Programs and Abstracts

Contractors’ Meeting
Separations and Analysis Program

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Chemical Sciences, Geosciences, & Biosciences Division
Office Of Basic Energy Science
U.S. Department Of Energy
The Separations and Analysis (S&A) Program traces its roots directly to the Manhattan Project and its successful development of processes to extract heavy elements from irradiated fuel. The scope of the S&A program has grown with that of the Department of Energy from the Atomic Energy Commission's focus on nuclear energy to today's more general interest in energy issues. As will be evident from the content of the meeting, the S&A program reflects that breadth and its results broadly impact the Department's missions.

The Separations and Analysis program supports basic research to advance the science that underlies both separations and analysis. By definition, basic research produces new knowledge and understanding. The researcher must learn. The first step in learning requires one to make the simple statement, “I don't know!” Research is, of course, guided by knowledge but is motivated by absence of knowledge. This deep absence of knowledge is the source of questions that drive research, and the hope of articulating characteristics of our collective and individual ignorance serves as the motivation for this meeting.

The purpose of this meeting is to identify major questions in underlying science that DEMAND continued effort. The meeting is not intended as a standard technical exchange, such as the American Chemical Society meeting of this week, though significant exchange among a gathering of researchers always occurs. Nor is the meeting meant to serve as some kind of “Program Review.” There are no external reviewers present and there will be no formal evaluation of the progress of the work. The meeting is intended to be a venue for open and candid discussion of the questions that will drive future research. A recurring question will be, “Where will a reduction in ignorance have the most impact?”

Your Program Manager appreciates the effort expended to prepare for this meeting, and thanks you in advance for your active and animated participation in the Summary Sessions.

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A wide array of ligands can be immobilized on polymer supports. Our research has focused on immobilizing groups on polymers wherein two different types of ligands are available for interaction with a target metal ion. Recent research includes polymers wherein one type of group is preorganized for ionic interactions.

We now report a method by which the calixarene molecule can be immobilized on a polymer and serve as a platform on which ion-binding ligands can be preorganized. Immobilization was optimized through nucleophilic substitution on poly(vinylbenzyl chloride) beads by the sodium salt of calixarene derivatives. Contacting immobilized calix[4]arene resin (HCR) with dilute cesium nitrate in 1 M NaOH gave 96.7% removal of the cesium ions from solution. Polyhydroxystyrene resin (HSR) gave only 35.1%Cs(I) complexation, indicating the importance of the calixarene ring to the observed affinity.

Bis(diethoxyphosphoryloxy)calix[4]arene resin (BPCR) was prepared and its affinity determined for Fe(III), Pb(II), Cu(II), and Ni(II) as 0.0001 N solutions in 0.01 M nitric acid. The percent complexation for the ions as listed above was 100%, 100%, 66.7%, and 37.5%, respectively. HCR, HSR, and the phosphorylated HSR all had less than 14% complexed of each of the metal ions, indicating that neither the cavity alone nor binding to phenolic or phosphoryl oxygens alone is responsible for the unique affinities displayed by the immobilized phosphorylated calixarene resin for transition metals. The high ionic affinities displayed by BPCR are thus ascribed to intra-ligand cooperation of the preorganized coordinating ligands on the ring.

Intra-ligand cooperation was further explored by combining the metal ion coordinating ability of polyamines with the ion exchange ability of phosphonic acid to produce immobilized aminophosphonic acid ligands on crosslinked polymers. The Mannich reaction was applied to the phosphorylation of resins with monoamine, ethylenediamine, diethylenetriamine, and tetraethylenepentamine ligands to give a series of bifunctional aminophosphonic acid resins. The affinity of the resins for Cu(II), Cd(II), Pb(II), and Eu(III) was evaluated from solutions buffered at pH 5. With all of the metal ions studied, the aminophosphonic acid resins showed higher complexing affinities than the monofunctional amine resins, except for Cu(II) which complexed well with all amine resins. When comparing the results to the phosphonic acid resin, it is evident that a supported ligand synergistic interaction is operative where both groups operating together complex more metal ion than either one alone. For example, 26% Cd(II) is complexed by the ethylenediamine resin (distribution coefficient of 26) and 49% Cd(II) is complexed by the phosphonic acid resin (distribution coefficient of 48), but the bifunctional amionophosphonic acid resin complexes 98% cadmium (distribution coefficient of 2300), which far exceeds the combined distribution coefficients of the monofunctional resins. Ion exchange by the phosphonic acid ligand and coordination by the amine ligand cooperate as a dual mechanism for metal ion complexation.

Intra-ligand cooperation to enhance the ion-binding affinity of the phosphoryl oxygen was the objective in a comparative study of the β-ketophosphonate (-C(O)CH₂P(O)(OH)₂), phosphonoacetate (-CH₂CHP(O)(OH)₂COOH), and phosphate (-CH₂P(O)(OH)₂) ligands immobilized on polystyrene beads. Intra-ligand hydrogen bonding was found to attenuate ionic affinities of an immobilized ligand and can be an important variable when quantifying cooperative interactions between two groups on a given ligand.
Recently there has been a great deal of attention focused on rare-earth doped nanocrystals (DNCs) as a new class of luminescent nanomaterials with novel and tunable optical properties. The luminescent wavelengths of the particles are defined primarily by the dopant ion and are not strongly sensitive to particle size or the choice of host material. However, some controversy exists as to the role of quantum confinement of the optical electron and particle size effects on the magnitude of the electric dipole transition moment. We describe recent results of experiments probing the luminescence properties of single europium and terbium ions in isolated yttrium oxide nanocrystals (2 -15 nm diam.). In our experiments, we used time-resolved fluorescence microscopy techniques similar to those used to probe single fluorescence molecules and semiconductor quantum dots, to image the luminescence from individual nanoparticles with a time resolution of about 100 ms. In contrast with luminescence from larger crystals containing several ions, small particles believed to contain single ions show fascinating on-off behavior on a variable time scale. In addition, the single-ion luminescence shows at least 3 well-defined discrete intensity levels, or "bright states". We propose that the on-off blinking and multiple bright state luminescence from single europium ions derives from local symmetry fluctuations in the host crystal.

New proton-ionizable, calixarene-based ligands for selective metal ion separations

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New extractants for divalent metal ions have been prepared by attaching two \(-\text{OCH}_2\text{C(O)NHSO}_2\text{X}\) groups to the lower rim of a calix[4]arene platform. By matching the number of proton-ionizable groups to the valency of the metal ion to be extracted, ion exchange provides an electroneutral extraction complex that avoids co-extraction of an aqueous phase anion. This is a critical factor for potential practical applications in which hydrophilic anions, such as chloride, nitrate, or sulfate would be involved. By varying the electron-withdrawing ability of \(X\) in the proton-ionizable group, the acidity of the extractant may be "tuned". For divalent metal ion species, conformationally mobile ligands 1-4 efficiently and selectively extract \(\text{Pb(II)}\) and \(\text{Hg(II)}\) from aqueous solutions into chloroform. Fluorescence quenching of ligand 5 due to \(\text{Hg(II)}\) coordination is unaffected by the presence of 100-fold excesses of alkali metal cations, alkaline earth metal cations, \(\text{Ag(I)}\), \(\text{Tl(I)}\), \(\text{Cd(II)}\), \(\text{Cu(II)}\), \(\text{Ni(II)}\), \(\text{Pb(II)}\), \(\text{Pd(II)}\), \(\text{Zn(II)}\) or \(\text{Fe(III)}\). By replacing the two \(-\text{OMe}\) groups with \(-\text{OBu}\) groups, the ligand structure becomes fixed in the cone, partial cone, and 1,3-alternate conformations. Currently being assessed are the influences of ligand conformation and identity of the \(\text{para}\)-substituent on the efficiency and selectivity of divalent metal ion extraction.

Linking together alternating aromatic units of a calix[4]arene with polyether units gives calixcrown compounds. Despite the high \(\text{Cs}^+/>\text{Na}^+\) selectivities of certain calixcrowns that is very attractive for removal of \(^{137}\text{Cs}\) from nuclear waste and nuclear fuel reprocessing solutions, applications are limited by low extraction efficiencies. Incorporation of a \(-\text{OC(O)NHSO}_2\text{CF}_3\) group into calix[4]arene-bis(crown-6-ether) 6 gives the mono-ionizable analogue 7. For competitive extractions of \(\text{Na}^+\), \(\text{K}^+\), and \(\text{Cs}^+\) from aqueous solutions into chloroform, the proton-ionizable ligand 7 exhibits high \(\text{Cs}^+\) extraction selectivity under conditions where alkali metal cation extraction by the non-ionizable analogue was undetectable.

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DROP FORMATION WITHOUT AND WITH ELECTRIC FIELDS: RECENT ADVANCES AND FUTURE CHALLENGES

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A recent workshop on drop and jet breakup that took place at the Institute of Mathematics and Its Applications (IMA) at the University of Minnesota in January 2001 and at which the author was invited to present a paper was remarkable from several standpoints. First, the workshop made the point that physicists, applied mathematicians, engineers, and materials scientists alike are interested in the science of drops. Second, one should not be too surprised by all this interest as drop and/or jet breakup is a problem of central importance in applications as diverse as separations, printing, and DNA arraying.

As at the IMA workshop, I will present at the DOE S&A Contractors’ Meeting the status of our research program at Purdue. Over the last few years, we have developed new algorithms that can simulate the dynamics of drop formation and breakup with such accuracy that the discrepancy between the calculations and the experiments is less than about 1%. Indeed, our calculations are now so accurate that their predictions accord with various scaling theories of drop breakup, a feat that had remained inaccessible until the publication of our results in the March 2001 issue of the Physics of Fluids. Another one of our recent notable achievements has been the first theoretical prediction of dripping of hundreds of drops from a nozzle in a sequence, a feat which had eluded dozens of investigators over the past two decades.

If we can calculate things with such great accuracy and have experimental capabilities that complement the theoretical predictions, can we then say that everything about drop breakup is now known? I will show in the second part of my talk and in greater detail during my poster presentation that this is far from the case. As the many participants in the IMA workshop noted, there are more things that we do not understand than we do know. For example, while we know a great deal about the dynamics of drops of simple Newtonian liquids or of such drops if they are perfectly conducting/insulating and when they are immersed in an electric field, we know virtually nothing about the response of drops of complex fluids and that of drops of leaky dielectrics immersed in an electric field. Complex fluids of interest to our group include ones containing surface-active species, e.g. surfactants, and polymer additives. Leaky dielectrics include all fluids that are neither metals nor perfect insulators and hence our existing knowledge base cannot even allow us to predict the dynamics of emission of drops of corn oil from the tip of a Taylor cone attached to an electrified nozzle. My talk will conclude with the approaches that we are about to undertake and/or are envisioning in solving these and numerous other future challenges to advance our understanding of drop dynamics in multiphase separations and other fields.

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PROTEINS AT MEMBRANE INTERFACES: WHAT DO WE KNOW?

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In this fundamental study, the interaction of proteins and a series of polymer surfaces characterized by their surface energies using spectroscopic and intermolecular force measurements was studied. Also, using a new algorithm with ATR/IR spectroscopy, the conformational changes in protein structure during adsorption was monitored.

FTIR/ATR has been used to show that during lysozyme (Lz) adsorption onto five different synthetic polymer membranes, its α-helix structure is reduced and its β-sheet structure is increased with decreasing wettability (cos θ) from 0.93 (regenerated cellulose) to -0.34 (PTFE). These structural changes were also related to the amount of protein adsorbed.

Using the Surface Forces Apparatus, normalized adhesion forces were measured below, at and above the pI of Lz and compared with permeation flux ratios from ultrafiltration experiments using the same solution conditions. Simple exponential correlations were obtained relating the normalized adhesion forces to several different permeation flux ratios. Also, the amount of protein adsorbed onto the membrane from solution during filtration was linearly related to the adhesion force through the choice of solution pH.

The intermolecular forces including adhesion between a model adhesive protein (mussel adhesive protein, Mefp-1) and a variety of different polymeric surfaces were measured using Atomic Force Microscopy. Seven polymeric materials of different critical surface tensions (γc, 17-43 mN/m) were used to correlate adhesion with wettability and the dispersion and polar components of the surface energy at high ionic concentrations (0.5 M). For γc >32 mN/m, the adhesion force increased linearly with γc. However, for γc <32 mN/m, the adhesion force was independent of γc. Also, adhesion appeared to increase with the increasing polar component of the surface energy but was unresponsive to the dispersive component.

References

We have designed and demonstrated polymer-based multilayer structures for use in chemical separations. To date we have focused on one type of polymer multilayer capable of efficient sequestration of metal ions and able to be used in the construction of a polarity gradient along the surface normal axis. For both of these applications, we use maleimide-vinyl ether alternating copolymers and, for this work, we use an \((\alpha,\omega)\)-diacid chloride for efficient interlayer connection.

When using maleimide-vinyl ether alternating copolymers for sequestration of metal ions, the structural strategy we employ is to use the maleimide substituents to facilitate interlayer covalent linkages and the vinyl ether side groups for interactions with selected metal ions. We chose initially to use a phosphonate-terminated \((R_2 =H_2O_3P-)\) vinyl ether as one monomer unit, and Zr\(^{4+}\) as an example metal ion. After the construction of a 4-layer interface of the polymer, exposure of the assembly to Zr\(^{4+}\) resulted in rapid metal ion uptake and substantial swelling of the polymer layers, as measured ellipsometrically. Quartz crystal microbalance (QCM) gravimetric measurements demonstrated the metal ion uptake in these polymer layers to be complete within seconds after exposure to a dilute metal ion solution.

These same polymer multilayers can be used for selective sorption of organic species and we have measured the adsorption isotherms for methanol and other volatile organic solvents and several different polymer structures. The experimental apparatus is comprised of a QCM housed in a cube where the partial pressure of selected adsorbate vapors is controlled using a gas-blending system. There is also an optical null ellipsometer associated with the system for in-situ measurement of the adlayer thickness simultaneous with the mass uptake QCM measurement. Data from these experiments are shown in Fig. 1, and they reveal a substantial structural dependence of sorption characteristics for methanol. Methanol adsorption onto bare gold yields the expected low efficiency, and sorption onto a polymer monolayer with exposed phosphonic acid \((R_2)\) functionalities is seen to be very efficient. The intermediate cases, where the \((R_1)\) functionality interacting with the methanol is 3-chlorophenyl maleimide or 3-bromophenyl maleimide, reveal interactions intermediate in strength, and dependent to some extent on polymer layer thickness, as expected. Current work in this area is focusing on the growth and characterization of polymer multilayer assemblies where each polymer layer has a different chemical identity. Adsorption isotherm data on these layers will reveal their ability to structurally mediate adlayer interactions.
MOLECULAR ASPECTS OF TRANSPORT IN THIN FILMS OF CONTROLLED ARCHITECTURE: NANOPORES AS INTELLIGENT INTERCONNECTING ELEMENTS FOR MICROFLUIDIC INSTRUMENTATION

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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. Increasingly these problems call for us to turn our attention toward the behavior of very small ensembles of molecules. Thus, we are working to extend microseparations technology by developing preparative separation technologies which target mass amounts down to the attomole (10^{-18} mole) range.

One approach to controlling molecular transport combines actively controlled molecular assemblies with transport in nanometer diameter channels, i.e., nanopores, to achieve transport which can be controlled based on: (a) applied bias, (b) molecular size, or (c) specific molecular recognition elements. Fluid flow and chemical reactions which occur in structures with nanometer characteristic dimensions are fundamentally different than the same phenomena in their larger µm-scale cousins. These differences can all be ascribed to the fact that characteristic length scales which describe important physico-chemical phenomena are approximately equal to the dimensions of the devices in which they occur. For example, the Debye length, \( \kappa^{-1} \), which characterizes the length scale of ionic interactions in solution, can be made to span the range \( 1 \text{ nm} \leq \kappa^{-1} \leq 50 \text{ nm} \) by adjusting the ionic strength of a buffer solution in the high-to-low mM concentration range. Thus, applied bias, solution ionic strength and surface charge density can all be varied to control transport.

Molecular size controlled transport is linked to the fact that both the molecular diameter, \( d \), as well as the hydrodynamic radius may be of the order of the channel diameter, \( a \). We are investigating ways in which the channel diameter may be altered under active control by coating the interior walls with a potential-sensitive hydrogel. Finally, as the figure shows, the channel interior walls may be decorated with specific molecular recognition sequences to generate nanoscale affinity columns.

Because the capacity factor, \( k' \), is governed by the phase ratio, it is huge in these structures, increasing by a factor of 117 as the inner diameter of a wall-coated open tubular column with a 10 nm thick coating shrinks from 20 µm to 200 nm. Selected examples of transport control using these principles will be presented.

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ION PAIR EXTRACTION USING CALIXARENE-CROWN ETHERS AND ALCOHOL SOLVATING AGENTS: PAST, PRESENT, AND FUTURE

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Ongoing research in our laboratories has included investigating factors, which control the strength of extraction of cesium by mono- and bis-crown-6 derivatives of calix[4]arenes in the 1,3-alternate conformation. These calixarene-crown ethers are remarkably selective for cesium over the smaller alkali metals; however, extraction strength is not governed only by the strength of complexation of the cation. To preserve electroneutrality, an accompanying anion needs to be co-extracted. Thus, to effectively extract the cation-anion pair, factors, which also enhance extraction of the anion, must also be considered. These factors include increasing anion partitioning to the solvent phase by enhancing anion solvation, employing hosts to physically accommodate or coordinate the anion, or using extractants that recognize and extract the complete ion pair.

Past research efforts regarding increasing anion extractability have included simply selecting an anion that partitions better to the solvent phase, and selecting diluents for the extractant that a given anion will partition better to. For the former, the Hofmeister series can be consulted, whereby anions such as perchlorate will partition preferentially over anions such as nitrate that possess higher hydration energies. For the latter, a given anion will partition more readily to a solvent that can better solvate it. For example, a given anion such as chloride or nitrate will partition more readily to a polar diluent such as an alcohol, ketone, or chlorocarbon than to an aliphatic or aromatic hydrocarbon.

Present research efforts have included a strategy similar to changing the diluent properties. Where it has been necessary to employ low-polarity diluents, lipophilic alcohols have been added to the diluent to enhance anion solvation. Recent investigations have shown that the extractability of cesium nitrate by a calix[4]arene crown-6 ether increases as the hydrogen bond donor ability of the alcohol solvating agent (also called a modifier) increases.

Future research efforts will focus more on the approach of accommodating both ions of an extracted ion pair at once. These research efforts will build on our understanding and controlling the critical role of the co-extracted anion through studies of the effects of ion-pairing interactions, especially the aforementioned solvation by lipophilic alcohols used in combination with alkali-metal selective ionophores. Ditopic hosts capable of simultaneous recognition of ion pairs will be designed and synthesized. Strategies entail building hydrogen-bond donor functionalities onto calixarene frameworks already possessing desirable cation binding properties. Target compounds include 1,2-mono-crown calix[4]arenes in the cone conformation bearing two hydroxyethyl lariats attached to the other phenolic groups on the lower rim. The hydroxyethyl groups can additionally possess substituents of variable electron-withdrawing capability attached to the carbon atom bearing the hydroxyl group.

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MOLECULAR RECOGNITION USING CONSTRAINED FACE-TO-FACE METAL COMPLEXES

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Molecules, 1, consisting of molecular spacers which constrain two square planar terpyridyl metal complexes to a face-to-face disposition separated by ~7Å have been prepared and characterized. Using linear linkers, such as 4,4'-dipyridyl, 2, and 1 (L = CH₃CN), the molecular rectangles, 3, were formed quantitatively. Both 1 (L = Cl⁻) and 3 incarcerate a variety of guest molecules, including aromatic molecules and square planar metal complexes. Guest incarceration is signaled by color changes.

Using, for example, 9-methylanthracene (9-MA) as a guest, 1 (L = Cl⁻) forms a tight 2:1 complex, whereas the oxidized spacer rectangle forms a 5:1 complex and the reduced spacer rectangle forms a 4:1 adduct. A crystal structure of the 2:1 complex of 1 (L = Cl⁻) formed by the reduced spacer, 4, shows a variety of stacking interactions. The 9-MA molecules reside within the cleft and on “top” of the terpyridyl-Pd-Cl units which also stack (see 5). These and other examples of molecular recognition will be presented in relation to selective separation. The potential for using these spacer-chelator systems for fabricating molecular switches and molecular machines driven by protomotive or electromotive forces will be discussed.

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PROBING MOLECULAR-LEVEL EVENTS IN SUPERCRITICAL FLUID SYSTEMS

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Supercritical fluids exhibit liquid-like densities, gas-like mass transfer, and their physicochemical properties (e.g., density) can be readily adjusted. Fluids like CO₂ are also considered to be environmentally benign. Given these factors, one should not be surprised to learn that supercritical fluids are attractive solvent systems for extractions, chemical reactions, and separations. However, many questions remain unanswered regarding supercritical fluid systems. The supercritical fluid work in our laboratories focus on four areas:

1. Determining how the local microenvironment surrounding a solute at an interface is affected by the presence of the interface. This work focuses on addressing questions of solute solvation when such is an actual part of a sample matrix and not just dissolved in solution. The results from these experiments impact supercritical fluid-based extractions.

2. Quantifying the tail-tail and junction point dynamics of polymers dissolved in neat and co-solvent modified CO₂. This work centers on understanding how polymer segment, junction, and tail mobility and tail accessibility can be modulated in supercritical CO₂. The results of these experiments have ramifications in areas ranging from the use of polymers as a means to control to more effective strategies for polymer synthesis using supercritical fluids as solvents.

3. Determining the behavior within and exploiting reverse micelle systems formed in supercritical CO₂. These efforts center on understanding the chemistry (e.g., pH, solute mobility) within the water pool, the transport of key materials into and out of the micelle core, and the ability of these micelles to serve as environmentally friendly nanoreactors for enzyme-based reactions.

4. The characteristics of ionic liquid/CO₂ systems. These experiments seek to determine the local microenvironment within these hybrid reaction media and understand the factors that govern the behavior of solute molecules when they are dissolved within these systems.

This presentation will briefly summarize our activities in each of these research areas.

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Deposition of layered polyelectrolyte films (LPFs) on highly porous supports produces ultrathin, highly selective ion-transport membranes. These membranes are attractive in part because of their convenient synthesis, which simply involves alternating adsorption of polycations and polyanions. Scanning electron microscopy (SEM) images, e.g., Figure 1, show that this simple deposition procedure results in defect-free membranes that cover porous supports without filling them. Because the polyelectrolyte film can be ultrathin, these membranes allow high flux.

The wide variety of polyelectrolytes capable of forming LPFs affords control over membrane properties and allows synthesis of membranes with remarkable monovalent/divalent ion selectivities. Initially, we deposited poly(styrene sulfonate) (PSS)/poly(allylamine hydrochloride) (PAH) films on porous alumina, and diffusion dialysis experiments showed that these materials have modest Cl⁻/SO₄²⁻ selectivities (5-10) and high Cl⁻/Fe(CN)₆³⁻ selectivities (>300). Poly(acrylic acid) (PAA)/PAH membranes have similar selectivities. Deposition of hybrid PSS/PAH + PAA/PAH films, however, results in dramatic increases in selectivity. The Cl⁻/SO₄²⁻ selectivity of 5-bilayer PSS/PAH + 2.5 bilayer PAA/PAH films is 280.

Variation of membrane composition suggests that the high selectivities of hybrid membranes are due in large part to Donnan exclusion at the membrane surface. Upon capping of hybrid membranes with PAH to change the sign of the surface charge, Cl⁻/SO₄²⁻ selectivities decrease by 2 orders of magnitude. Field-emission SEM images show that the surface of hybrid PSS/PAH + PAA/PAH membranes has a different topology than the surface of pure PAA/PAH membranes. We speculate that the PAA surface layer of the hybrid membranes is less strongly hydrated than in pure PAA/PAH membranes. Thus these surfaces would contain a high charge density that results in highly selective Donnan exclusion.

Post-deposition modifications of layered polyelectrolytes yield remarkably selective membranes. Adsorption of poly(amic acid)/PAH films followed by heat-induced imidization yields membranes with Cl⁻/SO₄²⁻ selectivities as high as 1000. Interestingly, these membranes also show K⁺/Mg²⁺ selectivities of 400. Monovalent/divalent ion selectivities for both cations and anions are not consistent with a simple Donnan model for transport through LPFs. Future work with these and other LPFs aims at using a combination of systematic synthetic variation of membranes, streaming potential measurements, diffusion dialysis experiments, and nanofiltration studies to better understand the unusual ion-selectivity of LPFs.
NEAR THRESHOLD AUTOIONIZATION BEHAVIOR OF ATOMS WITH PARTIALLY FILLED D- AND F-SHELLS

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Autoionization is the process where an atom (or molecule) is excited to a nominally bound state that lies above the ionization potential (IP) for the most loosely bound valence electron. The excitation energy is then rapidly transferred to the valence electron, usually through the Coulomb interaction, and ionization takes place. Because of strong coupling to the continuum, autoionization states typically have lifetimes on the order of $10^{-12} - 10^{-14}$ s, with corresponding resonance widths in the range of 5 – 500 cm$^{-1}$. When available, these autoionization resonances (AIR) can play an important role in developing laser-based ionization analytical methods; they improve the efficiency of ionization for the target species, or the same efficiency can be achieved using much smaller lasers, which also reduces background ionization of other species. For a given integrated line strength, a narrower AIR is preferable because the excitation cross-section, which will determine the excitation efficiency, is inversely proportional to the width.

The lanthanides and actinides are generally known to have a high density of relatively narrow AIRs, which can in part be attributed to poor communication between the optically excited electron and angular momentum states of partially filled d- and f-shells in the core. For example, an early pulsed laser study on gadolinium identified a single AIR with a near resolution-limited width of 0.07 cm$^{-1}$, with an estimated lifetime of 0.5 ns and excitation cross section of $8 \times 10^{-15}$ cm$^2$ [1]. Motivated by these observations and the need for ultrasensitive analyses for gadolinium in a number of fields [2], we have undertaken a comprehensive study of near threshold autoionization. In particular, we have used high-resolution triple-resonance excitation with single-mode cw lasers to investigate the first 260 cm$^{-1}$ above the Gd IP, corresponding to the region between the first two angular momentum states ($J = 5/2, 7/2$) of the Gd$^+$ ion ground term. In this region we observe literally thousands of AIRs with widths ranging from a few cm$^{-1}$ down to $2 \times 10^{-4}$ cm$^{-1}$. By comparing spectra derived from excitation schemes that access different $J$ values in the intermediate states, we have determined the $J$ value of the autoionization states in the range $J = 3 – 7$. Among these, there appears to be a general trend toward narrower width with increasing $J$, which may be interpreted in terms of inertial barrier effects and conservation of angular momentum that requires the departing electron to leave in a high angular momentum state (d- or higher partial wave).

Many observed AIRs can be assigned to Rydberg series converging to the $J = 7/2$ level of the ion ground term, while others must be attributed to (as yet unidentified) higher excited core configurations. Of particular interest are some extremely narrow $J = 7$ AIRs belonging to higher excited core configurations. Not only do they have widths as small as ~7 MHz, corresponding to a lifetime of ~20 ns, they are strong transitions with cross-sections as high as $10^{-13}$ cm$^2$, 6 orders of magnitude larger than nearby continuum ionization. They behave very much like normal, allowed bound atomic transitions; the main difference is that after a delay of some nanoseconds, they finally result in ionization of the atom. As such, we have observed many characteristics that are normally associated with bound atomic transitions. These include the first (to our knowledge) measurement of isotope shifts and hyperfine structure in autoionization states, and we have observed saturation of the ionization step with moderate-power cw lasers. For the strongest AIR we observed saturation of all excitation steps, including the final step leading to ionization, at powers reachable with solid-state diode lasers. This extremely efficient and selective photoionization has obvious and profound implications for a number of processes ranging from isotope separation to ultra-trace analysis of radionuclides in the environment.

LI-CONTAINING ZEOLITES FOR NON-CRYOGENIC AIR SEPARATION

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Aluminosilicate zeolites find widespread commercial applications in separation processes, and a detailed knowledge of the placement of the extraframework cations is crucial in the optimization of such materials for any particular application. For example, in lithium-containing zeolites, which are used for non-cryogenic air separation, it is desirable to maximize the numbers of Li⁺ cations in accessible positions where they can interact with adsorbed nitrogen. Unfortunately, the characterization of the Li⁺ positions by X-ray diffraction is impracticable, especially with powder samples, because lithium is a very poor X-ray scatterer. However, Li is a reasonable neutron scatterer, and ⁷Li is a useful nucleus for solid state NMR studies. We shall show how a combined neutron diffraction and NMR approach can be used to probe the lithium distribution in Li⁺-containing materials in great detail. In particular, we shall show that this combination of analytical tools is particularly powerful when used in mixed cation systems such as Li,Na-chabazites (Si/Al=2.4) (1) and Li,Na,K- chabazites (2).


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Metal solvent extraction data obtained with P,P'-di(2-ethylhexyl) methylene-, ethylene-, and butylenediphosphonic acids (H₂DEH[MDP], H₂DEH[EDP] and H₂DEH[BuDP], respectively) exhibit features that are difficult to explain without knowledge of the aggregation state of the extractants and their metal complexes. Extractant structure and diluent type determine these aggregation phenomena which, in turn, have a pronounced effect on metal extraction chemistry.

Information on the aggregation of the dialkylsubstituted diphosphonic acids in aromatic diluents has been obtained using the complementary techniques of vapor pressure osmometry (VPO), infrared spectroscopy, molecular mechanics and small angle neutron scattering (SANS). In toluene, H₂DEH[MDP], H₂DEH[EDP] and H₂DEH[BuDP] molecules form dimeric, hexameric, and trimeric aggregates, respectively.

SANS data indicate that the H₂DEH[EDP] hexameric aggregate assumes a spherical shape. In this structure, reminiscent of a reverse micelle, the alkyl groups are probably oriented outwards (toward the solvent) and a large hydrophilic internal cavity is available to accommodate metal cations and/or water molecules.

SANS investigations confirm that large aggregates form when solutions of H₂DEH[MDP] and H₂DEH[BuDP] are used to extract certain cations under high metal loading conditions. The largest aggregates were observed in the extraction of Fe(III) and Th(IV) by H₂DEH[MDP]. The Fe(III)-H₂DEH[MDP] aggregates are rods of constant radius whose length increases with the metal concentration in the organic phase. The Th(IV)-H₂DEH[MDP] and Fe(III)-H₂DEH[BuDP] aggregates are cylindrical but growth also occurs laterally as more metal is transferred into the organic phase.

With H₂DEH[EDP], the average aggregation number remained essentially unchanged after extraction of metal ions at high concentration. This result reaffirms the unique solvent extraction behavior of H₂DEH[EDP]. The highly aggregated state of H₂DEH[EDP], which is not disrupted by metal extraction, and the strong water absorption bands observed in the infrared for H₂DEH[EDP], confirm that this extractant in aromatic diluents behaves in a way similar to reverse micelles. The first-power extractant dependency observed in the extraction of various metal cations by H₂DEH[EDP] fully agrees with the results of the aggregation studies.
Our work has been concerned with the synthesis and structure of sorbents and ion exchangers for the removal of cesium, strontium and actinides from tank waste and ground water. Types of compounds studied include titanium silicates (CST, pharmacosiderites), titanates, sodium micas, pillared clays and others. By carrying out X-ray structural studies on the more crystalline tunnel type ion exchangers, we are able to characterize the ion exchange sites occupied by the ion of interest and their coordination. This information can be connected to the selectivities of the ions and a rational basis for the selectivities established. Based on this information as a guide, more focused synthetic processes were developed. At present, sorbents for Sr and actinides for both tank wastes and ground water use have been developed and are undergoing extensive testing.

Development of sodium micas and pillared clays for immobilization of radioisotopes in soils is under development.

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The motion of ions in rf ion traps is a focal point of our research. Quadrupole ion traps are extensively utilized as analytical tools. To enhance their performance, we have developed a simulation program, ITSIM, which closely mirrors experimental outcomes. ITSIM's collision model incorporates elastic and inelastic collisions, allowing for non-zero buffer gas atom velocities and velocity-dependent collision cross-sections. It also simulates energy transfer to internal degrees of freedom and fragmentation behavior, enabling the calculation of MS/MS spectra.

With these enhancements, ITSIM provides quantitative or near-quantitative agreement between simulation and experiment, particularly in miniature traps and arrays of ion traps. We observe that chemical structure impacts ion motion, especially in elastic and inelastic collisions, leading to "chemical mass shifts" and their dependence on the ion trap geometry. Enhanced shifts associated with resonance ejection have been explored and utilized as an additional ion structural characteristic.

An FT ion trap experiment based on non-destructive ion detection has been developed, with a focus on minimizing noise. Differential detection and noise suppression improve signal to noise ratios in these experiments. A SWIFT pulse, used at the secular and side-band frequencies, has enabled the excitation of ions into coherence, reducing the amplitude of the excitation pulse compared to a DC pulse, allowing for tailored waveforms.

Ion mobility measurements have been conducted using DC tomography, a method that examines the secular oscillation of a coherent group of trapped ions. In these experiments, resonance excitation is used to excite an initially cooled ion population into coherent motion. A subsequent DC probe pulse is employed to eject some of the ions, and the number of ions remaining in the trap after the probe pulse is measured to assess the secular velocity of the ions at the time of pulse application. The experiment is repeated with the probe pulse applied at different times, allowing for the measurement of the oscillation of the ion cloud and the collisional reduction of its amplitude.

Applications of ion traps have emphasized thermochemical measurements made using the kinetic method, a cluster ion dissociation experiment that provides affinity and other data. A recent extended version of this method uses a triple plot procedure to deduce relative entropic and enthalpic values.
Hierarchical structures can be found in nature from the macroscopic to the microscopic level. Biomaterials are selectively self-organized from molecular- to macro-length scales, with organized units of subassemblies that are generated to serve biological purposes. They are smartly chosen from a multitude of options. Recently, research has been initiated to mimic biomineralization processes and chemically produce hierarchical structures.\textsuperscript{1,2} Three methodologies have been developed to synthesize hierarchical materials. First, complex macroscopic morphological forms can be produced by fluctuating chemical processes involving local perturbations in the fluid-solid interface during mineralization. Secondly, organic assemblies such as micelles are used as scaffold-like templates to direct mineralization along, around, and between the organic-inorganic interfaces. Thirdly, patterned organic compartments (vesicles) are used to shape biomaterials through “organized reaction fields.” We have recently introduced a facile approach to the production of hierarchical microstructure and mesostructures.\textsuperscript{3} The essence of our new methodology is the combination of two powerful imprinting techniques at different scales: (1) molecular imprinting\textsuperscript{4} and (2) micelle templating synthesis.\textsuperscript{5} The motivation for synthesizing hierarchical materials with microscopic and mesoscopic form centers around the synergistic importance of stereochemistry, pore size, and surface area in determining such properties as flow and transport phenomena, capacity, and selectivity in separation efficiency. The general concept provides a rational way to synthesize hierarchical materials for separation applications. The design principles illustrated by these results highlight opportunities for application in areas such as selective sorption, chemical sensing, and catalysis.

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SELF-ASSEMBLED IONOPHORES: STRUCTURE, DYNAMICS AND FUNCTION

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We are studying a powerful approach for the selective coordination of metal cations. The method relies on self-assembly, whereby the metal ion serves as a template to bring together multiple organic ligands for its own encapsulation (Fig. 1). The ligands, lipophilic nucleosides, have self-complementary hydrogen bonding edges that enable formation of the macrocyclic receptor. In essence, we have prepared non-covalent analogs of crown ethers. Because synthesis is under thermodynamic control, ion-templated assembly is both efficient and reversible. Our major goals are: 1) to understand structural and dynamic factors that control self-association and cation binding, and; 2) to design new self-assembled ionophores that selectively bind cations.

Fig. 1. A self-assembled ionophore. Hydrogen bonds form a cation-binding host.

We have identified simple nucleosides that are selective for binding and transporting Cs+ and Pb+2, among other cations. We will present the results of these studies at this meeting. For example, in the presence of Cs+, the nucleoside, 5'-tert-butyl-dimethylsilyl-2', 3'-isopropylidene-isoguanosine (isoG 1) self-assembles to form a hydrogen-bonded decamer 3 in organic solvents. Pentamer 2, with five oxygen atoms in its central cavity, is the initially formed intermediate. Two hydrogen bonded pentamers give a sandwich complex, decamer, (isoG)10-M+ 3 (Scheme 1). The cavity size dictates the ion binding selectivity and X-ray crystallography shows that decamer 3 is optimal for binding Cs+. This basic knowledge has enabled us to better understand Cs+ coordination and transport. In the long-term, our approach may be useful for 137Cs+ separation, helping to minimize nuclear waste volume, and lower environmental risks associated with radioactivity.

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EXTRACTION OF ALKALI METALS BY A CALIX[4]ARENE BISCROWN-6 ETHER:
WHEN MODIFIERS MEET MODELING...

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Fundamental research on calix[4]arene biscrown-6 ethers, molecules known for their exceptional abilities to extract selectively cesium over other alkali metals, has led to new insights into the metal-binding properties of these useful compounds and deeper understanding of why solvation effects are so important.

Recent extraction results indicate that the calix[4]arene frame in the 1,3-alt conformation accommodates univalent cations larger than Cs⁺. Extraction data for the short-lived Fr-221 radionuclide were collected and evaluated based on modeling by the program SXLSQI. Understanding these results will be of value in addressing the issue of conformational flexibility and strain in calix-crowns. When the calix-crown extractants are used in aliphatic diluents, their solubility and extraction strength decrease drastically. However, the addition of fluoro-alcohol derivatives to the systems produces a dramatic increase in extraction strength. These derivatives are solvating components also known as modifiers. Anion solvation is believed to be one of the principal reasons modifiers yield such extraction enhancement. This hypothesis was confirmed following anion-mode electrospray mass spectrometry experiments. It was shown that the modifiers are associated as 1:1 complexes with various anions. Detailed equilibrium-modeling studies were carried out with extremely simple systems to learn how the modifier acts cooperatively with the calixarene-crown ether. Extraction of cesium was investigated for selected modifiers at various concentrations in dodecane diluent from simple aqueous mixtures containing only cesium nitrate in sodium or potassium nitrate. A complete speciation model was determined for all systems. The stoichiometry calix:cation:anion was confirmed as 1:1:1 in all cases. The number of modifier molecules involved in the complexes still needs to be determined with accuracy.

These fundamental results have proven to be of considerable value in USDOE Office of Environmental Management programs to remediate high-level waste. Such applied development has led to a new solvent-extraction process involving the first calixarene-crown compound to be used successfully in a commercially viable method for selective cesium removal. Testing of the process on Savannah River High Level Wastes has reached the engineering level and so far has shown that all the SRS requirements could be met or exceeded.

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ION FORMATION MECHANISMS IN MOLTEN GLASS ION EMITTERS

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Extensive experimental and computation work has been performed that for the first time provides a rational framework for the explanation of the thermal ion formation method commonly referred to as the silica gel method. This important analytical method has been in wide use for over 30 years as the preferred technique for the thermal ionization analysis of approximately 20 elements that volatize at relatively low temperatures and have high ionization potentials. Pb is the element most commonly analyzed by this method, usually in association with U/Pb age dating. The technique typically involves adding a small quantity of silica gel to a rhenium filament, adding the element of interest in a solution, adding a solution of boric or phosphoric acid and evaporating to dryness. This is then inserted into the instrument and slowly heated. We have identified these materials as molten glass ion emitters and shown with an ion source imaging instrument that ions originate from the surface of the molten glass.

We originally suspected that ions might be pre-forming in the molten glass and volatilizing, however, this has been disproved for at least ten of these elements, including Pb and Ag. Extensive experimentation with Ag ion emitting glasses were conducted that conclusively demonstrate that Ag is reduced to the elemental state in the molten glass. Special instrumentation was designed and constructed that allowed the thermal desorption curves to be measured for Ag ions and neutrals, and there was substantial overlap between the ions and neutrals. This demonstrated that the two species originated from the same species in the molten glass. The thermal desorption curves were also near overlaps with Ag neutrals from pure Ag compounds. Extensive thermodynamic computations were conducted on Ag and nine other elements, and these demonstrated that there is extensive reduction to the elemental state in the molten glass. This lends credence to the concept that ions originate by a Saha-Langmuir process with neutrals volatilizing from the surface and a certain percentage of these being stripped of an electron to form a positive ion.

The problem with this model is that the work function of the surface must be one to two eV higher than what would be normally expected for this type of surface. The work function of molten glass has never been measured, but judging by the measured work functions of various silicon and boron oxide surfaces, it would be expected to be about 5eV at the most. A work function of 6 to 7 eV would be required in order to account for the observed ion formation efficiency. An outcome of the thermodynamic modeling is the prediction that rhenium and its oxides are soluble to some extent in the molten glass, and previous work by Davis has shown that the work function of oxidized rhenium surfaces can be as high as 7.2eV. If the surface of the molten glass were to be coated with rhenium oxide, and the work function were to be in this range, quite high ion formation efficiencies could be expected.

Thus, a model is proposed against which future experiments will be designed. This model has the element dissolved in the molten glass in the zero oxidation state, with a work function sufficiently high to allow a relatively high percentage of neutrals volatilizing from the surface to be stripped of an electron to form a positive ion.

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SMALL-SCALE STUDIES FOR CONTROL OF ELECTRICALLY DRIVEN SEPARATION PROCESSES

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Electrically driven chemical processes have been pursued for several years because of their promise for enhanced performance and efficiency. The external control provides flexibility, and is particularly important for process intensification/miniaturization. In addition, electrically driven technologies may be considered environmentally friendly because of greater efficiency and reduced/eliminated chemical addition. Electric fields can be applied to chemical processes to increase mass transport by increasing interfacial area and mixing, to improve separation of phases by attracting dispersed entities, etc. Examples to be highlighted in this presentation include studies at the macroscopic scale of electric field effects on fluid dispersion, coalescence, mixing, flow, and sorption. As the scale of chemical processes is made smaller, interfacial phenomena become more dominant, presenting both challenges and opportunities for applying electric fields. Studies currently in progress will be described on electrohydrodynamic flows in the microscale, which could be used in microanalytical devices, for example, and on the effects of electric-double-layer overlap on electrosorption capacity in the micropores of sorbents. These studies are being pushed still further to explore the behavior of liquids in nanoscale channels and the additional questions that arise at this scale. Perspective will be given on the emerging experimental, theoretical, and computational approaches, which will be necessary to gain a greater understanding of electrical and interfacial effects on transport phenomena over the full range of size scales and on methods for bridging these scales to unify our approach to electrically driven chemical separations.

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TRANSIENT GRATING STUDIES OF THE PHOTOACOUSTIC EFFECT FROM PARTICLES AND PRODUCTION OF $^1\Delta$ OXYGEN BY PHOTODYNAMIC THERAPY AGENTS

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Here, two transient grating problems are discussed, the production of the photoacoustic effect by a point sources of heat, and, secondly, the production $^1\Delta$ oxygen by a photodynamic therapy agent. In the first problem, a theoretical description of the photoacoustic effect with linear and nonlinear source terms is given. The nonlinear effect is expected to be seen in water since its thermal expansion coefficient rises with temperature. Solutions to the wave equation for the displacement potential are found for the case of delta function heat liberation. The solution for the source linear in the temperature gives a fast rising exponential pressure pulse whereas the nonlinear source gives a bipolar pulse. The photoacoustic pressure for long laser pulses is found for the linear problem to be proportional to the first time derivative of the optical intensity. The solution for long pulses for the nonlinear problem is not so general: the functional form of the spatial and temporal profile of the temperature pulse must be specified in advance. For a Gaussian laser pulse, the photoacoustic wave generated by the point source is shown to resemble the second time derivative of the intensity profile, but with some diminution of the amplitude in time. The shape of the waveform can be understood as a heating pulse followed by what acts as a "cooling" pulse. The latter describes a diminution in the fluid density caused by heat diffusion from a region of space that has already been heated and compressed. The nonlinear effect is shown to be large in many experimental situations. The unique characteristics of a transient grating from such point particles is discussed and compared with experimental results.

We also describe transient grating experiments where a photodynamic therapy agent, zinc octakis (perfluoroisopropyl) perfluorophthalocyanine, F64-Zn-Pc, is excited by a pulsed dye laser. The presence of oxygen in solution is shown to produce a profound change in the character of the transient grating signal. A model is given based on energy transfer from the excited singlet state of the dye to an excited triplet state followed by chemical reaction of the excited triplet state with ground state oxygen in solution to produce excited $^1\Delta$. The resulting expression describes the experimental data and permits several kinetics parameters to be determined. The salient point of the study is that the transient grating method is highly sensitive to production of excited oxygen and that the efficiency of a dye for producing excited oxygen can be determined in a direct way through a straightforward physical measurement.

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THE “ONE-TWO PUNCH” APPROACH TO LASER MATERIALS INTERACTIONS WITH TRANSPARENT MATERIALS

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Wide bandgap insulators such as ionic crystals are highly transparent to most laser light yet can often be made to exhibit strong “interactions”. Plying crystals with two stimuli (the “one-two punch”), for example a laser beam plus:

- an electron beam
- a second laser beam
- mechanical stimulation

can generate high densities of defects causing dramatic increases in coupling to the laser. We present the consequences and synergisms that arise during simultaneous exposures of ionic single crystals including NaNO₃, a major component of Pu-high level waste materials at Hanford, NaCl (a model ionic crystal), CaCO₃ (an important component of the soil) and CaHPO₄·2H₂O (brushite--an important phosphate and biomaterial as well as a good model for hydrated ionic materials). One important aspect of these studies is careful characterization of the modification in morphology and in chemical composition that arises from these treatments. The influence of these modifications on both UV and near IR laser interactions have been studied. Physical models of these effects will be presented and the implications regarding material removal rates, plasma formation, and chemical analysis will be presented. The role of water has been found to be extreme in that it results in significant damage to crystals, transport of ions from the bulk to free surfaces (including voids), and the recrystallization/efflorescence of material. In addition, water from the gas phase can dramatically increase the rates of radiation induced decomposition of ionic materials, sometimes by factors of 10. This can lead to highly localized etching of material causing exotic topographical changes. As examples of this, we show two micrographs of this strong surface modification due to (a) electron irradiation and (b) 248 nm Excimer irradiation of single crystal brushite surfaces. In addition to interesting optical properties, these surfaces are highly sensitive to additional exposure to laser light in terms of ion, electron, and neutral emission.

(a) Electron Beam Generation of Nano-Cones on CaHPO₄·2H₂O (brushite)
(b) Micro-Flowers generated by 248 nm excimer laser irradiation of CaHPO₄·2H₂O (brushite).
Recently, the need for new and improved separations technologies, particularly for metal ions, has grown significantly. Solvent extraction (SX) is frequently the method of choice for both process-scale and (with suitable modifications) analytical-scale metal ion separations, a direct result of its physical simplicity and versatility. Although there are a number of both physical and chemical parameters in any liquid-liquid system that can be varied to enhance the efficiency and selectivity of the system for extraction of a particular ion, in the final analysis, the success of a given extraction process is frequently governed by the efficiency and selectivity of the extractant itself. For this reason, there has long been considerable interest in the design and synthesis of extractants of improved specificity for selected metal ions.

Recent work in our laboratory has focused on the use of macrocyclic polyethers (crown ethers) for the separation and preconcentration of various metal ions, both in liquid-liquid extraction and in ion-exchange and chromatographic systems. Of particular interest in our work has been the elucidation of the factors governing metal ion extraction from acidic media by crown compounds and the exploitation of these factors in developing improved methods for the separation of selected fission product (i.e., alkali and alkaline earth) cations. Previous work has established that a number of structural features of a crown molecule determine the strength and selectivity of its interaction with a given metal ion and thus, its usefulness as a metal ion complexing agent / extractant. Although the effect of many of these parameters has been thoroughly investigated, the influence of crown ether stereochemistry has received relatively little attention. In collaboration with Pacific Northwest National Laboratory, we have recently demonstrated the utility of molecular mechanics methods in establishing the relative extraction efficiency of various crown ether stereoisomers, identifying appropriate synthetic targets, and understanding the often substantial differences in extraction behavior observed for commercially available crown ethers. In conjunction with these studies, we have sought improved methods by which selected stereoisomers can be either synthesized or isolated from commercial preparations, and these efforts have led to both improved routes to the preparation of several isomers of dicyclohexano-18-crown-6 and to a combined chromatographic/ selective precipitation approach to the isolation of several stereoisomers of its di-t-butyl-substituted derivative.

In an effort to avoid stereochemical influences on complexation/extraction behavior, we have also been examining the application of simple, unsubstituted crown ethers (e.g., 18-crown-6), compounds generally regarded as having little utility in SX systems due to their significant water solubility, in metal ion separations. Certain of these compounds have been found to have a significant effect (i.e., selective enhancement of retention) on the elution behavior of alkaline earth cations on strong-acid cation-exchange resins, and it has been demonstrated that these effects can be exploited to devise improved methods for their separation. Follow-up studies using the same crown ethers in an SX system employing lipophilic sulfonic acid cation exchangers in o-xylene indicate that selective synergistic enhancement of cation extraction is also possible in these systems. Both of these observations offer additional opportunities for the design of efficient and selective metal ion separation schemes. The application of solvent effects offers a similar range of opportunities for the development of novel systems for metal ion separations.

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INVESTIGATION OF MASS EFFECTS ON THE UNIMOLECULAR DISSOCIATION OF DIATOMIC IONS IN QUADRUPOLE ION TRAPS

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Experimental and theoretical studies in our laboratory have focused on characterizing the unimolecular dissociation processes that occur in the multicollisional environment of quadrupole ion traps.(1-3) We have extended our investigations of polyatomic organic ions to strongly bound diatomic metal oxides such as TaO+ (D_o = 8.2 eV) which represent an extreme case in terms of dissociation energy and degrees of freedom. Recent investigations characterized the conditions required to reliably measure collision induced dissociation (CID) rates.(1) Mass effects influencing CID are described in this work and our observations have led to a novel approach to determining dissociation energy. This approach is a modification of the original rate determination method, and it accounts for shifts in secular frequencies with excitation time, voltage, and ion densities.

A Teledyne 3DQ quadrupole ion trap is used to collect ions produced from a pulsed glow discharge ion source. Metal oxide ions are then obtained by ion-molecule reactions with molecular oxygen. Previously optimized CID conditions for diatomic ions are 0.5 mTorr Ne and q_z=0.67. Resonance absorption curves for a suite of lanthanide (plus yttrium) oxides were collected at a fixed voltage (250 mV_{ppp}) and time (20 ms). The maximum percent dissociation was normalized to an internal standard (PrO+) before plotting as a function of mass (for a constant bond strength) or bond strength (for a near-constant mass).

Initial CID rate comparisons showed no direct relationship to bond strength. Center-of-mass effects were thought to be the primary factor influencing the results. A series of experiments using lanthanide oxides was designed to probe mass effects on CID rates. A modification of our experimental approach was required because the dissociation rate measurements incurred several problems. The secular frequency for a given m/z shifts as a function of ion density, excitation amplitude, and excitation time. Also, the dissociation rate varies as a function of ion density, even when excitation remains on-resonance.

Resonance excitation absorption curves were measured to alleviate the problems of resonance frequency shifts. Normalized percent dissociation, obtained from the absorption curves, was plotted as a function of oxide ion mass for oxides having the same dissociation energy (within experimental error). A linear dependence on mass was established. The percent dissociation for the remaining oxide ions was plotted as a function of bond dissociation energy. Using the mass correction, the dissociation rate falls on a linear curve with respect to bond energy. The results indicate that ion mass is clearly a first order correction and that metal oxides of different masses can be compared on a calibrated scale for absolute dissociation energy measurements. Future studies will focus on higher mass ions (actinide oxides) and the effect of counter ion identity and size (e.g., alkanes, sulfides, hydroxides, methoxides) on unimolecular dissociation.

Although the plus six oxidation state of iron has been known for more than 150 years, there have been comparatively few kinetic studies reported of this powerful oxidant until fairly recently. Preparation of \( \text{K}_2\text{FeO}_4 \) by the hypochlorite oxidation of ferric hydroxide is straightforward and the brown salt can be stored indefinitely in a desiccator. Atmospheric pressure and variable high pressure stopped-flow visible spectroscopic data and EPR spin trap data have been combined with reaction product analyses to elucidate the mechanism of the oxidation of alkaline aqueous phenol by the \( \text{FeO}_4^{2-} \) ion. Reactions have half-lives of the order of seconds. Results will be compared with similar data obtained for the oxidation of alkaline aqueous aniline by the ferrate(VI) ion. In both cases reaction proceeds by a pathway involving free radicals. Negative activation volumes are deduced from the pressure dependence of the rate constants suggesting the formation of highly structured transition states. Practical applications of iron(VI) chemistry will be considered. Future work will include the use of ring-substituted anilines and N-substituted anilines to achieve a more comprehensive view of the oxidation mechanism. In an unrelated future study, a pulse-quench flow reactor and a high-temperature high-pressure diffuse reflectance reaction cell will both be used with our Bruker IFS 66/S FTIR spectrometer to examine adsorbed reaction intermediates in gas phase reactions catalyzed by supported heterogeneous catalysts.
HIGHLY SELECTIVE MEMBRANE MATERIALS FOR THE REMOVAL OF CARBON DIOXIDE FROM MIXTURES WITH LIGHT GASES

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The selective removal of carbon dioxide and other acid or polar gases from mixtures with light gases such as H$_2$ is an important step in the purification of synthesis gas that cannot be performed economically or efficiently with current generation polymer membranes because they are more permeable to H$_2$ than to CO$_2$. This research program focuses on new classes of polymer membrane materials that are simultaneously much more permeable to CO$_2$ than to H$_2$ and have extremely high CO$_2$ permeability. These membrane materials would be the cornerstone of a new, low energy route to concentrate CO$_2$ from mixtures with light gases (e.g., H$_2$, N$_2$, etc.) in order to simultaneously purify the light gases and produce a concentrated CO$_2$ stream for further utilization or sequestration. The new materials for this application would be heterophase block copolymers where one block (the soft block) is selected to have exceptional CO$_2$ permeability and selectivity and the other (the hard block) provides mechanical strength and processing flexibility. In a departure from traditional gas separation membranes, these materials are designed to be more permeable to larger molecules (e.g., CO$_2$) than to small molecules (e.g., H$_2$). The addition of salts to the polymer matrix can enhance both permeability and selectivity of acid gas components.

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At elevated temperatures, it is possible to increase the cation-to-anion coordination without changing the chemical composition of the systems. At moderate- to low concentrations and under ambient conditions, most cations and anions would normally be fully dissociated. However, at high temperatures the contact-ion pairs form. Thus, for aqueous systems containing simple salts, one can explore both the hydration and the contact-ion-pair chemistry. In contrast, the chemistry of organic ligands is a great deal more complex because the symmetry and binding are strongly influenced by the structure of the ligand. Hence, the coordination structure derived from these simple aqueous solutions is relevant to building a better understanding of the coordination chemistry of metal ions to large organic ligands or to biomolecules. Furthermore, these results are also of interest for comparison to ab initio and density functional methods because of the simple nature of the ligand structure.

The method used in this characterization is x-ray absorption fine structure spectroscopy (XAFS) which accurately measures the first-shell structure about ions. For aqueous systems, an understanding of this first-shell structure is paramount to defining the controlling thermodynamics of the system. Only recently has the utility of this technique been realized for probing aqueous systems well above 200°C.

As an example, at elevated temperatures, the linear dichloro Cu\(^{1+}\) species, [CuCl\(_2\)]\(^-\), is especially stable and it is predominant from 100°C to 325°C in the presence of excess Cl\(^-\). Even for solutions with 2.0 m NaCl, only the dichloro Cu\(^{1+}\) species is observed with no evidence of higher Cl\(^-\) coordination. There is no evidence of hydration waters in the first solvation shell of this unusual dichloro-species.

The behavior of Ni\(^{2+}\) is different. At room temperature, the octahedral Ni\(^{2+}\)(H\(_2\)O)\(_6\) species persists at all salt concentrations, but at higher temperatures it is replaced by four-coordinate structures. Above 425°C the stable structures are a family of four-coordinated species where the degree of Br\(^-\) adduction and replacement of H\(_2\)O in the inner shell depends upon the overall Br\(^-\) concentration. These results are of interest for predicting salt solubilities in hydrothermal processes including the separation of ionic species from aqueous waste streams. They are also applicable to the areas of geochemistry and to power plant corrosion chemistry in which analogous chemical systems are found.

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SURFACE-INDUCED DISSOCIATION (SID) POLYATOMIC IONS

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Our research is concerned with the collisional activation and dissociation of molecular ions—the fundamental processes involved in tandem mass spectrometry. Our approach utilizes molecular beam methods to define experimentally energy transfer in the collisional activation step and uses RRKM theory based modeling of energy-resolved fragmentation efficiency curves obtained in a Fourier Transform mass spectrometer to define the energetics of unimolecular decomposition of excited ions. The thrust of recent investigations is to extend these methods to the decomposition of complex molecular ions which are generated by electrospray ionization. An important class of complex molecules we are investigating is model peptides. This has the objective of improving our understanding of and devising improved strategies for determining the amino acid sequence in peptides of moderate complexity. Several salient features of the decomposition of large ions include substantial kinetic energy shifts, requiring large excess internal energy to drive the decomposition in the time frame sampled by mass spectrometry. To induce decompositions of these ions current practice involves multiple collision activation in ion traps and the operation of electrospray ion sources with several Townsend extraction fields to introduce substantial amounts of internal energy into protonated peptides while stripping solvent molecules.

Our current research focus is achieving a detailed understanding of energy transfer in multiple collision gas phase activation and in surface collisional activation of complex ions. By controlling the pressure in an ion cyclotron resonance cell pressure and applying progressively higher amplitude RF in sustained off-resonance irradiation (SORI) large amounts of internal energy can be transferred to the ion. However, the effective mass resolution of ICR decreases by orders of magnitude because of collisional dephasing of coherent ion motion while SORI is applied. Restoring high mass resolution requires time delays of several seconds to pump out the collision gas, effectively limiting ICR studies to slow decomposition processes. An attractive alternative is surface-induced dissociation (SID) using self-assembled monolayers of alkyl-thiols on gold. Utilizing a “soft” collider semi-conductor surface maximizes energy transfer into the surface, minimizes recoil kinetic energy in the molecular ion and enables immediate determination of the fragmentation pattern at high mass resolution. Modeling and experiment support the hypothesis that collisions with “soft” surfaces are qualitatively similar to sequential multiple collision activation in SORI. Quantitative differences are readily rationalized by considering competing energy loss processes in gas phase collisions sustained over substantial fractions of a second while SORI is applied. For peptide ions radiative energy loss during the “cooling” period of several seconds to pump out the collision gas is an additional competing process.

Our poster will provide details of new experimental apparatus constructed for characterizing dynamics of these processes and summarize recent results.

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A primary goal of our ongoing work is investigation of the ion processes occurring in the unique environment of quadrupole ion traps. Because the underlying principles for many of the phenomena are not yet fully understood, in-depth study of them will likely indicate directions for improving mass spectrometric approaches to solving molecular measurement problems, and conceivably, altogether new analytical measurements. For example, collision-induced dissociation (CID) is generally used to obtain macro-ion sequence information from the spectrum of charged products arising from unimolecular decomposition. Yet, the multiple collision nature of ion trap collisional activation also makes it possible to use the measurement of CID kinetics to derive the Arrhenius activation energy and the entropy change leading to the transition state. There is considerable interest in developing and refining methods to derive still other fundamental information for such species. Thus, we will discuss the possibility of using ion trap CID rate data to make a new kind of measurement, namely the determination of cross-sections for activated ions.

Although it is still uncertain as to how closely gas-phase conformations are related to those in solution, accurate measurements of collision cross-sections can improve the understanding of the specific conformations of peptides and proteins. Among the most popular techniques for making collision cross-section determinations is ion mobility spectrometry, a technique based on measuring the transport velocity of gas-phase ions through a buffer gas while under the influence of a DC electric field. Ion velocity in an electric field depends on charge state, z, collision cross-section, and ion-neutral reduced mass, which is independent of ion mass for macro-ions. The ion trap CID method generally involves the use of an AC electric field in resonance with ion secular motion to increase the velocity of stored ions. The corresponding effective temperature for ions undergoing dissociation can be established using Arrhenius parameters. With the effective temperature in hand, the expression below can then be used to determine ion velocity, and subsequently, the collision cross-section.

\[ T_{\text{eff}} = T_{\text{buffer}} + \frac{m_{\text{buffer}}}{3k} v_{\text{ion}}^2 \]

In this case, the relevant cross-section is that for the activated ion. The charge dependence can become complex if macro-ions adopt an enlarged conformation with higher charge state to reduce the increasing coulomb repulsion energy. In addition, a complex dependence on effective temperature could result if variation in ion internal energy disrupts the relatively weak intramolecular interactions that contribute to ion conformation, thereby affecting the cross-section.
A semiempirical model is developed for an optically thick inhomogeneous laser induced plasma (LIP). The model describes time evolution of the plasma continuum and specific atomic emission after a laser pulse has terminated and interaction with a target material has ended. Local thermodynamic equilibrium (LTE) is assumed allowing application of the collision-dominated plasma model and standard statistical distributions. Calculations (Figure) are performed for a two-component Si/N system.

The model input parameters are the number of plasma species (or plasma pressure) and the atomic ratio of silicon to nitrogen which ranged from 0.01 to 10. Functions are introduced which describe evolution of temperature and size of the plasma. All model inputs are measurable in the experiment. The model outputs are spatial and temporal distributions of atom, ion, and electron number densities, evolution of an atomic line profile and optical thickness, and the resulting absolute intensity of plasma emission in the vicinity of a strong non-resonance atomic transition. Practical applications of the model include prediction of temperature, electron density, the dominating broadening mechanism. The model can also be used to choose the optimal line for quantitative analysis.

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NEW NMR APPROACHES FOR STUDYING GAS BINDING AND GAS SEPARATIONS IN ZEOLITES, LITHOSILICATES AND HALOZEOTYPES

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The talk will describe our work in two research areas: (i) the development of new NMR approaches to study gas sorption in molecular sieves and (ii) gas sorption and structural studies of novel zeotypes. Two new classes of materials have been investigated, namely lithosilicates and copper aluminum chlorides. In collaboration with John Parise (SUNY Stony Brook) and Hermann Gies (Ruhr University of Bochum), we have been investigating the sorption properties of a new lithosilicates, where lithium has been substituted for silicon, into the zeolite framework. Substitution of a monovalent cation requires charge balancing by an additional three M⁺ cations, resulting in large numbers of extraframework cations. Lithium also has very different coordination preferences, yielding novel framework types such as RUB-29.¹ Copper aluminum chlorides have recently been shown by James Martin et al. (North Carolina State University) to reversibly sorb small molecules such as ethylene and carbon monoxide.² We, in collaboration with the N.C. State group, have identified a series of ethylene-loaded copper aluminates, by using time-resolved X-ray diffraction (XRD) measurements. Both XRD and double resonance NMR experiments were used to identify the ethylene binding site and the effect of gas binding on the MCl₂ (M = Al³⁺ and Cu⁺) framework.

The binding of larger molecules to a surface will be determined by a number of often competing interactions. In order to separate some of these contributions, we have been examining how different parts of the same molecule are coordinated to the internal surfaces of zeolites, and the surface of -Al₂O₃, by using a series of double resonance NMR experiments. For example, cross polarization (CP) NMR experiments have been used to study the binding of the asymmetric hydrofluorocarbons (HFCs) CF₃CFH₂ (HFC-134a), CF₃CF₂H (HFC-125) and CF₂HCFH₂ (HFC-143) on zeolites NaX and NaY. By exploiting the very large differences in ¹⁹F chemical shifts for the -CF₃, H₃ end groups of each molecule, individual ¹⁹F → ²³Na CP build-up curves involving polarization transfer from different parts of the molecule have been obtained. CP efficiencies in the order CF₃ < CF₂H < CFH₂ were found, indicating that the hydrogen-containing groups are bound more strongly to the zeolite framework. This effect is most pronounced for the lowest-sodium content zeolite studied (NaY: Si/Al = 7.6), and increases with HFC loading. These results are explained by a competition of the two end groups for the available Na cations and a less effective averaging (due to residual motion) of the Na-F dipolar coupling for the more strongly bound end groups. Extensions of this work to study interactions with the oxygen atoms of the zeolite framework will be described.

The surface of all adsorbents is heterogeneous. This phenomenon arises mainly from the tendency of the elemental impurities of the material making the bulk of the adsorbent (e.g., boron or iron in silica) to segregate at the surface. Foreign elements are more concentrated on the surface of adsorbents than in their bulk and only high purity adsorbents have relatively homogeneous surfaces. The presence of various element impurities on the surface and the strains of the bonds involving polyvalent atoms at the solid interface cause a nonuniform distribution of the adsorption energy of the probes used to study the surface. The profile of this distribution, particularly the number, width, and position of its modes, may characterize the heterogeneity of the surface. Numerous authors have attempted to relate the experimental isotherms of different probes and the characteristics of their adsorption energy distribution. However, the theory is complex. The derivation of the adsorption energy distribution from the isotherm results in a numerically ill-posed problem. Unfortunately, there are no valid tests of these relationships because there are no reference surfaces for which the adsorption energy would be known or could be determined straightforwardly.

We are investigating the application of conventional methods of determination of the adsorption energy distribution to adsorbents specially synthesized. Selected chiral ligands are chemically bonded to porous silica for HPLC. These ligands can form different association complexes with the two enantiomers of a probe compound. In this case, the contributions of nonselective interactions to the energy distributions will be the same for the two enantiomers. The difference between the adsorption energy distributions of the two enantiomers will be entirely explained by the differences between the interactions that take place between the ligands and the two enantiomers. These interactions can be determined separately. Various methods of validation of the results obtained will be presented. This approach should permit the validation of a procedure of determination of the adsorption energy distribution of a surface. Such a procedure would allow quantitative studies of the surface properties of many heterogeneous adsorbents.
DEVELOPMENT OF VIBRATIONAL SPECTROSCOPY METHODS TO CHARACTERIZE ADSORPTION AND BINDING PROCESSES AT LIQUID/SOLID INTERFACES

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The theme of this research is the development of surface-sensitive vibrational spectroscopies for studying chemical structure and reactions at liquid/solid interfaces. These spectroscopic tools lead to new understanding of interfacial chemistry that impacts both analytical methods (chromatography, solid-phase extraction, and optical sensors) and environmental transport and remediation (metal-ion complexation to bound ligands, adsorption interactions at oxide surfaces). We are developing in situ vibrational spectroscopies, both Raman and infrared, to probe the chemical structure of adsorbed and bound species at silica/solution interfaces. We are using these tools to investigate metal-ion complexation at silica-immobilized ligands and the specific molecular interactions responsible for adsorption, solid-phase extraction, and molecular recognition at both bare and chemically-modified silica surfaces. The chemistry of metal-ion complexation to silica-immobilized ligands is being monitored through the use of an in situ fiber-optic Raman probe. This probe has been used to investigate the interfacial chemistry of surface-bound 8-hydroxyquinoline, both its acid-base chemistry, its binding of several different metal ions, and the influence of surface potential on these processes. Surface-enhanced Raman spectroscopy (SERS) is being used to study site-dependent charge-transfer interactions at metal surfaces as a prelude to using SERS to probe the local electric field at polarized interfaces. The latter goal will be achieved through the measurement of Stark-tuning rates of C≡N stretching frequencies of cyanoalkanethiols chemisorbed to silver surfaces. The methodology is being adapted to electric-field perturbation experiments to investigate the influence of potential on the adsorption or binding of ionic species at insulating surfaces. We have also deposited hydrophobic insulating layers over SERS-active gold surfaces to accumulate PAH compounds from aqueous solution for high-sensitivity Raman-scattering detection.

In order to acquire in situ infrared absorption spectra of monolayers on the surfaces of silica in contact with liquids, we have captured a thin layer of colloidal silica particles onto internal-reflection elements to provide a high area surface for internal-reflection infrared measurements. This approach opens up a spectral window to the entire mid-infrared range and provides a 100-fold greater surface area for rapid detection of submonolayer species. We have used this technique to carry out a complete study of the adsorption chemistry responsible for non-linear adsorption behavior in normal-phase chromatography. This phenomenon was shown to arise from site heterogeneity on the silica surface and not bilayer adsorption or adsorbate delocalization, as was proposed in the chromatography literature. Competitive adsorption was also studied which is an important process for solute displacement and elution in normal-phase chromatography. We are presently adapting this technology to studies of enantiomerically selective interactions at chiral ligands immobilized on silica.

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The pulsing of a glow discharge offers several advantages over continuous operation, including high transient sputtering, excitation, and ionization. Although high power levels are obtained during pulse operation, the limited duty cycle means that sample heating problems can be reduced. An additional important consideration, particularly in mass spectrometry, is the opportunity for temporal resolution by separating in time the ion signals of the discharge and background gases from those of the ions arising from sputtered sample species. Time-of-flight (TOF) mass spectrometry permits optimum effectiveness of such time resolved measurements.

The pulsed glow discharge serves to interface well with the TOF by nature of its transient source of ions, something that is required for TOF operation anyway. A critical element in obtaining optimum temporal separation lies in the design of the ion extraction and transport system. Each pulse injects a packet of sample atoms into the glow discharge for collisional excitation and ionization. The integrity of this sample injection as it subsequently diffuses across the sample cell is influenced by discharge pressure, gas flow rate, and cell configuration. We have studied a series of samplers and skimmers as interfaces between our pulsed Grimm-type glow discharge and the TOF system. Many factors are interactive in defining success (or not), including sample to sampler distance, sampler to skimmer distance, orifice sizes, pressure differentials, etc. The opportunity presents itself to study fundamental aspects of ion interactions and transport, balanced against the resulting trace analysis measurements. We will report on the configurations evaluated to date and some initial analytical data.
Although inductively coupled plasma atomic emission spectrometry (ICP-AES) sources have been commercially available for almost two decades, the ICP still suffers from sample-related matrix effects. That is, the presence of other constituents in a sample influences the signal that is obtained from a given analyte concentration. Commonly, these inaccuracies are ignored; at best they are minimized through use of tedious, time-consuming procedures such as matrix matching, internal standardization, and standard additions. A better approach, in our view, is to characterize the processes that occur in the ICP and to overcome the interferences on a rational basis. In turn, a detailed picture of ICP behavior can be developed by measuring the fundamental plasma parameters of gas-kinetic temperature, electron temperature and electron concentration. It is these parameters that are directly responsible for sample volatilization, analyte excitation and analyte ionization. Furthermore, the measurement of atom and ion number densities and emission intensities yields information on the spatial distribution of analyte and plasma-gas species within the discharge and about their excitation. While it is desirable to study these processes on the plasma as a whole, additional information can be obtained by observing single particles introduced into the plasma.

In the inductively coupled plasma, the plasma structure and the emission intensities of analyte atoms and ions are controlled by the fundamental parameters. Accordingly, the effect of a sample matrix on the analyte emission intensity in an ICP might be attributable to changes in these fundamental parameters caused by the matrix elements. In recent studies, a plasma imaging instrument that combines Thomson scattering, Rayleigh scattering, laser-induced fluorescence and computed tomography has been employed to measure the above-mentioned parameters in the presence and absence of introduced matrix elements. The data thus obtained were all collected on a spatially resolved basis without the need for Abel inversion or any assumption of spatial symmetry in the ICP. Ca and Sr were used as analytes, while Li, Cu, and Zn were introduced as matrix elements. Comparing the data in the presence and absence of the matrix elements allows us to determine the extent to which each fundamental parameter changes in the presence of a matrix element, and to better understand the nature of the matrix effects that occur in the ICP.

The ICP has become very popular as an ion source for mass spectrometry and a great deal of research has been undertaken to clarify why the mass spectrum changes with plasma conditions. However, almost nothing has been done to determine whether and how an ICP-MS sampling interface influences the plasma itself. Not surprisingly, the plasma properties undergo a dramatic change when the flow passes the sampling-cone orifice, given the reduced pressure within the interface. However, it is unclear whether the fundamental properties of the plasma upstream of the interface will also be affected, considering the large gas flow taken in by the sampling-cone orifice, the relatively high thermal conductivity of the ICP, and the water-cooled metallic surface that directly touches the hot plasma. To observe what really happens to the plasma upstream of the sampling interface, Thomson scattering, Rayleigh scattering and laser-induced fluorescence have been measured on an inductively coupled plasma with and without a sampling interface in place. Radial distributions of $T_e$, $n_e$, $T_g$ as well as calcium and strontium ion number densities $n_i$(Ca) and $n_i$(Sr) were measured.
AQUEOUS BIPHASIC SYSTEMS: LINEAR FREE ENERGY RELATIONSHIPS AND SOLVATOCHROMIC PARAMETERS

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Aqueous biphasic systems (ABS) based on the critical phase separation of mixtures of polymers or polymers and salts in aqueous solution, may represent a useful alternative to conventional biphasic systems based on volatile organic solvents in a number of areas. We have demonstrated their application to the separation of metal ion species, small organic molecules, and their application to the separation of lignin species from cellulosics in a variant of the Kraft pulping process. ABS are also widely applied to protein recovery and purification in biotechnology. It has also been suggested that ABS represent the best hope for the molecular property characterization of a new generation of biopharmaceuticals, arising from our increased genomic knowledge, for which organic solvent systems such as octanol/water will be totally unsuited. In all these applications a thorough understanding of the nature of the solvent medium and its interactions with the solute is of paramount importance.

We are currently engaged upon a variety of studies in this area. ABS have been characterized by the free energy of transfer of a methylene group. Distributions of a wide range of small organic solutes have been compared to partitioning in the 1-octanol/water system. A Linear Free Energy Relationship based on the Gibbs energy related solute descriptors of Abraham has been developed enabling still wider comparison to conventional solvent systems and to similar micellar extraction systems. We have also begun characterization of ABS using Kamlet and Taft solvatochromic descriptors (π*, α, β). As a result of these studies a relatively consistent picture of the solvent properties of these systems is beginning to emerge which should be of considerable utility in the design of further applications, and in furthering our understanding of their major application to date, the purification and characterization of proteins.

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Glucose glasses are very effective amorphous solids for acquiring both solid-matrix fluorescence (SMF) and solid-matrix phosphorescence (SMP) at room temperature from aromatic compounds. An understanding of the photophysical aspects and physicochemical interactions of the lumiphors in the glasses is very important for developing novel glasses for trace organic analysis. The glucose glasses prepared from a melt have properties that are much more favorable than glasses prepared from crystalline glucose. For example, there was a 2- to 4-fold enhancement of SMP from heterocyclic aromatic amines. Near-infrared spectrometry, differential scanning calorimetry, NMR spectrometry, and solid-matrix luminescence spectrometry were used to investigate heterocyclic aromatic amines in glasses prepared from crystalline glucose and glucose melts. The experiments were performed to develop a better understanding of how the lumiphors interact in the glasses and to determine the properties of the glasses that are important for SMF and SMP.

A near-infrared method was developed for the determination of water in the glasses. The data obtained were used to generate quenching models for SMP and determine the effects of moisture on glass transition temperatures of the glasses. The SMP quenching model showed that random packing of the water molecules in the glasses resulted in narrow channels of free space. Thus, a fraction of the water molecules could move through these channels and cause dynamic quenching. Another portion of the water molecules altered the hydrogen-bonding network in the glasses and caused SMP matrix quenching. The glass transition temperatures of the glasses, which were acquired by differential scanning calorimetry, showed that these temperatures were very sensitive to the moisture content in the glasses. Also, the molecular mobility of glasses near the glass transition temperature was important for understanding the macroscopic changes that were associated with the glass transition temperature and ultimately how SMP was affected.

NMR spectrometry experiments showed that the anomic ratios of α- to β-glucose glasses were not significant for obtaining strong SMP. The water content of the glasses was more important in affecting SMP. Data acquired from SMP intensities and lifetimes from room temperature to 93K indicated that the excited phosphor was coupling with low-frequency vibrational modes in the glucose glasses and that β-relaxation phenomena in the glucose glasses were partly responsible for the nonradiative transition from the excited triplet state of the phosphor.

Several fundamental questions and future research opportunities have surfaced from our research in solid-matrix luminescence. For example, a few fundamental questions are: How do low-frequency vibrational modes in a solid matrix couple with an excited triplet-state probe molecule? Why is SMP dynamic quenching by oxygen and moisture inefficient in solid matrices? Some future research opportunities are: solid-matrix vibronic luminescence spectrometry, the direct determination of multiple intact carcinogenic DNA adducts, and sugar glasses in spectrometry.
INFLUENCE OF COVALENCY, COMPLEX STRUCTURE, 
AND SOLVATION ENERGETICS ON ACTINIDE COMPLEXATION 
IN SEPARATIONS-RELATED SYSTEMS

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The fundamental facets of solution phase actinide chemistry play an important role in the separation of the actinide elements from other groups of the periodic table and from each other. The primacy of hard-hard interactions, the variety of accessible oxidation states and the importance of the “-yl” ions, the flexibility of coordination numbers, the importance of cation dehydration in aqueous reactions, and the near equivalence of the trivalent lanthanide and actinide cations are all well documented themes. This work is concerned with providing quantitative measures of these effects in selected systems to expand our understanding of actinide chemistry at the outer limits of actinide solution chemistry, and to underpin ongoing work in heavy element separations chemistry.

Working with the Argonne Actinide Synchrotron Facility and BESSRC, the actinide (Am, Cm) and lanthanide (Nd, Sm) complexes with dioxo-, oxo(thio)- and dithiophosphinic acid extractants were studied using EXAFS, optical spectroscopy, and solvent extraction. The dithiophosphinic acid has been reported to extract Am\textsuperscript{3+} 6000 times more strongly than Eu\textsuperscript{3+}, presumably because of greater covalence in the Am complex. However, it was not known if the hypothesized covalency is manifested in measurable differences in the solution structures of the complexes. Even though the Cm-dithiophosphinate complex is extracted much more strongly than the Sm-dithiophosphinate complex, the metal-sulfur bond distances are indistinguishable for the Sm and Cm complexes in dodecane. For each ligand the coordination number of the metal and the metal-oxygen (2.30-2.33 Å) or metal-sulfur (2.80-2.81 Å) bond distances are independent of the metal cation, when the slightly different crystal radii (ca. 0.02 Å) of the cations is considered. Also, only sulfur donors are detected in the inner-sphere of the dithiophosphinate complexes despite the affinity of trivalent f-element cations for the water and nitrate present in the system.

To better understand the impact of aqueous solvation on the energetics of actinide complexation, we have been attempting to answer the question: how much of the reaction energy arises from intrinsic interactions between metal cations and ligands, and how much arises from the rearrangement of solvent molecules when the complex is formed. Isotopic substitution of the solvent has been employed to quantitatively fractionate the enthalpies, entropies, and free energies of complexation into solvent based and complex based contributions for the 2,6-pyridinedicarboxylate complexes of a several metal ions. In the case of a transition metal cation like Cu(II) that is prone to form bonds with more covalent character, the contribution of solvation to the enthalpy of complex formation is negligibly small. The energy of metal-ligand bond formation dominates. By contrast, a significant fraction of the complexation enthalpy of 2,6-pyridinedicarboxylic acid comes from solvent rearrangement when complexes with harder cations like Ca(II) or Nd(III) are formed.

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AGGREGATION PHENOMENA IN HEAVY ELEMENT CHEMISTRY

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A close collaborative effort between chemists and physicists involved in separations science, heavy element chemistry, solid state chemistry and physics, chemical thermodynamics, optical spectroscopy, and techniques employing synchrotron radiation has been initiated to expand our understanding of the origins, mechanisms, bonding, and morphology of heavy element aggregates in amorphous system. The combination of this expertise and these experimental techniques allows the examination of short and long range order and the energy that drives aggregation in a wide range of amorphous solid and liquid phases important to DOE activities in actinide separations processes, the remediation of contaminated sites, radioactive waste disposal, nuclear safety, and stockpile stewardship.

Most closely related to separations science are current studies of third phase formation in actinide/nitric acid/tributylphosphate/alkane systems. This previously studied system is understood phenomenologically, but a molecular level understanding of the nature of the third phase and its formation is absent. Visible and infrared absorption spectroscopy, EXAFS, small angle neutron scattering, and high energy x-ray scattering have been used to reexamine the U(VI)/nitric acid/tributylphosphate (TBP)/n-dodecane system with the objective of gaining coordination chemistry and structural information on the species that are formed in the organic phase at the onset of organic phase splitting. The infrared stretching vibrations of the phosphoryl and nitrate groups shift on extraction, indicating that uranyl cations replace HNO₃ hydrogen-bonded to the extractant, the nitrate ions are bound to the metal in a chelate bidentate or bridging environment, and molecular HNO₃ is present in the heavy third phase. Absorption spectroscopy and L₃-edge EXAFS data indicate that the inner coordination sphere of the U(VI) species present before the onset of third phase formation and the uranium species present in the light organic phase are the same. However, the inner coordination sphere of the uranyl cations in the heavy organic phase is distinctly different, incorporating fewer nitrate oxygens than the light phase complex. Both before and after phase splitting, the small-angle neutron scattering data reveal the presence of large cylindrical aggregates in the organic phase whose formation seems to depend more on the extraction of HNO₃ than that of U(VI).

Other systems under investigation include other third phase forming systems such as U(VI)/nitric acid/octyl(phenyl)-N,N-diisobutylcarbamoymethylphosphine oxide (CMPO)/n-dodecane, actinide-phosphate solids, aqueous colloids and polymers, and solutions of highly charged polyoxometallate anions.

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A fundamental understanding of steric stabilization in supercritical fluids is being utilized to design novel colloids including microemulsions and silicon nanoparticles. The properties of surfactants and polymeric stabilizers at solid or liquid interfaces in the presence of carbon dioxide are being studied by spectroscopic ellipsometry. The thickness and refractive index of poly(dimethylsiloxane) (PDMS) thin films on silicon, exposed to high pressure carbon dioxide, have been measured in-situ. The swelling of the film is determined from the thickness and the sorption of CO\textsubscript{2} from the refractive index. The sorption and swelling for the thin films exceed the values for bulk films. These increases may be attributed to excess CO\textsubscript{2} at the polymer thin film-CO\textsubscript{2} and polymer-silica interfaces, and the influence of the silica surface and CO\textsubscript{2} on the orientation of the polymer. Large surface excesses of CO\textsubscript{2} on the reference wafer were observed in regions where CO\textsubscript{2} is highly compressible due to critical adsorption. The formation of water-in-carbon dioxide microemulsions with a cationic perfluoropolyether trimethylammonium acetate surfactant, PFPE-C(O)-NH-CH\textsubscript{2}-N\textsuperscript{+}(CH\textsubscript{3})\textsubscript{3} CH\textsubscript{3}COO\textsuperscript{-}, is reported over a range of temperatures (25 – 90 °C) and pressures (87.3 – 415 bar). Spherical droplets are observed by SANS with radii ranging from 16 to 36 Å for water-to-surfactant molar ratios ($W_w$) from 9.5 to 28. Porod analysis of the SANS data indicates an area of approximately 60 Å\textsuperscript{2}/surfactant molecule at the water-CO\textsubscript{2} interface, in reasonable agreement with the value of 72 Å\textsuperscript{2} determined from the change in the droplet radius with $W_w$. The CO\textsubscript{2}-phobic functionality between the surfactant head group and perfluoropolyether tail reduces CO\textsubscript{2} penetration of the tails, resulting in a smaller area/surfactant than in the case of an anionic perfluoropolyether surfactant [Langmuir, 13, 3934 (1997)]. A relatively rigid film, with a mean film rigidity (2$K$ + $\overline{K}$) of approximately 1 $k_B$T, along with the strong partitioning of the surfactant towards CO\textsubscript{2} versus water, lead to the small, rigid, spherical water droplets in CO\textsubscript{2}. Highly monodisperse ‘artificial atoms’ of silicon, 15 Å in diameter, with discrete electronic and photoluminescence transitions have been synthesized in solution utilizing a capping solvent heated and pressurized above its critical point. Significant quantities of these nanocrystals are produced by thermally degrading the precursor diphenylsilane in supercritical octanol (T\textsubscript{c} = 385 °C, P\textsubscript{c} = 34.5 bar) at 500 °C and 345 bar. These nanocrystals are stable in solution at room temperature, even in the presence of oxygen, and exhibit discrete electronic absorption and photoluminescence transitions previously unobserved. Furthermore, these octanol-capped clusters show efficient band-edge photoemission with a luminescence quantum yield of 23 %. This study also confirms that nanoparticles of silicon do not undergo a change from an indirect to a direct semiconductor but that excitons in these very small clusters remain strongly coupled to phonons.

References:
EXCITATION AND IONIZATION IN A MS PULSED GLOW DISCHARGE PLASMA:
IMPLICATIONS FOR ATOMIC AND MOLECULAR DETERMINATIONS

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The use of glow discharge plasmas is now well established for trace element determinations. Their use is also well established in the materials science community in plasma vapor deposition for the production of novel thin film materials, i.e. diamond-like films. It is well known that the ability to generate a film of a desired composition, quality, or purity is linked directly to the operating parameters of the deposition plasma. To a large extent, this arises because these parameters also control the rich chemistry inherent in these plasmas. Similar to the case in analysis, the parameters of the plasma are tuned to optimize the chemical processes desired. It is clear that in order for such varied chemistry to occur, the chemical composition of the plasma must be tunable as well. In collaboration with Dr. Vahid Majidi’s group at Los Alamos National Laboratory, we have been exploring how this rich variation in glow discharge plasma chemistry might be utilized to afford chemical speciation, and how we optimize this chemistry to obtain optimal analytical performance in this application.

Our efforts have focused principally on glow discharges operated in a pulsed power mode. Because excitation and ionization processes vary widely over the pulse cycle, we can temporally select the chemistry to be observed and thereby generate spectra with elemental or molecular information. Coupling such temporal resolution with spatial resolution provides the optimum selectivity and sensitivity for a specific analysis. This work employs a simple coaxial cathode argon-glow discharge operating in a pulsed power mode, typically at 50 Hz with a 25% duty cycle. When coupled with time-of-flight mass spectrometry, this provides information regarding the elemental composition, molecular structure, and molecular weight for simple organic molecules. Temporally and spatially resolved optical spectroscopy of the plasma provides insight into the processes leading to the excitation (or dissociation) and ionization of both atomic and molecular species.

Early in the collaboration we demonstrated that depending on the time of observation in the plasma operating cycle, we could obtain mass spectra for BTEX compounds that were dominated by the molecular ion, as in CI, or fragment ions, as in EI. In recent work a GC has been coupled with the pulsed GD-ToFMS to yield GCMS data with alternating EI or CI spectra for the analyte. A subsequent investigation employing tungsten hexacarbolyl demonstrated a marked change in the energy imparted to molecules during the prepeak, plateau, and afterpeak time regimes of the plasma. Most interesting was that the energy imparted in the afterpeak agreed well with the known potential energy of the metastable argon atoms at 11.5 eV. From previous work it was known that metastable argon atom formation is enhanced during the afterpeak time regime of these pulsed glow discharges.

Temporally and spatially resolved optical spectroscopy of the glow discharge provides insight into the variation of temporally dependent processes as a function of distance from the cathode surface. Of particular interest is the distribution of the electron excitation/ionization v. Penning ionization within these plasmas. It was found that the population maximum for these species shifts from 1-2 mm beyond the cathode surface during the prepeak or plateau time regimes to 4-7 mm beyond the cathode surface during the afterpeak time regime. The maximum population of metastable argon atoms during the afterpeak arises principally through recombination processes; whereas, their population in the prepeak appears to arise through electron excitation to higher levels followed by radiative decay. Spectroscopic study of copper atoms and ions in the plasma reveal that: 1) electron excitation/ionization processes dominate within about 2 mm of the cathode during the prepeak and plateau time regimes, and 2) Penning processes involving metastable argon atoms dominate at about 5 mm from the cathode surface during the afterpeak time regime.

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Our project focuses on understanding and tailoring two classes of high performance materials that show superior performance compared to conventional polymers used in membrane-based gas separations and pervaporation. The materials being studied include: (i) molecular sieving carbons and (ii) crosslinked polymers. Separation of economically important, but technologically challenging feeds such as high pressure natural gas (e.g., CO$_2$/CH$_4$), olefin-paraffin (e.g., C$_3$H$_6$/C$_3$H$_8$) and aromatic-aliphatic (e.g. toluene-isooctane) are model systems that are being studied.

We have produced carbon molecular sieve materials that greatly surpass the upper bound selectivity vs. productivity performance of traditional polymer membranes for gas separations. Separation of C$_3$H$_6$/C$_3$H$_8$, O$_2$/N$_2$ and CO$_2$/CH$_4$ pairs will be discussed to illustrate these achievements. The effects of systematic changes in the pyrolysis parameters used to produce the various carbons will be illustrated and discussed.

Our work with the second group of materials, crosslinkable polyimides, suggest that they probably provide the most practical avenues to the next generation of practical natural gas and aromatic-aliphatic separation membranes. Aromatic polyimides are rigid materials in the pure polymer solid state with thermal softening points above 350°C in many cases. The solid state rigidity of polyimides derives in part from their intrachain resistance to segmental rotation. Rigidity is also promoted by the well-packed segmental natures of penetrant-free polyimides, which inhibits segmental motions. In the presence of solvent, polyimides show adequate flexibility to be dissolved and processed. This combination of solution processability and solid state matrix rigidity allows polyimides to be economically processed to form thin-skinned high productivity asymmetric membranes with high intrinsic selectivity for similarly sized penetrants. Nevertheless, the advantage offered by the solubility of polyimides in solvents ultimately makes them partially swellable in actual process feed streams. The swelling “loosens” intersegmental resistances to motion and partially undermines the attractive high intrinsic selectivity of these materials.

It is conventional to refer to the swelling-induced increase in segmental motion responsible for selectivity loss as “plasticization”. This process can result from the presence of the permeating components themselves or even from impurities present in the feed. In any case, this selectivity loss is undesirable. Our work on tailored crosslinking of solution-processable polyimides will enable rapid implementation in practical membrane systems. We are focusing on a model crosslinkable monomer, diamino benzoic acid (DABA) to provide a functional group to enable the crosslinking to occur.

By incorporating various amounts of the trifunctional DABA unit in the backbone, suppression of losses in selectivity due to swelling-induced plasticization are found for 50:50 CO$_2$/CH$_4$ feed mixtures. In typical realistic natural gases, polar and polarizable penetrants like CO$_2$, H$_2$S, and H$_2$O are present and may disrupt hydrogen bonds responsible for the improvement seen even in some of the uncrosslinked samples containing DABA compared to samples without DABA. For robust protection, therefore, we feel that the covalent crosslinking crosslinking strategy is required.

Surprisingly, we have found that in some pervaporation applications, ionic crosslinks appear to actually be superior to covalent crosslinks for achieving practically useful matrix stabilization. These two extreme cases emphasize the importance of understanding the pros, cons and differences of both methods of matrix stabilization.

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Phosphorus-31 Nuclear Magnetic Resonance (\(^{31}\)P NMR) is shown to be effective for following the clay-catalyzed decomposition of two organothiophosphate pesticides, methyl parathion and chlorpyrifos. These commonly used agricultural pesticides were adsorbed onto kaolin and montmorillonite clays at high concentration (typically 5 to 10 % by weight), and analyzed by both solid-state \(^{31}\)P NMR (using cross-polarization and magic-angle spinning) and by liquid-state \(^{31}\)P NMR of DMSO and acetonitrile extracts. The montmorillonite was used in four different ion-exchanged forms (Ca\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\) and Al\(^{3+}\)), and the pesticides were adsorbed on both dehydrated and partially-hydrated clays.

When initially adsorbed onto the clay minerals, both pesticides appear by solid-state \(^{31}\)P NMR to exhibit significant motion on the molecular level, resulting in almost liquid-like spectra. Over a period of days or weeks, the signal due to unreacted pesticide diminishes and was replaced by new \(^{31}\)P NMR signals arising from various decomposition products, including hydrolysis products and the oxon form of each pesticide. The \(^{31}\)P NMR signal characteristics suggest that these decomposition products are much more tightly bound to the clay than are the starting organothiophosphate pesticides. The detected species are compared to the spectrum of a phosphorylated silica gel.

The rate of pesticide decomposition was found to vary greatly, depending on the cation present in montmorillonite. The fastest initial decomposition (disappearance of unreacted pesticide) occurred with the Cu\(^{2+}\) and Zn\(^{2+}\) exchanged montmorillonites.

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We are interested in understanding the chemistry of macro-ions in the gas phase. Such species have become important in analysis scenarios because new ionization methods are now capable of forming gaseous ions of high mass molecules and complexes. This capability enables high quality mass analysis to be performed on the ions thereby yielding the valuable information content available via mass spectrometry. To maximize this information it is important to understand the unimolecular, ion/molecule, and ion/ion reactions of gaseous macro-ions.

Unimolecular dissociation chemistry is of particular importance within the context of mass spectrometry because it is the reaction type that yields information about ion structure, at least from the standpoint of atom connectivity. We are studying the thermal dissociation kinetics of macro-ions in the quadrupole ion trap environment (roughly 1 mtorr light bath gas). Due both to the relatively high collision rates in the ion trap and the large numbers of degrees of freedom of the macro-ions, it is possible to derive Arrhenius rate parameters thereby yielding both dynamic (entropy associated with the transition state) and thermodynamic (activation energy, which is related to enthalpy) information. Our initial studies have focused on relatively weak binding; e.g., proton and hydrogen bonding. Initial measurements have been made on complexes between polypeptide ions and strong gaseous acids such as hydroiodic acid. This constitutes an example of a strong gas-phase dipole-dipole bond. Other examples include the study of proton-bound dimers and the study of the dissociation of relatively weak covalent bonds.

Ion/molecule reaction chemistry of high mass macro-ions remains a poorly explored area. Most studies have focused on proton transfer reactions involving multiply protonated macro-ions and strong gaseous bases. As alluded to above, it has been shown that strong gaseous acids will attach to polypeptide ions via relatively strong dipole-dipole interactions. The latter reaction has been shown to provide useful information about the composition of polypeptide ions. That is, the sum of the maximum number of acid molecules that will attach to an ion and the total charge of the ion indicates the number of arginines, lysines, histidines, and N-termini. We have also described nucleophilic substitution chemistry that can yield useful structural information. Therefore, we are studying other potentially interesting reactions. For example, we have noted that chemical functionalities other than loosely held protons (acidic groups) lead to attachment to polypeptide ions. We are in the process of determining the underlying factors that lead to binding with an eye towards the development of novel analytical useful ion/molecule reactions.

We have recently turned our attention to the study of weakly-bound macro-ions using ion/ion reactions to manipulate ion charge. In particular, solvated species are of high current interest in that they can serve to bridge the gap between condensed-phase and gas-phase ion chemistry. We have succeeded in forming polypeptide ions highly solvated by methanol. Remarkably, reducing the charge states of the ions via ion/ion proton transfer reactions does not lead to a significant degree of desolvation. These studies are expected to lead to new insights into ion solvation, at least in the gas phase.
The phenomenon of surfactant adsorption on mineral surfaces is of significant importance in many particulate processes ranging from mineral flotation and enhanced oil recovery to pharmaceutics, paint technology and the casting of ceramics. Stability of the suspensions is related not only to the amount of adsorbed surfactant but also to the structure of the adsorbed surfactant molecules at the interface. This structure greatly depends on the type of surfactant and the hydrophobicity or hydrophilicity of the surface. The “packing parameter” theory has been able to explain to a great extent the self-assembled structures of surfactants in the bulk. However, the recent soft contact atomic force microscopy (AFM) images of surface surfactant structures were found to be different from those of the bulk and even the concentrations at which self-assembly takes place are found to be much lower than that in bulk. This highlights the strong catalytic role being played by the surface in promoting the aggregation of surfactants. But there is no clear understanding about how and to what extent the factors such as surface charge density, crystallinity, hydrophobicity and other surface properties would influence the self assembly of surfactants at the surface. In general, at hydrophilic surfaces, like mica, the surfactants adsorb through electrostatic interactions with their polar moiety fixed at the surface. In the latter case, the electric charge of the surface and surfactant plays a crucial role in the surfactant adsorption process. In contrast, on hydrophobic surfaces, like graphite, surfactants adsorb regardless of surface charge by van der Waals/hydrophobic interactions with hydrocarbon chains accommodated at the surface. The nature of these surfactant structures at both hydrophilic and hydrophobic surfaces will be discussed.
DIRECT SAMPLE INTRODUCTION INTO ANALYTICAL PLASMAS

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Our research programs explore the production of excited species, ions, and interfering species in plasma atomic emission spectrometry and mass spectrometry. This subject is tied to the introduction of sample into the plasma and the fundamental properties of these high-temperature sources. Our ultimate aim is to use the combined knowledge from our fundamental studies as the foundation for developing measurement technologies that will, compared to the existing technology: (1) offer better selectivity, sensitivity, precision, reliability, and ease of operation, (2) allow chemical analysis at lower cost with less sample consumption and minimal waste generation, (3) reduce instrument size, and (4) simplify analytical measurements.

Among various sources, atmospheric-pressure inductively coupled plasmas (ICPs) are the most practical sources for elemental and isotopic ratio analysis. The sample introduction system, however, typically consumes 1 to 2 mL/min of sample solution and ultimately transfers only 1 to 20% of the original solution to the plasma. The nebulizer-spray chamber arrangement also suffers from a number of shortcomings including analyte loss, memory effects, interferences, and inferior precision, which are mainly attributed to the spray chamber. A reduction in the sample volume requirement and an increase in the analyte transport efficiency are desirable, particularly in the analysis of limited, expensive or hazardous samples, or for interfacing microbore chromatography and capillary electrophoresis with plasma detection.

To overcome these challenges, sample solutions should be directly introduced into the plasma. This presentation focuses on the development of (1) new micro- and nanonebulizers for direct injection of sample into plasmas, (2) novel aerosol diagnostic techniques that can quickly provide aerosol properties in three dimensions, and (3) new numerical models that can predict the motion and the fate of sample droplets in ICP spectrometries. These and other advances collectively present a roadmap for what remains to realize the full benefits of elemental and speciation analysis using plasma spectrometry.


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ANION SELECTIVITY IN ION-PAIR EXTRACTION OF ALKALI METAL SALTS USING CATION AND ANION RECEPTORS

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It is widely understood that non-ionizable cation hosts such as crown ethers extract alkali metal salts most efficiently when the co-extracted anion is large and hydrophobic. However, since it would be useful if this restriction could be lifted so as to permit efficient separations from common acid or salt matrices, a portion of the research in this program has been devoted to understanding those factors that control the selectivity for the anion.

In considering this problem, we introduced the concept of bias, which characterizes the selectivity of many separation systems where the relative ability to separate a solute depends monotonically on a single variable. In the case of anions, the charge density is most influential, and it is commonly found that separation strength toward univalent anions increases as the anion thermochemical radius increases. In effect, this phenomenon has long been recognized in the Hofmeister series. Since one may always find a more extractable anion by choosing one with lower charge density or larger radius, bias-type selectivity may be distinguished from true recognition.

Experiments with a variety of neutral crown ethers and calixarenes have revealed that bias may be a powerful tool in separating pairs of anions, such as in the removal of traces of pertechnetate ion (TcO₄⁻) from high concentrations of the smaller nitrate anion. Plotting the logarithm of distribution ratios for alkali metal salts between aqueous salt solutions and organic solutions of crown ethers or calixarenes vs. the reciprocal of the anion thermochemical radius gives a nearly linear trend, whose slope may be equated with bias. The bias may be quite steep, depending on the solvating ability of the solvent system, as explored in other parts of the program. Other influential effects include ion-pairing and specific interactions with added anion receptors via hydrogen bonding.

Ion-pairing tends to lower bias, because it strengthens with shorter inter-nuclear distance and therefore favors small anions. Jean-Marie Lehn (Nobel laureate, 1987) suggested ligand thickness to be an important consideration in the design of host molecules for cation recognition. We have recently expanded the role of this simple ligand property by demonstrating a system in which ligand thickness markedly influences anion discrimination. It was found that in the extraction of sodium nitrate and perchlorate by a simple crown ether, bis(t-octylbenzo)-14-crown-4 (BOB14C4), the normal strong preference for perchlorate is almost completely lost when the complex cation has the "open-face sandwich" vs. the "sandwich" structure.

Bias may also be counteracted by the use of anion receptors via hydrogen bonding, since such interactions again favor small anions. Potent meta-benzenedisulfonamide anion receptors were found to strongly enhance CsX extraction (X = Cl⁻, Br⁻, I⁻, OAc⁻, NO₃⁻, ClO₄⁻) by calix[4]arene-bis(benzo-18-crown-6). Synergistic factors were observed as low as 2.1 for the most hydrophobic anion, perchlorate, and as high as 620 for the most hydrophilic anion, acetate. Thus, an overall attenuation of the normally dominant Hofmeister selectivity is observed. Surprisingly, while the bidentate nature of the disulfonamide receptor confers a strong interaction, the enhancement is remarkably non-specific with regard to breaking the simple dependence on anion size.

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THE ROLE OF EXTERNAL ELECTRIC FIELDS IN MEMBRANE-BASED
SEPARATION PROCESSES

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We have used the method of molecular dynamics to examine the role of external electric fields on the separation rate in membrane-based processes. In the results to be reported we have used thin ZK-4 zeolite membranes to study the separation of a wide range of mixtures/solutions including supercritical aqueous electrolyte mixtures. Our results show that zeolite membranes can be used to separate ions from supercritical aqueous mixtures, even though the size of the ions is generally smaller than that of water molecules. This is a consequence of the ions forming stable clusters with water molecules surrounding the ions (even under supercritical conditions) and thus increasing their effective size considerably more than the pores (about 4.2 Å) in ZK-4.

Our results have also shown that external electric fields can very significantly increase the separation rate of a wide range of mixtures. The increases are most pronounced when alternating electric fields are used. Direct fields lead to the accumulation of the electrolytes (ions) on the membrane surface, and this results in the blocking of the membrane pores.

We have also observed that the increases due to external electric fields are considerably larger in structured membranes such as thin zeolites, compared to simple one layer molecular membranes based on FCC structures, for example. Our results point to a simple and efficient method of increasing the rates of membrane-based separations, which has not been widely exploited in industrial separations.

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METAL ION RECOGNITION THROUGH ORGANIZED MICROSTRUCTURES

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Our research program addresses the recognition of metal ions by ligands placed in predetermined locations in organized molecular assemblies such as micelles, vesicles, and dendrimers. The hypothesis being tested and substantiated is that high metal ion selectivities can be achieved by chelating moieties in highly organized nano- and micro-environments. Such systems are being obtained by the self-assembly of systems with chelating moieties. The chelating moiety in these self-assembled systems are present in predetermined locations which imparts high selectivities on them compared to their presence in micelles by distribution or in traditional solvent extraction systems (random macro systems). An example of a self-assembling acylpyrazolone ligand (Brijpyrz) is displayed below:

This ligand as the mobile phase in HPLC separations employing a C18 stationary phase provides baseline separations of the transition metal ions as shown below:

Separation with Brijpyrz at pH = 3.2

Our research to date on the synthesis of the self-assembling systems and the separations with HPLC and capillary electrophoresis will be discussed with an emphasis on the selective separations that can be achieved and the fundamental factors that influence the metal ion recognition of these organized molecular assemblies.

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NEW MATERIALS BASED ON PEG TAILS

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The design of new chemical materials that respond to chemical or energy stimuli is an important avenue to new measurements of chemical properties. Our research has produced a diverse family of semi-solid room temperature molecular melts and molten salts, based on attaching short ethylene and propylene glycol (PEG and PPG) oligomers to interesting chemicals. The essential advantage of "melting" these chemicals is to produce a soft material that will exhibit a reproducible molecular scale contact to hard electrode surfaces, and the consequent ability to invoke the quantitative relations of modern voltammetry. Examples of such molecular melts include a) a molten salt containing DNA as the anion and a mixture of PEG-tailed ammonium cation and PEG-tailed iron bipyridine complexes and which exhibits a semi-solid state, redox mediated, electrocatalytic oxidation of the guanine bases, b) PEG-monolayer protected Au nanoparticles that are mixed ionic-electronic conductors (nanoparticle/polymer electrolyte composites), c) mixed valent PEG tailed metal complexes that exhibit optically driven electron transfer reactions and associated NIR absorption (reactions unobservable in ordinary fluid solutions), and d) PEG-tailed ruthenium complex films that exhibit redox reactions in contact with supercritical fluid CO$_2$ phase. Some properties of these materials will be described, that may yield analytical utility.

References:
  b)  Langmuir, 2001  
  d)  unpublished work.

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MAKING A CASE FOR BASIC RESEARCH TO REVIVE ACTINIDE PROCESSING IN THE U.S.

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In the world today, France, Japan, and the United Kingdom process nuclear fuels for energy production purposes with good financial success and comparatively little environmental impact. In addition, at least a half dozen other countries are engaged in research on the development of such capability either for defense purposes or possible future commercial opportunities. Though the basic concepts of actinide separations were developed in the U. S. and were practiced for 40+ years producing plutonium for defense purposes, we have indulged in only one brief, aborted foray into commercial recycle of fissile materials.

The pace of research on actinide separations science for actinide recycle steadily increased world-wide during the last decade of the 20th century. The technology developed from that science will likely have increasing impact around the world as “conventional” (i.e., fossil) energy sources become increasingly scarce and expensive. During this “renaissance”, the scientific research establishment in the U. S. has mostly remained on the sidelines in this growing trend. We have instead focused our efforts on cleanup of the radioactive contamination left over from our 40 years of plutonium production for defense. This 40 years of defense-driven plutonium separations experience actually provides a great deal of education on how to approach (or in some cases how not to approach) actinide recycle in a manner acceptable for the 21st century.

The accumulated experience of commercial reprocessing (in the U.K. and France) has been widely publicized in both the scientific/technological and popular press. This storehouse of knowledge is therefore also readily available to guide the development of new science and technology in the field. Further, in the current environment of growing energy demand coupled with greater unreliability of fossil energy supplies and concern about global warming, the attractiveness of nuclear power, which emits no atmospheric pollutants, is on the rise. An additional motivation for increased attention to the enormous potential of actinide recycle is provided by the extremely difficult task of insuring the integrity of high level waste in a geologic formation for the legislated 10,000-100,000 year lifetime of a repository.

In this presentation, the arguments for and against the revival of actinide recycle options will be discussed. Concepts for improved hydrometallurgical approaches to more “environmentally-friendly” actinide recycle will be offered with primary emphasis on those aspects that could most benefit from fundamental investigations.

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Metal and semiconductor particles on the nanometer scale have unique optical, electronic, and structural properties that are not available in either isolated molecules or bulk solids. These properties are currently under intense study for potential uses in microelectronics, quantum dot lasers, chemical sensors, data storage, and a host of other applications. With the use of surface-enhanced Raman scattering (SERS), we have recently examined the optical properties of single metal nanoparticles and nanoaggregates. The results indicate that the intrinsic enhancement factors are as large as 14-15 orders of magnitude, much larger than the values derived from population-averaged measurements. This work has important implications for ultrasensitive vibrational spectroscopy at the single-molecule level and for understanding the mechanisms of SERS. Research in our group has also linked luminescent quantum dots (ZnS-capped CdSe) to biological molecules for ultrasensitive imaging and detection (Chan and Nie, SCIENCE 281, 2016-2018, 1998). This new class of luminescent labels is 20 times brighter, 100 times more stable against photobleaching, and 3 times narrower in spectral linewidth when compared with organic fluorescent dyes. Quantum dots labeled with the protein transferrin undergo receptor-mediated endocytosis in cultured HeLa cells, and those dots that were labeled with immunomolecules recognize specific antibodies or antigens. These quantum-dot bioconjugates are expected to have a broad range of biological applications such as ligand-receptor interactions, real-time monitoring of molecular trafficking inside living cells, multicolor fluorescence in-situ hybridization (FISH), high-sensitivity detection in miniaturized devices (e.g., DNA chips), and fluorescent tagging of combinatorial chemical libraries.

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Particle size and composition are the two most fundamental properties of aerosol particles. Our laboratory has two concurrent projects aimed at developing methods for characterizing the physical and chemical properties of aerosols. The first project is the construction and deployment of the BNL Single Particle Laser Ablation Time-of-flight Mass Spectrometer (SPLAT-MS), an instrument designed to characterize the size and composition of individual particles in situ. The second project is the investigation of the thermochemistry of particles as a function of size from 3 nm to 100 nm using a laboratory-based Tandem Nano Differential Mobility Analyzer (TNDMA) system.

**SPLAT-MS:** Recently, we have completed the construction, testing, and initial deployment of the first generation SPLAT-MS. SPLAT-MS is currently capable of detecting and sizing particles as small as 70 nm at a rate of 30 particles per second. The instrument was deployed for its maiden voyage during the Texas 2000 Air Quality Study in Houston, TX. During the Houston study, over a million particles were detected and characterized with respect to size and composition. A second version of the instrument is under construction. It will employ a two-step ion generation using a CO$_2$ laser for particle evaporation and an excimer laser to ionize the gaseous plume that forms. A second modification is designed to prevent particle evaporation during transit through the aerodynamic lens allowing for sampling under ambient relative humidity. The combination of this new feature with a DMA and a humidifier at the inlet will produce a new instrument for the rapid characterization of hygroscopicity and composition of individual particles. Both of these will be tested in the field during the ACE-Asia field study.

**TNDMA:** We have constructed the initial components of a humidified TNDMA system at BNL. This system is designed to study the thermodynamic and kinetic properties, including deliquescence and water activities, of nanoparticles. The initial configuration of the TNDMA relies on a TSI Electrospray Aerosol Generator to produce a nearly monodispersed aerosol which will be conditioned with respect to temperature and humidity and subsequently analyzed using either a TSI Nano DMA connected to a particle counter, or the Pulse-Height Analysis, Ultrafine Condensation Nucleus Counter (PHA-UCPC). The size change, and hence water content and phase, of the particles are then directly correlated with the relative humidity and temperature. In this way, the TNDMA will be used to examine monolayer changes in particle size due to evaporation or condensation, with the purpose of investigating the thermodynamics of particles down to sizes that can be best described as large molecular clusters. Future configurations will include a second NDMA to size-select monodisperse particles from polydisperse aerosol produced by direct evaporation of the neat substance in an oven and subsequent homogeneous nucleation. This generation system will allow us to investigate particles with a wide range of compositions, including organic compounds, metals, and semi-conductor materials. Once produced, these monodispersed samples will be conditioned by exposure to elevated or reduced RH environments, or other semi-volatile gases and temperature changes as desired. When more than one volatile substance is involved the conditioned particles will also be probed with SPLAT-MS.

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CHARACTERIZATION OF ALKYLSILANE STATIONARY PHASES BY RAMAN SPECTROSCOPY

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In order to better define retention mechanisms in reversed-phase liquid chromatographic (RPLC) separations, an understanding of the intermolecular interactions between the alkyl moieties of commonly employed alkylsilane stationary phases, solutes, and the mobile phases is essential. Raman spectroscopy is a powerful tool for the characterization of conformational changes in alkyl chains and is being successfully used for such studies in this laboratory. A brief overview of the types of detailed molecular information that can be obtained from Raman spectral characterization of stationary phases will be presented.

Recent studies have focused on characterization of high surface density stationary phase materials that exhibit shape selectivity.\textsuperscript{1} This work is being done in collaboration with Dr. Lane C. Sander at the National Institute of Standards and Technology. To date, five octadecylsilane stationary phase materials have been studied including stationary phases made from trichloro-, dichloromethyl- and monochlorodimethyl-octadecylsilane precursors and fabricated using surface polymerization and solution polymerization approaches. Spectra from these stationary phases have been acquired in air as a function of temperature and in a series of organic solvents exhibiting a wide range of solvent characteristics including polarity, dipole moment, hydrogen bonding, shape and size (water, methanol, ethanol, 1-butanol, acetonitrile, acetone, tetrahydrofuran, hexane, benzene, toluene, p-xylene, chloroform, aniline, anisole, pyridine, and acetic acid.) In general, the results indicate subtle to substantial changes in alkyl chain conformational order as a function of surface coverage, temperature, and mobile phase solvent. Higher surface coverages, lower temperatures and polar solvents result in more conformationally-ordered alkylsilanes. The first two dependencies are expected. The latter is somewhat contrary to popular pictures of alkylsilane stationary phase collapse in water. Molecular modeling studies support the increased ordering of high-density alkyl chains in the presence of simple polar solvents. Although the five stationary phase systems available to date span three important experimental variables (surface coverage, alkylsilane precursor, surface versus solution polymerization) sufficient molecular insight into alkyl phase structure as a function of chemical environment has been attained to provide guidance for additional future studies.


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Carbon-based materials are used extensively as substrates in electroanalytical chemistry and as stationary phases in liquid chromatography [1, 2]. In spite of widespread use, fundamental details related to adsorption of these materials remains poorly understood. Electrochemical descriptions of adsorption focus primarily on the role of edge plane sites (i.e., multiple adsorption sites) [1], whereas chromatographic descriptions view interactions with the basal plane (i.e., a single adsorption site) to be the basis of adsorption [2].

This presentation examines issues related to adsorption on carbon materials within the context of retention data obtained using electrochemically-modulated liquid chromatography (EMLC). EMLC is a separation strategy that couples electrochemistry and liquid chromatography, exploiting the ability to manipulate analyte retention through changes in the potential applied to conductive stationary phases like glassy carbon and porous graphitic carbon [3]. To examine the merits of the two descriptions of adsorption, we examined the retention dependence of a series of model compounds (i.e., monosubstituted benzene sulfonates) as a function of the concentration and identity of the supporting electrolyte and the applied potential. The importance of surface oxides on adsorption was also investigated by varying the oxygen content by oxidizing and reducing plasma treatments. The results of these experiments will be examined within the context of prevailing interpretations as well as within the context of classical electrical double layer theory.


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Nanofluidics, the active transport of material through nanoscale (<100 nm) conduits, is essentially an unexplored area and promises dramatic new opportunities for basic and applied science and engineering. The ability to fabricate fluidic structures that have cross-sectional dimensions at the molecular scale will allow fundamental studies of fluid transport at the smallest possible dimension. Moreover, tools for the analysis of molecular species such as biopolymers (DNA and proteins) could well result from nanofluidic studies and the practical implementation of such strategies will only be possible through the ability to fabricate nanofluidic architectures. Moreover, nanofluidic devices might be used to mimic processes in biological systems, to carry out single-molecule chemical reactions, and to fabricate nanoscale components by mechanical or molecular assembly. Nanofluidics is essentially unexplored territory. Prior efforts have been limited to random arrays of nanopores in polymeric membranes or biological nanopores inserted into lipid membranes. Many benefits will accrue from the ability to fabricate conduits confined in two dimensions.

The transition from microscale fluidic devices to those with nanometer features is not a simple matter. Fabrication strategies must be developed to push the lateral dimensions of fabricated channels to molecular dimensions. Another uncertainty in the extrapolation of fluidics from the micron to nanometer scale is the physics of fluid transport. When conduits approach molecular dimensions, the fluid species primarily interact with the conduit walls rather than with each other. Thus wall interactions can play a dominant role in such situations and must be controlled through appropriate interfacial chemistry. Successful demonstration of fabricated nanoscale fluidic devices will potentially enable a broad spectrum of capabilities as suggested above.

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Cyanometallates are molecular frameworks based on M-CN-M’ linkages. Traditional cyanometallates are nonmolecular solids (e.g., Prussian Blue, PB, KFe₂(CN)₆) that exhibit interesting semiconducting and ion-selection properties. Under DOE-sponsorship, we have developed families of soluble (molecular) cages that are structurally related to the PB solids. Overall this project demonstrates the contributions of organometallic synthesis to the design of molecular containers with potential applications in separations and analysis.

Molecular boxes arise upon the interaction of L₃M(CN)₃⁻⁻ and tritopic Lewis acids. The cationic box [Cp*Rh(µ-CN)₃]₄[Mo(CO)₃]₄⁻⁻ has an internal volume of ~135 Å³ but displays no inclusion properties. In contrast, the anionic box [Cp*Rh(µ-CN)₃]₄[Mo(CO)₃]₄⁻⁻ selectively binds Cs⁺ (vs. K⁺), mirroring behavior of PB.

We have discovered two new classes of cyanometallate cages, both with affinities for alkali metal ions. Trigonal prismatic Mo₆(□-CN)₉ cages are templated by Cs⁺ (r = 181 pm) and K⁺ (r = 152 pm), whereas tetrahedral cages Mo₄(□-CN)₆ are templated by the smaller Na⁺ (r = 116 pm) and Li⁺ (r = 90 pm). Using alkali metal NMR we have obtained qualitative thermodynamic and kinetic insights. For example Cs⁺ displaces Na⁺ from Na@Mo₄(CN)₆⁵⁻ to give Cs@Mo₆(µ-CN)₉⁸⁻. The observation that Mo(CN)₃(CO)₃⁻ is an inferior cage precursor provides insights into the M-CN-M linking patterns.

Cages based on redox-active metals (e.g., Ru²⁺) are being investigated for the design of electroactive receptors. Progress is being made with nest-shaped cages of the stoichiometry M₇(CN)₉. In these cases, alkali metal binding occurs without framework rearrangement.

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Aqueous biphasic systems (ABS) result from the critical phase separation of mixtures of polymers, or polymers and salts, in aqueous solution. ABS based on the separation of polymers and salts are a variant of Cloud Point Extraction in which the critical point has been lowered by the presence of structure making (S+) salts. Many such systems may represent useful alternatives to conventional organic solvent-based extraction systems in a number of areas. The simple systems we have examined have been applied to the separation of metal ions, organic molecules, proteins, organelles, and cells. They have even been applied to high temperature reactive extraction processes, for example, in the delignification of cellulose by alkaline hydrolysis. Understanding the nature of the phase separation process and the distribution of solutes is clearly of importance in their application.

We have extensively studied the distribution of small organic solutes in these systems. Their distribution depends, not on the particular salts, with which the system is formed but on their S+ properties. Thus, the same properties which bring about changes in the concentration of polymer and salt required for phase separation, also control the degree of phase divergence and distribution of solutes. Both increase in temperature and increase in salt concentration appear to act similarly in a manner analogous to a field strength. Since like other critical phenomena correlation lengths increase greatly approaching critical concentrations (C_c) or temperatures (T_c), it may be wondered whether phase separation represents the sorting of pre-existing domains of PEG and salt into interfacially separated phases. Several lines of evidence support this suggestion. Both crosslinked PEG-gels and PEG-derivatized resins (ABEC™) display differential partition of solutes at concentrations of salt below C_c. Certain solvatochromic dyes report only on the environment of the PEG chains when present in mixed solutions with salt. (This is so even when the salt concentration is very low compared to C_c).

We have also found that mixtures of PEG and salt have quite different effects on the colligative properties of water depending on whether the salts are S+ or water structure breakers (S-). For S+ salts the effects of the PEG and the salt on the osmotic pressure or freezing point of water are distinct and additive, whereas for S- salts the effects are quite different. Understanding the nature of these interactions is important since S+ are the phase forming salts, whereas S- are important system additives in many extraction procedures.

Finally, we have found that S+ salts cause profound conformational changes in PEG in aqueous solution as judged from the shrinkage of covalently linked PEG gels. On the other hand, we anticipate that planned photon correlation spectroscopy results will show increases in correlation length with salt concentration. Taken together these results suggest that PEG-salt solutions exist as separated PEG and salt domains well below the critical point and that phase separation represents their sorting into distinct phases with consequent interface formation driven by a lack of free water. Examination of these phenomena may lead to important advances in our understanding of phase separation and solute distribution in these systems.

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PHOTODISSOCIATION AND ION MOBILITY SPECTROMETRY FOR STUDIES OF GAS-PHASE ION CHEMISTRY

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In our studies of chemical reactivity and reaction mechanisms of gas-phase ions we employ a variety of cutting-edge mass spectrometry experiments involving laser ionization/excitation, esp. matrix-assisted laser desorption ionization (MALDI) and laser-ion beam photodissociation, as well as ion-neutral and ion-surface collisions, e.g., collision-induced dissociation (CID) and surface-induced dissociation (SID).

Many of our studies emphasize protonated peptides, peptide-transition metal ion complexes and transition metal ion clusters. We also utilize high-level computational chemistry methods, e.g., MO theory, PMO theory and density functional theory, to evaluate candidate structures and for determining binding sites and binding energies. We are currently developing two new experimental capabilities, time-resolved photodissociation to measure rates of photofragmentation as a function of photon energy and ion mobility-TOF-MS. We anticipate that these experiments will provide important information concerning reactivity and ion structure. This presentation will focus on the use of surface-induced dissociation (SID) in combination with IM-TOF-MS. We will also discuss development of IM-TOF-MS for synthesize and characterize novel transition metal ionic clusters, which can be “soft-landed” on to surfaces and studied by fluorescence spectroscopy and microscopy (STM/AFM).

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LASER ABLECTION FOR CHEMICAL ANALYSIS: FROM PICOSECONDS TO MICROSECONDS

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Laser ablation is an optical technology used to transform a solid sample into vapor phase constituents, which then can be chemically analyzed by atomic spectrometry. Ablation brings many exciting capabilities to the field of chemical analysis, primarily because of the laser-beam properties. The ability to directly analyze any solid sample without sample preparation and minimal sample-quantity requirements are just some of the benefits. The fundamental mechanisms underlying laser ablation processes are quite complicated, which include laser-solid interactions at the target, plasma initiation off the target, and laser interactions with the expanding plasma. These processes occur over many orders of magnitude in time, from the initial absorption of photon energy to the ejection of large particles. On the picosecond time scale, electrons are emitted from the surface, followed by atomic/ionic mass ejection on the nanosecond time scale, followed by surface explosion with ejection of large particles (> micron), microseconds after the laser pulse is finished. In many laser ablation experiments, plasmas are formed above the target surface. The plasma can absorb incident laser energy, thereby shielding the target and decreasing the efficiency of laser energy available for mass ablation. A brief introduction to laser ablation sampling for chemical analysis will be presented, followed by a description of several time-resolved processes, from picoseconds to microseconds.


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The underpinning theme of our work is the rational design and fundamental development of molecular recognition systems for chemical separations, spectroscopic detection, and trace-level sensing. A successful interplay of modeling, synthesis, and broad-based utilization in chemical analysis will be presented. Molecular mechanics (MM) and molecular dynamics (MD) are used to target macrocyclic reagents that are expected to provide desirable molecular recognition properties and to help in understanding reagent performance in chemical analysis. Interaction energies involving the inclusion of organic analytes with commercial and new synthetic cyclodextrins (CDs), obtained using commercial MM/MD force fields, are shown to be sufficiently accurate to predict elution orders in CD-mediated capillary electrophoresis (CE) separations and correctly identify potentially effective new CDs. New classes of single isomer CDs have been synthesized using multi-step synthetic procedures. The reaction schemes create carboxymethyl-, thio-, or Si-tertbutyl-functionalities at the C6 positions of the CD to provide, respectively, mobility for electrophoresis, a means to chemically attach to metal surfaces, and increased volatility for vapor deposition. Substitution at the C2 and C3 positions is aimed at influencing inclusion selectivity. These reagents are shown to possess utility as running buffer additives for achiral and chiral CE separations. Among the attributes of these reagents in CE are good mass transfer characteristics for high efficiency, the ability to rationally combine CDs to tune selectivity, and high mobility for wide elution windows. Although laser induce fluorescence is the staple high-sensitivity detection technique in CE, we have recently demonstrated surface enhanced Raman scattering (SERS) as an alternative that exhibits good sensitivity. Both on-column and off-column SERS approaches are possible and both provide information-rich spectra for analyte identification and/or high selectivity. In all cases nanoparticles of silver or gold are employed with inexpensive instrumentation to achieve enhancements sufficient for effective utilization in CE. In some cases distinctive spectra are obtained for injection amounts in the attomole range. The SERS process is very complex and several fundamental factors contribute, sometimes dramatically, to observed enhancements. Evaluation of thiolated CDs and other reagents as sequestering reagents on the surfaces of the nanoparticles are underway and represent a means to adjust analyte-metal surface geometry and chemical interactions. The aforementioned macrocycles are also useful molecular recognition and signal enhancement reagents when immobilized onto the surfaces of microcantilevers in micro-electro-mechanical systems. Chemi-mechanical responses of the cantilevers provide for both sensing and actuation. Responses in both gas and liquid phase systems are found to increase dramatically when new modes of analyte-induced surface stress are generated on specially prepared nanostructured cantilevers. These advances may lead to interactive devices that are powered solely by chemi-mechanical interactions.
SECONDARY ION MICROPROBE IMAGING USING AN ION TRAP MASS SPECTROMETER

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We have modified our original triple quadrupole based secondary ion microprobe by replacing the triple quadrupole MS/MS mass filter with an ion trap, as shown in Figure 1. The ion trap does not suffer from mass discrimination for m/z>200 as do the quadrupole mass filters, but like the triple quadrupole system, permits MS/MS on selected ions. The disadvantages of the ion trap include the fact that mass selection is not instantaneous, and that it must be operated at a pressure of greater than 10^-4 torr. The time required to obtain an image using the ion trap is about 20 minutes. For each resolution element on the sample, about 50 ms is required to generate, mass select and detect ions. This is about 15 times as much time as is required with the quadrupole system. Differential pumping on the housing of the ion trap and microprobe permits the pressure difference between microprobe and ion trap. Originally, we anticipated that we would need an octapole ion guide to allow for the pressure differential, but because we could focus the secondary ions down to about 200 microns, a simple aperture/barrier proved adequate.

At present, the instrument is configured with two computers and data systems. One system controls the microprobe (imaging) components, and the other controls the operation of the ion trap. Although awkward, the system is functional, and permits several primitive operations, such as single ion image acquisition. Ultimately, we plan to replace this system with an integrated data system. For this meeting, we will discuss performance of the instrument, and some early results.

Figure 1. Secondary Ion Microprobe/Trap

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FAST KINETICS OF ION PRODUCTION IN MATRIX-ASSISTED LASER DESORPTION IONIZATION

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Gas-phase ion production from intact macromolecules is an enabling technology for a host of research fields. Matrix-assisted laser desorption ionization (MALDI) continues to offer unique capabilities for the accurate mass analysis of biomolecules and synthetic polymers. While there is an emerging consensus about the nature of the desorption event, the explanation of ion production in MALDI has remained an elusive goal.

To interrogate the kinetics of ion formation in MALDI, a special pump-probe experiment is used (Figure 1). To achieve MALDI, two coaxial laser pulses are projected onto the sample surface with irradiances kept below the ion generation (but not the neutral generation) threshold. Spatial and temporal coincidence of the laser pulses results in ion production. Introducing a delay time between the laser pulses allows the investigation of dynamics and relaxation processes in the generated plume.

Figure 1. Schematic view of the pump-probe experiment based on the third harmonic of a mode locked Nd:YAG laser and a variable optical delay line. This system is ideally suited for studying fast processes with up to 30 ps time resolution.

Studying the delay time dependence of the ion yield for matrix and analyte ions gives insight into the mechanism of ionization. Based on the kinetic information we expect to distinguish between ionization from an excited state, cluster ionization in the dense plume, gas phase ionization from a metastable state and ionization via exciton pooling and clusters. The characteristic times of these processes can be determined and correlated with the phase transition and plume density data.

In order to explore the internal energy (IE) content of ions generated by MALDI, we use a method analogous to the "survival yield" technique. This method has been used to derive characteristic temperatures for ions generated in electrospray ionization. In this project we take an analogous approach to characterize the mean IE and the IE distribution of ions generated by MALDI. This powerful technique in combination with the pump-probe experiments will enable us to explore the consequences of excitation, relaxation and the cooling effect of the matrix plume on the IE of the generated ions.

Based on these experiments, new insight is expected into the fundamental dynamics of microplumes in MALDI. Consequently, more stable and higher efficiency ion sources may become feasible for the gas phase spectroscopy of macromolecular ions.

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129Xe NMR spectroscopy was first used to study the structure of zeolites and similar microporous solids in the mid 1980s (Demarquay and Fraissard 1987). Xenon is an ideal probe for these studies; it is non-reactive with a large electron cloud sensitive to its immediate environment, and the 129Xe isotope is abundant so the NMR signal is strong.

Early work determined that the interaction between xenon atoms contributed to the chemical shift. In order to correct for this influence, several samples with varying xenon densities must be prepared and the pressure dependence of chemical shift (normally linear for zeolites with monovalent counterions) determined. This dependence could then be extrapolated to zero pressure, which is interpreted as the chemical shift of an isolated xenon atom interacting only with the walls of the porous system.

The zero pressure chemical shift can be correlated with pore size (as determined through X-ray crystallography). However, the correlation was not strong enough to provide an accurate technique for measurement of pore size. Surface chemistry also exerts a strong influence on chemical shift.

In 1995 Cheung (Cheung 1995) studied the effect of thermal vibrations of xenon atoms confined in small cavities using molecular simulations, and predicted that the temperature dependence of chemical shift should correlate with pore size. Thus the chemical shift of a single sample at a variety of temperatures should provide information about pore size, and perhaps a better size measurement technique.

In this work, we study this prediction experimentally. Several different zeolite structure types (MFI, LTA, FAU) have been examined for the effects of geometry (cylindrical vs. spherical cavities) and chemistry (different counterions in the same zeolite structure). Chemical shift for each zeolite was measured at six different temperatures over a 240°C range. Xenon occupancy effects are also examined by preparing samples of the same zeolite at different xenon pressures.

The temperature dependence of the chemical shift is highly linear for zeolites with monovalent counterions, while zeolites with divalent counterions show some curvature. Plotting the slope of the chemical shift (\(\partial \delta / \partial T\)) vs temperature curves shows a trend with cavity size for spherical pores with monatomic counterions; larger counterions such as ammonium do not correlate as well. The temperature gradient of chemical shift (\(\partial \delta / \partial T\)) is compared to several parameters associated with the pore geometry, including pore diameter, mean free path of diffusing xenon, and pore volume.

### References


Living polymer films will have impact in many areas of technology where the nanometer-scale structure of a material is crucial to its performance. Potential applications include coatings for capillary electrophoresis, chromatographic stationary phases, substrates for functional lipid bilayers, stable ion-exchange films for remediation of waste-water, biocompatible surfaces for medical devices, substrates for DNA and protein arrays, and protective coatings for heat-exchangers in power plants. In each case, only a nanometer-thick film of polymer is needed, yet the film must be uniform on the nanometer scale. Advances in the understanding of the growth of living polymer films on surfaces are needed to control their uniformity on the nanometer scale in order to realize their full applicability. The key questions that address the nanoscale structuring of the films are the nature of the ultimate termination reactions and the processes that control the uniformity of the density of films. We have employed a battery of techniques to address these questions, including single-molecule fluorescence spectroscopy, AFM, NMR, FTIR, XPS, contact angle measurements, and microanalysis to study film growth and structure. We have studied the living polymerization of both acrylamide and styrene. The results explain the boundaries under which film properties can be controlled.

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HIGHLY SELECTIVE BINDING BY POROUS METAL-ORGANIC MATERIALS.

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Metal-organic frameworks (MOFs) are an emerging class of porous materials that combine inorganic and organic building blocks. For example, in designing an MOF we take a conceptually very simple cubic framework and use a cluster of tetrahedra, in a recent case ZnO₄ tetrahedra, as a building unit. These units are then linked by the long and rigid organic material known as terephthalic acid (or 1, 4-benzenedicarboxylic acid = BDC) to make a very open framework (shown here). As prepared, the cavities of the structure are filled with solvent molecules, however these can be removed without disrupting the framework and a remarkably empty structure results. We believe in fact that this is the most porous material ever made—over 80% of the structure is empty space. Such structures are the first to be prepared free of solvent molecules. Of crystalline materials stable at room temperature and pressure, only elemental lithium (the lightest metal) has lower density. The secret of success lies in using both clusters of atoms as the nodes of the network and a rigid planar rod of atoms (the terephthalate anion) as the linking unit to provide a rigid framework consisting only of strong bonds (C-C, C-O and Zn-O). This material absorbs voluminous amounts of gases and organic vapors. This presentation will discuss strategies for designing open metal sites in MOFs where highly selective binding and the luminescent sensing of organics can be accomplished.


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The conformational dynamics and adsorption/desorption behavior of individual λ-DNA molecules at liquid-solid interfaces were monitored by imaging within the evanescent-field layer using total-internal-reflection fluorescence microscopy. At a fused-silica surface, molecular conformation and adsorption behavior were found to depend both on pH and on buffer composition. A histogram of individual λ-DNA adsorption durations measured by hydrodynamically flowing molecules along the interface exhibited nearly identical asymmetry as the corresponding elution peaks found in capillary liquid chromatography (CLC) and capillary electrophoresis (CE). The accessibility of the surface to the molecules, which is proportional to the capillary surface-area-to-volume ratio, can be correlated with the capacity factor and the relative adsorption factor. At a C18 surface, the dynamics of individual DNA molecules changed with the addition of organic solvent as well as with pH. Hydrophobic interaction rather than electrostatic interaction was the major driving force for adsorption of individual DNA molecules.
Understanding on a molecular level the intermolecular interactions underlying separations and extractions in supercritical fluids is important to extend these useful solvents to new separation and chemical synthesis technologies. The approach involves the use of spectroscopic techniques such as, time-resolved FT-IR, and NMR. These investigations in supercritical fluids result in an improved understanding of condensed phase thermodynamics and kinetics by bridging the gap between the gaseous and liquid states. The nuclear shielding for both the $^1$H and $^{19}$F nuclei of both neat samples of CH$_3$F and CHF$_3$ along with CO$_2$ mixtures of these fluorocarbons was investigated as a function of pressure and temperature. Molecular dynamics simulations were undertaken to describe the pair distribution functions for both the neat samples and mixtures to aid in the interpretation of the $^1$H and $^{19}$F nuclear shielding determined from high pressure NMR. The NMR of the neat fluoromethanes and their CO$_2$ mixtures suggests that there are no distinct or specific interactions between the fluoromethanes and CO$_2$ and that as temperature increases the multi-body effects play less of a role in nuclear shielding.$^1$

Time-resolved, step-scan FTIR investigations of the kinetics of molybdenum radical self-termination reactions in supercritical fluids will be discussed. The kinetics of (n-butylCp)Mo(CO)$_3$ (where n-butylCp is n-butyl-$\eta^5$-cyclopentadienyl) radical self-termination to form a nonequilibrium mixture of trans- and gauche-[n-butylCp]Mo(CO)$_3$$_2$ and the kinetics of the gauche-to-trans isomerization have been determined in xenon (350 bar) and CO$_2$ (350 bar) at 283 K. The overall rate constant for the disappearance, $2k_R$, of the (n-butylCp) Mo(CO)$_3$ radical increases with decreasing solvent viscosity as expected, except in CO$_2$, which is anomalously slower. The slower overall termination rate in liquid CO$_2$ is consistent with the formation of a transient molybdenum radical-CO$_2$ complex. The first determinations of the radical self-termination-to- gauche rate constants, $k_G$, are presented. The values of $k_G$ are much slower than the corresponding recombination to trans, $k_T$, reflecting a steric contribution to the rate. The rate of isomerization (rotation about the molybdenum-molybdenum bond) from gauche to trans is unaffected by the solvent and is 3 times faster than the reported isomerization rate for the nonsubstituted [CpMo(CO)$_3$)$_2$ molecule.$^2$

The basic knowledge and new technologies generated from this research effort related to the chemistry and physics of supercritical fluid solutions will find many ready applications in separation technologies, solvent substitution processes, carbon management and environmental remediation.


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