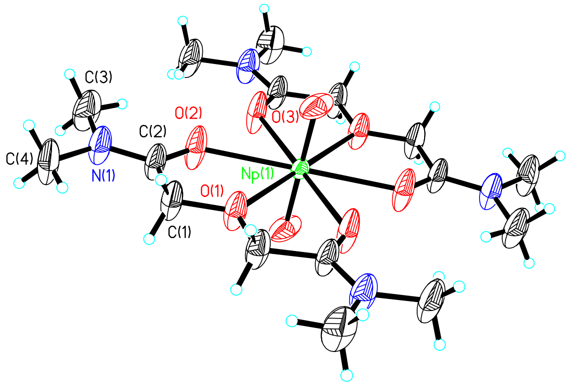


Fig.3. ORTEP of the 1:2 Np(V)/TMOGA complex.

Specific objectives for 2005-2006

- To study the complexation of Np(V) with oxalate, oxydiacetate (ODA), thiodiacetate (TDA) and iminodiacetate (IDA), U(VI) with oxalate, TDA and IDA at elevated temperatures.
- To study the hydrolysis of Th(IV) and Pu(VI) at elevated temperatures.
- To conduct further experimental and computational studies on the complexation of An(III) and Ln(III) with dithiophosphinic acids.
- To determine the thermodynamic, spectroscopic and structural properties of actinide complexes with a series of related amides in solution.

References of work that were supported by this project

1. T. G. Srinivasan, P. Zanonato, P. Di Bernardo, A. Bismondo, L. Rao, “Complexation of Thorium(IV) with Malonate at Variable Temperatures,” *J. Alloys and Compounds*, accepted (2005).
2. L. Rao, T. G. Srinivasan, A. Yu. Garnov, P. Zanonato, P. Di Bernardo, A. Bismondo, “Hydrolysis of Neptunium(V) at Variable temperatures (10 - 85 ^{o}C),” *Geochim. Cosmochim. Acta*, 68, 4821-4830 (2004).
3. P. Zanonato, P. Di Bernardo, A. Bismondo, G. Liu, X. Chen, L. Rao, “Hydrolysis of Uranium(VI) at variable temperatures (10 - 85 ^{o}C),” *J. Am. Chem. Soc*. 126, 5515-5522 (2004).
4. L. Rao, Z. C. Zhang, P. Zanonato, P. Di Bernardo, A. Bismondo, S. B. Clark, “Complexation of Thorium(IV) with Acetate at Variable Temperatures,” *J. Chem. Soc. Dalton Trans*. 2867-2872 (2004).
5. X. Y. Chen, L. Rao, G. K. Liu, “On the Physical Nature of Uranyl Charge Transfer Vibronic Interactions,” *Mat. Res. Soc. Symp. Proc*. Vol. 802, DD4.6.1-DD4.6.6 (2004).
6. G. Tian, T. Kimura, Z. Yoshida, Y. Zhu, L. Rao, “Fluorescence and IR studies on the hydration state of lanthanides(III) and curium(III) in the complexes extracted with purified Cyanex301, Cyanex302 and Cyanex272,” *Radiochim. Acta*, 92, 495-499 (2004).
7. L. Rao, A. Yu. Garnov, J. Jiang, P. Di Bernardo, P. Zanonato, A. Bismondo, “Complexation of Uranium(VI) and Samarium(III) with Oxydiacetic Acid: Temperature Effect and Coordination Modes,” *Inorg. Chem*. 42 (11), 3685-3692 (2003).
8. A. Bismondo, P. Di Bernardo, P. Zanonato, J. Jiang, L. Rao, “Complexation of Thorium(IV) with 2-Furoic Acid and 2-Thenoic Acid in Aqueous Solution,” *J. Chem. Soc. Dalton Trans*., 469-474 (2003).

Probing Metal-Ligand Interactions with Neoteric Solvent Systems

Mark L. Dietz, Mark R. Antonio, Mark P. Jensen, Paul G. Rickert, Julie A. Dzielawa and Dominique C. Stepinski
mdietz@anl.gov
Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

Collaborators: Millicent A. Firestone, Larry A. Curtiss, and Peter Zapol, Materials Science Division, ANL; Sönke Seifert, Advanced Photon Source Division, ANL.

Overall research goals: In general terms, our research program seeks an improved understanding of the nature of the atomic-scale interactions between metal atoms/ions and ligands and the changes in them brought about by physical or chemical transformations, with the ultimate objective of controlling their strength and selectivity. To this end, the effects of solvation and redox activity on metal-ligand interactions in both conventional and "neoteric" media are explored. In these studies, it is our objective to determine the relative importance of metal-ligand bonding and metal-solvent, ligand-solvent, complex-solvent, and solvent-solvent interactions in influencing metal-ligand equilibria.

Significant achievements in 2003-2005: In prior work under this program,[1] we showed that the transfer of Sr^{2+} from aqueous nitrate solution into the ionic liquid (IL) 1-pentyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($C_5mim^+Tf_2N^-$) containing a crown ether (CE) proceeds *via* exchange of the cationic 1:1 strontium:CE complex for the cationic component of the IL. Such behavior contrasts with that of conventional solvents, for which simple partitioning of a neutral strontium nitrato-crown ether complex is observed. Because such a transfer mechanism has significant negative implications for the "greenness" of ionic liquids as solvents in the L-L extraction of metal ions, we have sought means to inhibit ion exchange as a mode of strontium transfer. Recently, we have shown that the predominant mode of strontium ion transfer shifts from cation-exchange to conventional nitrato complex partitioning as the IL cation hydrophobicity is increased.[2,3] This shift is accompanied by a significant decrease in the efficiency of strontium extraction under a given set of conditions, however, thus diminishing a significant advantage of ILs as extraction solvents over ordinary molecular diluents. In an effort to overcome this difficulty, we have begun a systematic study of synergistic effects, in which a pair of extractants is employed to obtain extraction efficiencies not achievable with either extractant alone, in ILs.[4] Unexpectedly, this work has shown that the extraction of strontium from acidic nitrate media into various 1-alkyl-3-methylimidazolium salts by dicyclohexano-18-crown-6 is enhanced by addition of tri-*n*-butylphosphate (TBP). The magnitude of the synergistic effect is, in fact, both much greater than that observed in conventional, polar diluents and readily correlated with the hydrophobicity of the IL cation. In related work, we have shown that $C_4mim^+Tf_2N^-$ behaves as a liquid *anion* exchanger in the extraction of lanthanides by 2-thenoyl-trifluoroacetone (Htta).[5] That is, in contrast to non-polar molecular solvents (*e.g.,* xylene or chloroform) into which hydrated, neutral complexes, $M(tta)_3(H_2O)_n$ (n = 2 or 3) are extracted, europium and neodymium are extracted into the ionic liquid as anionic $M(tta)_4^-$

complexes with no water coordinated to the metal center. The presence of anionic lanthanide complexes in the IL is made possible by the exchange of IL anions into the aqueous phase for the lanthanide complex. Finally, building on our earlier work in this program demonstrating that addition of an appropriate concentration of water to certain ionic liquids can trigger their self-assembly and conversion to a rigid gel,[6] we have employed infrared and NMR spectroscopy to establish the probable mechanism of gelation and X-ray scattering to determine the relationship of the nature of the IL anion and the water content of a gel to its mesoscopic structure.[7]

Specific objectives for 2005-2006: Our investigations of synergistic interactions between extractants in ionic liquids and their influence on metal ion partitioning in these novel solvents will be continued, as will our systematic examination of the physicochemical properties of IL-based gels and their relationship to IL characteristics.

References:

1. M. L. Dietz, M. P. Jensen, J. V. Beitz, J. A. Dzielawa, "Room-temperature ionic liquids as diluents for the liquid-liquid extraction of metal ions: Promise and limitations", in *Hydrometallurgy 2003, Volume 1: Leaching and solution purification*, C. A. Young, A. M. Alfantazi, C. G. Anderson, D. B. Dreisinger, B. Harris, and A. James (Eds.), TMS, New York, 2003, pp. 929-939.
2. M. L. Dietz, J. A. Dzielawa, I. Laszak, B. A. Young, and M. P. Jensen, "Influence of solvent structural variations on the mechanism of facilitated ion transfer into room-temperature ionic liquids", *Green Chem*. **5**, 682-685 (2003).
3. M. L. Dietz, J. A. Dzielawa, M. P. Jensen, J. V. Beitz, M. Borkowski, "The road to partition: Mechanisms of metal ion transfer into ionic liquids (ILs), and their implications for the application of ILs as extraction solvents", in *Ionic liquids IV: Fundamentals, progress, challenges and opportunities*, R. D. Rogers and K. R. Seddon (Eds.), ACS, Washington, DC, 2005 (in press).
4. D. C. Stepinski, M. P. Jensen, J. A. Dzielawa, M. L. Dietz, "Synergistic effects in the facilitated transfer of metal ions into room-temperature ionic liquids", *Green Chem*. **7**, 151-158 (2005).
5. M. P. Jensen, J. Neuefeind, J. V. Beitz, S. Skanthakumar, L. Soderholm, "Mechanisms of metal ion transfer into room-temperature ionic liquids: The role of anion exchange", *J. Am. Chem. Soc*. **125**, 15466-15473 (2003).
6. M. A. Firestone, J. A. Dzielawa, P. Zapol, L. A. Curtiss, S. Seifert, M. L. Dietz, "Lyotropic liquid-crystalline gel formation in a room-temperature ionic liquid", *Langmuir* **18**, 7258-7260 (2002).
7. M. A. Firestone, P. G. Rickert, S. Seifert, M. L. Dietz, "Anion effects on ionogel formation in N,N'-dialkylimidazolium-based ionic liquids", *Inorg. Chim. Acta* **357**, 3991-3998 (2004).

Organization of Solutes in Solvent Extraction

Renato Chiarizia, M. P. Jensen, J. R. Ferraro, P. G. Rickert, D. Stepinski, M. R. Antonio
Chemistry Division, Argonne National Laboratory, Argonne, Illinois
e-mail: chiarizia@anl.gov

Collaborators: P. Thiyagarajan and K. C. Littrell (IPNS Division, ANL); M. Borkowski (Carlsbad Operations, LANL), K. L. Nash (Washington State University), A. W. Herlinger (Loyola University, Chicago)

Overall research goals:

The general objective of this research is to develop a molecular- and supramolecular-level understanding of the interactions and forces that drive and limit the aggregation of solutes. Our emphasis is on self-assembly processes in which solute molecules interact with each other, possibly leading to formation of new phases. Third phase formation in solvent extraction, a generally unwanted and potentially hazardous phenomenon, is the present main focus of our research, because a comprehensive description of its mechanism and energetics is still lacking.

Significant achievements in 2003-2005:

We have investigated third phase formation in the extraction of $UO_2(NO_3)_2$, $Th(NO_3)_4$ and $Zr(NO_3)_4$ by tri-*n*-butyl phosphate (TBP) in *n*-alkane diluents (1-7), and the aggregation phenomena taking place in the extraction of trivalent f-elements cations by a tetraalkyldiglycolamide (8), by using distribution and small-angle neutron scattering (SANS) measurements. Our SANS data were interpreted with a model based on particle interactions. To calculate the short-range interactions between particles, the Baxter model for hard spheres with surface adhesion (aka the "sticky spheres" model) (9) was used. This model allows the calculation of the energy of interaction between small reverse micelles assumed as incompressible spheres.

In all systems investigated, the application of the Baxter model to our SANS data provided a mechanistic explanation for third phase formation (3-7): TBP at high concentrations in *n*-alkanes, in contact with aqueous phases containing nitric acid and uranyl, thorium or zirconium nitrates, forms small reverse micelles containing up to four TBP molecules. Water, nitric acid and metal nitrates are incorporated into the polar core of the micelles and these interact through van der Waals forces between their polar cores. The TBP micelles are subjected to two contrasting physical forces. On one hand, the thermal energy (k_BT, where k_B = Boltzmann constant) keeps the micelles dispersed in the diluent; on the other hand, the energy of intermicellar attraction makes the micelles stick together. As long as these two energies are comparable, the organic phase is stable. The separation of most of the solute particles in a new phase takes place when the energy of attraction between the particles in solution becomes about twice the average thermal energy k_BT. Upon phase splitting, most of the solutes in the original organic phase (TBP, water, HNO_3 and metal nitrates) collect in a separate and denser third phase containing interspersed layers or pockets of *n*-alkane.

By creating third phases using different metal ions having a wide range of charge/radius ratios, such as UO_2^{+2}, Zr^{+4} and Th^{+4}, we were able to rationalize the effect of the metal cation on third phase formation. The critical energy of attraction of about 2 k_BT was reached more readily for cations possessing a higher hydration enthalpy (6).

Specific objectives for 2005-2006:
Our future program consists in testing the generality of the intermicellar interaction model by investigating third phase formation in systems involving: 1) mineral acids with different hydration properties of the anion (NO_3^-, Cl^-, ClO_4^-, HSO_4^-, $H_2PO_4^-$); 2) extractants with different basicities of the donor groups (phosphates vs. phosphonates vs. phosphine oxides); 3) extractants with different alkyl groups (straight vs. branched); 4) multidentate extractants (i.e., of the carbamoylphosphine oxide (CMPO) type).

We plan to extend our studies on solute organization to polyoxometalate (POM) solutions. Through use of small-angle X-ray scattering (SAXS) and other techniques, we intend to obtain information on the effect of solvent, countercation and redox factors on the short- and intermediate-range fluid structures of POMs.

References of work supported by this project
1. Chiarizia, R.; Jensen, M. P.; Borkowski, M.; Ferraro, J. R.; Thiyagarajan, P; Littrell, K. C. (2003), SANS Study of Third Phase Formation in the U(VI), HNO_3 / TBP, *n*-Dodecane System. *Sep. Sci. Technol.,* **38**, 3313-3331.
2. Borkowski, M.; Chiarizia, R.; Jensen, M. P.; Ferraro, J. R.; Thiyagarajan, P; Littrell, K. C. (2003), SANS Study of Third Phase Formation in the Th(IV), HNO_3 / TBP, *n*-Octane System. *Sep. Sci. Technol.,* **38**, 3333-3351.
3. R. Chiarizia, M.P. Jensen, M. Borkowski, J.R. Ferraro, P. Thiyagarajan and K.C. Littrell (2003), Third Phase Formation Revisited: The U(VI), HNO_3-TBP, *n*-Dodecane System, *Solv. Extr. Ion Exch.,* **21**, 1-27.
4. Chiarizia, R.; Nash, K. L.; Jensen, M. P.; Thiyagarajan, P; Littrell, K. C. (2003), Application of the Baxter Model for Hard-Spheres with Surface Adhesion to SANS Data for the U(VI) - HNO_3 / TBP, *n*-Dodecane System. *Langmuir,* **19**, 9592-9599.
5. Chiarizia, R.; Jensen, M. P.; Borkowski, M.; Thiyagarajan, P.; Littrell, K. C. (2004), Interpretation of Third Phase Formation in the Th(IV) - HNO_3, TBP - *n*-Octane System with Baxter's "Sticky Spheres" Model. *Solvent Extr. Ion Exch.* **22,** 1-27.
6. Chiarizia, R.; Jensen, M. P.; Rickert, P. G.; Kolarik, Z.; Borkowski, M.; Thiyagarajan, P. (2004), Extraction of Zirconium Nitrate by TBP in *n*-Octane: Influence of Cation Type on Third Phase Formation According to the "Sticky Spheres" Model. *Langmuir,* **20**, 10798-10808.
7. Chiarizia, R.; Jensen, M. P.; Borkowski, M.; Nash K. L. (2005), A New Interpretation of Third Phase Formation in the Solvent Extraction of Actinides by TBP. In *Separations for the Nuclear Fuel Cycle in the 21th Century,* Lumetta, G. J., Nash, K. L., Clark, S. B., Friese, J. I., Eds., ACS Symposium Series, *in press*.
8. Yaita T.; Herlinger, A. W.; Thiyagarajan, P; Jensen, M. P. (2004), Influence of Extractant Aggregation on the Extraction of Trivalent f-Element Cations by a Tetraalkyldiglycolamide. *Solvent Extr. Ion Exch.* **24,** 553-571.

Other References
9. Baxter, R. J. (1968), Percus-Yevick Equation for Hard Spheres with Surface Adhesion. *J. Chem. Phys.* **49**, 2770-2774.

Studies of Solvation Processes in Supercritical Fluids and Ionic Liquids

Frank V. Bright, PI
G.A. Baker, S.N. (nee Daniel) Baker, M.A. Kane, C.A. Munson, W.E. Gardinier, P.M. Page, and T.A. McCarty, Graduate Research Assistants
Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY 14260-3000
chefvb@acsu.buffalo.edu http://www.chem.buffalo.edu/Bright.html

Overall research goals:
We aim to develop a molecular-level view of solute solvation and dynamics in supercritical fluids and room temperature ionic liquids – two classes of replacement solvents.

Significant achievements in 2003-2005:
Oligomer and polymer dynamics. We have investigated the tail-tail cyclization and unfolding kinetics of poly(dimethylsiloxane) end-labeled with pyrene (Py-PDMS-Py) in pure supercritical CO_2 ($scCO_2$). There are at least two forms of Py-PDMS-Py 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; however, its dominance wanes as the CO_2 density increases. Our results are also consistent with the presence of upper and lower critical solution pressures/densities for dilute PDMS dissolved in $scCO_2$.

When Py-PDMS-Py is dissolved in liquid ethyl acetate (EA, a theta solvent for PDMS) or methanol (M, a poor PDMS solvent) at 308 K as a function of added CO_2 (0 – 1 mole fraction) the tail-to-tail cyclization rate increases as the CO_2 mole fraction increases. The tail-to-tail unfolding rate is CO_2 independent, and generally slower in comparison to the cyclization rates. As CO_2 is added, toluene (T, a good solvent for PDMS) and EA move toward becoming poorer PDMS solvents. At a given CO_2 mole fraction in the liquid phase, the theta solvent (EA) quality for PDMS decreases ahead of and in greater magnitude than the good solvent (T). The overall effects of solvent and CO_2 mole fraction on the Py-PDMS-Py dynamics in CO_2-expanded liquids is captured by a simple model.

We have studied a PDMS-based three-armed junction that contains a single dansyl reporter group (DJ). In pure CO_2 at low fluid densities, the local microenvironment sensed by the dansyl residue in DJ appears to be rich in PDMS, indicating that the solvent quality is poor and the PDMS segments interact strongly with the dansyl residue. Increasing the density increases the solvent quality, and PDMS segments become better solvated by the CO_2. At the highest densities, solvent quality decreases resulting in a local increase in the PDMS composition around the average dansyl residue. DJ aggregates form in the fluid phase at low densities. As the density is increased, these aggregates are disrupted and isolated DJ molecules appear to be the major species above a reduced density of ~1.5 and up to ~1.9. DJ aggregates are present in the CO_2/M mixture at all fluid densities studied. At low mixture densities there is enrichment in the local methanol concentration surrounding the dansyl residue in DJ. Thus, it appears as if the PDMS segments in DJ augment/enhance the M concentration surrounding the dansyl residue in DJ. These results demonstrate the dramatic role density and composition can play in tuning the local microenvironment surrounding a polymeric junction point.

Solute-fluid-surface interactions. We have prepared a series of dansyl-labeled controlled pore glass (D-CPG) particles with dansyl to amine molar ratios (DR) that cover five orders of magnitude. At high DR, the majority of the dansyl groups are solvated by other dansyl moieties and solvent does not significantly alter the dansyl's local microenvironment (i.e., cybotactic region) to any significant level. At intermediate DR, the average distance between the dansyl groups increases, and solvent is able to access/solvate/wet the dansyl groups and alter their cybotactic region. At the lowest DR studied, the dansyl moieties are localized within solvent inaccessible/restrictive SiO_2 sites (e.g., small pores).

Room temperature ionic liquids. We have reported the picosecond time-resolved fluorescence of 6-propionyl-2-(N,N-dimethylamino)naphthalene (PRODAN) dissolved in [bmim][PF6] at 298 K as a function of solubilized water in the [bmim][PF6] phase. The solvent relaxation dynamics are described by three components with apparent relaxation times below 15 ps and up to 10 ns. The average relaxation dynamics increase as the water concentration in the [bmim][PF6] 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 sub-15 ps dynamics. The sub-ns dynamics are consistent with [PF6] anion relaxation. This process is water dependent, slowing as the amount of solubilized water in the [bmim][PF6] phase increases. We suggest that this process arises from formation of 1:2 H-bonded [PF6]-HOH-[PF6] complexes. The ns dynamics are consistent with the cation, decreasing slightly with an increase in the amount of solubilized water.

We have also written an invited review on ionic liquids as environmentally-responsible designer solvents in analytical chemistry.

Specific objectives for 2005-2006:
Research will center on the following area: (1) Studies on oligomer/polymer tail and junction point accessibility, dynamics, and mobility in pure and cosolvent-modified ionic liquids. (2) Solute-fluid interactions at interfaces in contact with pure and cosolvent-modified $scCO_2$ and ionic liquids. (3) Solvent properties of room temperature ionic liquids as a function of dissolved cosolvents and pure CO_2.

References of work that were supported by this project(2003-2005):

1. X. Yang, A.L. Brown, M. Furukawa, S. Li., W.E. Gardinier, E.J. Bukowski, F.V. Bright, C. Zheng, X.C. Zeng and B. Gong, “A New Strategy for Folding Oligo(m-phenylene ethynylenes),” *Chem. Commun.* **2003**, 56-57.
2. 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.
3. F.V. Bright and C.A. Munson, “Time-Resolved Fluorescence Spectroscopy for Illuminating Complex Systems,” *Anal. Chim. Acta* **2003 500**, 71-104.
4. 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** *20*, 1551-1557.
5. W.E. Gardinier, M.A. Kane and F.V. Bright, “Effects of Added CO_2 on the Dynamics of Poly(dimethylsiloxane) Oligomers Dissolved in a Theta and Poor Solvent,” *J. Phys. Chem. B* **2004**, *108*, 18520-18529.
6. P.M. Page, C.A. Munson and F.V. Bright, “Dansylated Controlled Pore Glass: A Model for Silica-Liquid Solvation,” *Langmuir* **2004**, *20*, 10507-10516.
7. C.A. Munson, P.M. Page and F.V. Bright, “Effects of Fluid Density on a Poly(dimethylsiloxane)-Based Junction in Pure and Methanol-Modified Carbon Dioxide,” *Macromolecules* **2005**, *38*, 1341-1348.
8. W.E. Gardinier and F.V. Bright, “Temperature-Dependent Tail-Tail Dynamics of Pyrene Labeled Poly(dimethylsiloxane) Oligomers Dissolved in Ethyl Acetate,” *J. Phys. Chem. B*, submitted for publication.
9. G.A. Baker, S.N. Baker, S. Pandey and F.V. Bright, “An Analytical View of Ionic Liquids,” *Analyst*, submitted for publication.

Fundamental Phase Partitioning for Supercritical Fluids

Clement R. Yonker and John L. Fulton
Postdoctoral Associates: Matthew C. Henry and Yongsheng Chen
Pacific Northwest National Laboratory
Chemical Sciences Division
Fundamental Sciences Directorate
Mail Stop K1-83
902 Battelle Battelle Blvd.
Richland, WA 99352
clem.yonker@pnl.gov / john.fulton@pnl.gov
www.pnl.gov/supercriticalfluid/index.stm

Overall Research Goals:
It is important to understand, on an atomic/molecular level, the intermolecular interactions underlying separations and extractions in supercritical fluids. The objectives of this research program are (1) to describe at the molecular level, the structure and chemistry of solute/solvent interactions in supercritical fluids; (2) to investigate reaction chemistries in supercritical fluids; and (3) to describe the intermolecular interactions leading to organized molecular structures in supercritical fluids. The scope of studies spans the range of solute/solvent interactions from ion-pair formation and hydrogen-bonding, to solvent clustering phenomena. Supercritical fluids offer an important opportunity to investigate solution structure and dynamics due to the ability to control the number of molecular interactions and molecular distance through fluid density. Molecular level studies in supercritical fluids will provide an improved understanding of these interactions by bridging the gap between the gaseous and liquid states. Continuing investigation of supercritical fluid solvation structure and solution dynamics involves the elucidation of the thermodynamics and kinetics of solute/solvent and solute/solute interactions over a complete range of densities, temperatures, and pressures coupled with an understanding of the structure/function relationships related to solubility and catalysis in fluids. The experimental effort entails the use and expansion of various high-pressure spectroscopic techniques such as NMR, X-ray absorption spectroscopy (XAFS), and time-resolved FTIR for supercritical fluids. The basic knowledge related to solution chemistry and physics generated in this research effort during this grant period will find many applications in novel separations technologies, solvent substitution processes, carbon management/CO_2 sequestration, environmental remediation, hydrothermal solutions and reaction chemistries in supercritical fluids.

The “Fundamental Phase Partitioning for Supercritical Fluids” Project at PNNL combines two mutually supportive research areas. The first of these areas deals with determining the molecular structure in supercritical water by probing ion hydration and contact ion pairing. This research effort is led by John L. Fulton. The second area investigating reaction kinetics and dynamics in supercritical fluids is led by Clement R. Yonker. The focus of this area is on understanding the role of cage effects, solvent viscosity and molecular diffusion on reaction rates and path control under various thermodynamic conditions. This basic investigation studies the dynamics of organometallic radical photochemical reactions in supercritical carbon dioxide as a function of pressure and temperature. The fundamental understanding of reaction dynamics in this specific system can be related to reaction chemistries in fluids in particular and to the role of pressure effects on solute/solvent interactions associated with molar volume changes in liquids in general.

Specific achievements in 2003-2005:

By using a unique capillary FTIR cell, thermodynamic investigations of supercritical fluid solutions were studied at pressures up to 3.1 kbar for the keto-enol tautomeric equilibrium of acetylacetone and its tri- and hexafluorinated analogs as neat liquids and in CO_2. The acetylacetonates are in a pressure dependent equilibrium between their keto and enol forms. The slope of a plot of ln Keq versus pressure is proportional to the change in partial molar volume between these two forms of this molecule. It is interesting that the partial molar volume change for both trifluoroacetylacetone and acetylacetone analogs are larger in a supercritical CO_2 solution than in the neat liquid, which is indicative of the role of CO_2 solvation in this equilibrium process. The fundamental understanding of equilibrium processes in supercritical fluids regarding the role of pressure and temperature effects on solute/solvent interactions associated with molar volume changes and enthalpy changes is necessary to enhance the overall use of supercritical fluid solvents.

Specific objectives for 2005-2006:

Extending preliminary organometallic photolysis reactions in liquids investigating molybdenum radical self-termination to supercritical fluid conditions. Experimental efforts include the kinetic and thermodynamic investigation of the effect of viscosity and solvent cage dynamics between the radical and the fluid over a wide range of physical conditions. The solvent environment (density, viscosity, dielectric) about a solute molecule can be continuously changed as a function of pressure without having to alter the solvent composition. This is important in physicochemical investigations of reaction mechanisms, chemical equilibria, or solution dynamics because of the wide range of solvent conditions that can be sampled as a function of pressure (and temperature). The structural information available from time-resolved FTIR allows a definitive identification of the reaction pathway and dynamics in compressible supercritical fluids. Therefore, from high-pressure rate experiments using this specific system, one could expect to obtain fundamental molecular level information about a wide range of chemical and dynamic processes in solutions for both liquids and supercritical fluids.

References of work supported by this project:

1. “Understanding the Effects of Concentration on the Solvation Structure of Ca^{2+} in Aqueous Solution I: The Perspective on Local Structure from EXAFS and XANES”, J. L. Fulton, S. M. Heald, Y. S. Badyal, J. M. Simonson, *J. Phys. Chem. A*, **107**, 4688-4696, (2003)
2. “EXAFS Spectra of the Dilute Solutions of Ca^{2+} and Sr^{2+} in water and methanol”, L. X. Dang, G. K. Schenter and J. L. Fulton, *J. Phys. Chem. B*, **107**, 14119-14123 (2003).
3. “High-pressure, high temperature XAFS transmission cell for the study of aqueous ions with low absorption-edge energies”, J. L. Fulton, Y. Chen, S. M. Heald, and M. Balasubramanian, *Rev. Sci. Instruments*, **75(12)**, 5228-5231, (2004).
4. “A High-Pressure NMR Investigation of Reaction Chemistries in a Simple Salt Hydrate”, C.R. Yonker, J.C. Linehan, *J. Supercritical Fluids*, **29**, 257-263 (2004).
5. “FT-IR studies of acetylacetonates in supercritical CO_2 using a capillary cell at pressures up to 3.1 kbar”, M.C. Henry, C.R. Yonker, *Anal. Chem.*, **76**, 4684-4689 (2004).

Participant List
and
Abstracts Index

Participant List
and
Abstracts Index

Last Name	First Name	Affiliation	Email	Abstract Number	Page Number
Albrecht-Schmitt	Thomas	Auburn University	albreth@auburn.edu	O3-5	61
Alexandratos	Spiro	Hunter College / City University of New York	alexsd@hunter.cuny.edu	O1-2	5
Antonio	Mark	Argonne National Laboratory	mantonio@anl.gov	O5-4	87
Assefa	Zerihun	Oak Ridge National Laboratory	assefaz@ornl.gov	O2-4	19
Bartsch	Richard	Texas Tech University	Richard.Bartsch@ttu.edu	O2-2	15
Basaran	Osman	Purdue University	obasaran@purdue.edu	O6-2	129
Batista	Enrique R.	Los Alamos National Laboratory	erb@lanl.gov	O4-2	69
Belfort	Georges	Rensselaer Polytechnic Institute	belfog@rpi.edu	P1-1	27
Blanchard	Gary	Michigan State University	blanchard@chemistry.msu.edu	O5-3	85
Bohn	Paul	University of Illinois	bohn@scs.uiuc.edu	O5-6	91
Booth	Corwin	Lawrence Berkeley National Laboratory	chbooth@lbl.gov	O5-7	93
Bosnich	Brice	University of Chicago	bos5@uchicago.edu	O1-1	3
Bright	Frank	The State University of New York, Buffalo	chefvb@acsu.buffalo.edu	O6-6	137
Bruening	Merlin	Michigan State University	bruening@cem.msu.edu	O3-3	57
Bursten	Bruce	Ohio State University	bursten@chemistry.ohio-state.edu	Keynote	1
				P2-2	103
Chiarizia	Renato	Argonne National Laboratory	chiarizia@anl.gov	O6-5	135
Choppin	Gregory	Florida State University	choppin@chem.fsu.edu	P1-2	29
Clark	David	Los Alamos National Laboratory	dlclark@lanl.gov		
Clearfield	Abraham	Texas A&M University	clearfield@mail.chem.tamu.edu	O3-2	55
Conradson	Steven	Los Alamos National Laboratory	conradson@lanl.gov	O4-5	75
Custelcean	Radu	Oak Ridge National Laboratory	custelceanr@ornl.gov	O3-4	59
Dai	Sheng	Oak Ridge National Laboratory	dais@ornl.gov	O5-9	99
Davis	Jeffery	University of Maryland	jd140@umail.umd.edu	O2-3	17
Dietz	Mark L.	Argonne National Laboratory	mdietz@anl.gov	O6-4	135
Duckworth	Douglas	Oak Ridge National Laboratory	duckworthdc@ornl.gov	P2-3	105
Edelstein	Norman	Lawrence Berkeley National Laboratory	nmedelstein@lbl.gov		
Fiechtner	Gregory J.	US DOE Office of Basic Energy Sciences	gregory.fiechtner@science.doe.gov		
Freeman	Benny	University of Texas, Austin	freeman@che.utexas.edu	P1-4	33
Gibson	John	Oak Ridge National Laboratory	gibsonjk@ornl.gov	O4-7	79
Gorden	Anne	Lawrence Berkeley National Laboratory	agorden@berkeley.edu	P1-5	35
Grey	Clare	Stony Brook University	cgrey@notes.cc.sunysb.edu	P2-5	109

Participant List
and
Abstracts Index

Last Name	First Name	Affiliation	Email	Abstract Number	Page Number
Groenewold	Gary	Idaho National Laboratory	gary.groenewold@inl.gov		
Haire	Richard	Oak Ridge National Laboratory	hairerg@ornl.gov	P1-6	37
Harris	Joel M.	University of Utah	harrisj@chem.utah.edu	P2-6	111
Hay	Benjamin	Pacific Northwest National Laboratory	ben.hay@pnl.gov	O4-1	67
Heaven	Michael	Emory University	mheaven@emory.edu	P1-7	39
Houk	Sam	Ames Laboratory	rshouk@iastate.edu	P2-7	113
Hupp	Joseph	Northwestern University	j-hupp@northwestern.edu	O2-1	13
Ibers	James	Northwestern University	ibers@chem.northwestern.edu	O3-6	63
Jensen	Mark	Argonne National Laboratory	mjensen@anl.gov	O4-6	77
Kiplinger	Jaqueline	Los Alamos National Laboratory	kiplinger@lanl.gov	O2-6	23
Kong	Deyuan	Texas A&M University	kong@mail.chem.tamu.edu		
Koros	William	Georgia Institute of Technology	william.koros@chbe.gatech.edu	O5-1	81
Lian	Jie	University of Michigan	jlian@umich.edu	P2-4	107
				O6-6	137
Liu	Guokui	Argonne National Laboratory	gkliu@anl.gov	P2-8	115
Maciel	Gary	Colorado State University	Maciel@lamar.colostate.edu	P2-9	117
Marceau	Diane	US DOE Office of Basic Energy Sciences	diane.marceau@science.doe.gov		
Meyer	Karsten	University of California, San Diego	kmeyer@ucsd.edu	O2-5	21
Miller	Jan	University of Utah	jdmiller@mines.utah.edu	P1-8	41
Miller	John	US DOE Office of Basic Energy Sciences	john.miller@science.doe.gov		
Millman	William	US DOE Office of Basic Energy Sciences	william.millman@science.doe.gov		
Morss	Lester	US DOE, Office of Basic Energy Sciences	lester.morss@science.doe.gov		
Moyer	Bruce	Oak Ridge National Laboratory	moyerba@ornl.gov	P2-10	119
Nitsche	Heino	Lawrence Berkeley National Laboratory	hnitsche@lbl.gov	P1-10	45
Paine	Robert	University of New Mexico	rtpaine@unm.edu	O1-3	7
Pemberton	Jeanne	University of Arizona	pembertn@u.arizona.edu	P1-11	47
Peralta	Juan	Rice University	juanp@rice.edu		
Pitzer	Russell	Ohio State University	pitzer.3@osu.edu	P2-11	121
Ramsey	Michael	University of North Carolina - Chapel Hill	jmramsey@email.unc.edu	Keynote Lecture 2	65
Rao	Linfeng	Lawrence Berkeley National Laboratory	lrao@lbl.gov	O6-3	131
Ray	Asok K.	University of Texas, Arlington	akr@uta.edu	O4-4	73

Participant List
and
Abstracts Index

Last Name	First Name	Affiliation	Email	Abstract Number	Page Number
Raymond	Kenneth	University of California, Berkeley	raymond@socrates.berkeley.edu	O1-4	9
Rogers	Robin	The University of Alabama	rdrogers@bama.ua.edu	O6-1	127
Scuseria	Gustavo	Rice University	guscus@rice.edu	P1-12	49
				O4-3	71
Selby	Hugh D.	Colorado State University/LANL	hds@lanl.gov	P1-3	31
Sepaniak	Michael	University of Tennessee, Knoxville	msepaniak@utk.edu	P2-12	123
Sessler	Jonathan	University of Texas	sessler@mail.utexas.edu	O1-5	11
Shuh	David	Lawrence Berkeley National Laboratory	DKShuh@lbl.gov	P2-13	125
Soderholm	Lynda	Argonne National Laboratory	LS@anl.gov	O5-5	89
				P2-1	101
Stevens	Walter	US DOE Office of Basic Energy Sciences	walter.stevens@science.doe.gov		
Stoyer	Nancy	Lawrence Livermore National Laboratory	stoyer2@llnl.gov	P1-9	43
Sudik	Andrea	University of Michigan, Ann Arbor	asudik@umich.edu	O3-1	53
Sykora	Richard	Oak Ridge National Laboratory	sykorare@ornl.gov		
Tian	Guoxin	Lawrence Berkeley National Laboratory	gtian@lbl.gov		
Tsouris	Costas	Oak Ridge National Laboratory	tsourisc@ornl.gov		
Wagner	Albert	Argonne National Laboratory	wagner@tcg.anl.gov		
Way	Douglas	Colorado School of Mines	dway@mines.edu	O5-8	95
Wirth	Mary J.	University of Arizona	mwirth@email.arizona.edu	P1-13	51
Yeung	Edward S.	Ames Laboratory	yeung@ameslab.gov	O5-2	83
Yonker	Clement	Pacific Northwest National Laboratory	clem.yonker@pnl.gov	O6-7	139