Chemistry & Physics of Complex Systems Facility

The Chemistry & Physics of Complex Systems (CPCS) Facility supports the Department of Energy's (DOE) mission of fostering fundamental research in the natural sciences to provide the basis for new and improved energy technologies and for understanding and mitigating the environmental impacts of energy use and contaminant releases. This research provides a foundation for understanding interactions of atoms, molecules, and ions with materials and with photons and electrons. Particular emphasis is on interfacial processes.

A distinguishing feature of research at the National Laboratories is their approach to problem solving. Significant scientific issues are addressed by using focused and multidisciplinary investigative teams with each team member bringing a particular skill and capability to bear on the problem. This accelerates progress. The same approach is inherent in how we manage the CPCS Facility, which involves numerous groups of scientists within the program as well as collaborators from throughout PNNL and the external scientific community.

The CPCS Facility has particular expertise in the preparation and spectroscopic analysis of molecular clusters; high-resolution biological imaging and studies of cellular processes including DNA damage and repair and lowdose radiation processes; ultra-fast and non-linear optical spectroscopies; ultra-high resolution spectroscopy for measurements of electronic and geometric structures and dynamics; surface and interface structure, chemical reaction dynamics, and kinetics; ionmolecule traps and storage technology; and specialized chambers, instruments, and models for chemical reactivity and analysis of atmospheric species including aerosols.

Our research underpins the fundamental understanding of chemical transport and reactivity in the condensed phase. It addresses the underlying uncertainties in thermal and nonthermal (i.e., radiation) chemistry, interfacial molecular and ionic transport, and other processes in complex natural and human-made systems related to energy use, environmental remediation, waste management, and understanding biological response to environmental stresses. One focus is on structures and processes of molecular and nano-scale systems in complex environments such as condensed phases and interfaces. Research guides the development of new materials and approaches for clean and efficient energy use.

Instrumentation & Capabilities

- Reaction mechanisms at solid, liquid, and gas interfaces
- High-energy processes at environmental interfaces
- Cluster models of the condensed phase
- Single molecule spectroscopy and biomolecular sciences
- Ultrasensitive and environmental analysis

Another central feature is the development of innovative experimental methods with broad applications to research in the natural sciences. In addition to this core research, the CPCS Group has expanded its interests into two major new areas: 1) the detection and monitoring of trace atmospheric species, including gaseous and particulate matter, and 2) biological processes important in the environment and health, including live cell imaging to observe the reaction dynamics of functioning biological systems in real-time, single-molecule spectroscopy to understand proteinprotein interactions and DNA damage and repair, and novel instrumentation for studying cellular responses to low-dose radiation.

The CPCS Facility emphasizes the following five research theme areas:

1. Reaction Mechanisms at Solid, Liquid, and Gas Interfaces
   This research area focuses on developing fundamental molecular information about processes occurring at the interfaces between environmentally important liquids, solids, and gases.
2. High-Energy Processes at Environmental Interfaces
   This research area focuses on obtaining a mechanistic understanding of chemical transformations of molecules and materials driven by thermal, radioactive, or optical sources.
3. Cluster Models of the Condensed Phase
   This research is aimed at providing a molecular-level understanding of solvation and subsequent reactions in simple and complex systems as they relate to the chemistry of complex wastes, contaminated solids and groundwater, and other systems found in nature.
4. Single-Molecule Spectroscopy and Biomolecular Sciences
   This research emphasizes single-molecule spectroscopy and high-resolution biological imaging techniques for studying biological systems.
5. Ultrasenstive and Environmental Analysis

Development of an Environmental Laboratory for Single Particle Aerosol Characterization Using Computer Controlled Scanning Electron Microscopy with Energy Dispersed Analysis of X-rays (CCSEM/EDX)

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Aerosols affect air quality as heterogeneous reaction sites that alter the trace gas-phase species, and may directly lead to increased health problems upon inhalation. Ambient atmospheric aerosols are a diverse mixture of particles of many different sizes, each having different origin, composition, and physical and chemical properties. This mixture will also evolve strongly with time. To assess the impact of aerosols on the environment, one would like to have detailed information about the size and chemical composition of individual particles as a function of time. The development of analytical instrumentation for a detailed, size- and time-resolved speciation of aerosol composition at the single-particle level is one of the highest priorities in modern aerosol science.

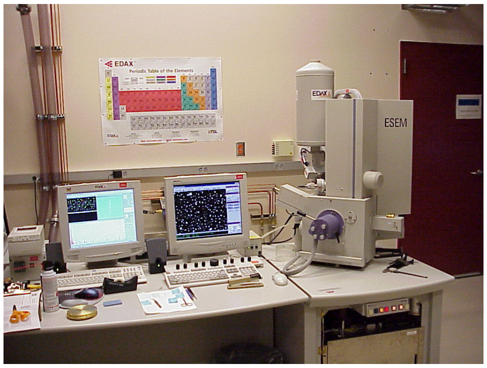

Figure 1. Environmental Scanning Electron Microscope (FEI FEG-XL30) located within EMSL. The instrument is equipped with custom modified commercial system (EDAX, Inc) for CCSEM/EDX single particle analysis.

CCSEM/EDX is one of the electron probe microanalysis methods in which individual particles are bombarded by a computer controlled electron beam and resulting X-ray fluorescence is then monitored by an EDX spectrometer (Figure 1). The method has been extensively used in the past to characterize the size, morphology, and elemental composition of individual particles collected in different field campaigns. However, most previous studies focused on a precise (sometimes at the level of tenth of a percent) quantitative analysis of few thousand individual particles collected in just a few time-integrated samples. For such detailed particle speciation, X-ray counting times of 50–100 s per particle were typically necessary to obtain enough counting statistics with sufficiently small peak-to-background ratio.

Our goal is somewhat different: to obtain the time-resolved aerosol composition data, we need to analyze thousands of particles in tens or even hundreds of sequential samples (Figure 2). To make CCSEM/EDX analysis to be an effective tool for such a task the throughput of analyzed particles must be substantially higher than most of the CCSEM/EDX researches have previously employed. In order to make the analysis feasible in a reasonable period of time (20–25 samples per day) the X-ray counting time must be

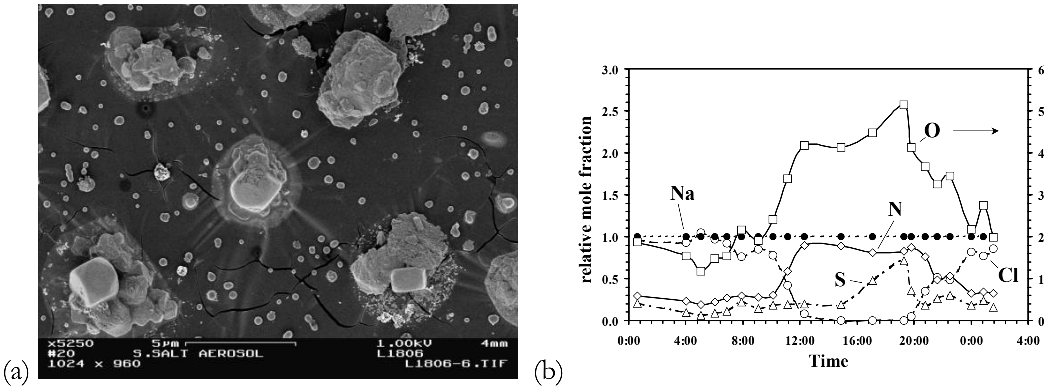

Figure 2. (a) SEM micrograph of partially reacted sea salt particles observed in TexAQS 2000 samples. (b) Time-resolved evolution of the composition of the sea salt particles as detected by the CCSEM/EDX single particle analysis. Markers represent average mole ratios of major particle elements, lines connect the symbols of the same element (Laskin et al. Environ. Sci. Tech. 2002)

reduced to the level of 1–5 s per particle. We demonstrated that the use of grid-supported ultra-thin carbon films as deposition substrates is crucial to the performance of single-particle CCSEM/EDX analysis. The carbon films of ~50 nm thickness give an exceptionally low background in the EDX analysis and allow superior automated analysis of particles down to 0.1-0.2 mm size, including semi-quantitative detection of low-Z elements (C, N, and O) at counting times as short as 1–5 sec.

We have also developed an automated Time-Resolved Aerosol Collector (TRAC) that deposits aerosol samples onto grid-supported thin films unattended, with a programmable sampling time as short as one sample per minute (Figure 3). The TRAC was successfully deployed for operation in number of recent field studies (Texas, Pacific Northwest, Boston region, and California) where aerosol samples with a time resolution of 10 min were taken and stored covering the entire periods of field campaigns. We were able to follow the time evolution in the relative contribution of non-volatile particles such as ammonium sulfate, mineral dust, sea salt, carbonaceous, etc. in the aerosol make up. The results showed, among other things, the diurnal cycles in appearance of fine carbonaceous and ammonium sulfate particles and substantial mixing/coating of mineral particles with ammonium sulfates. We have demonstrated that TRAC-CCSEM/EDX approach made it possible to follow in detail the time evolution of sea salt particles within a diverse aerosol mixture. Progress of the nitrate formation in individual sea salt particles was detected as a function of time using aerosol samples collected during the TexAQS 2000 experiment.

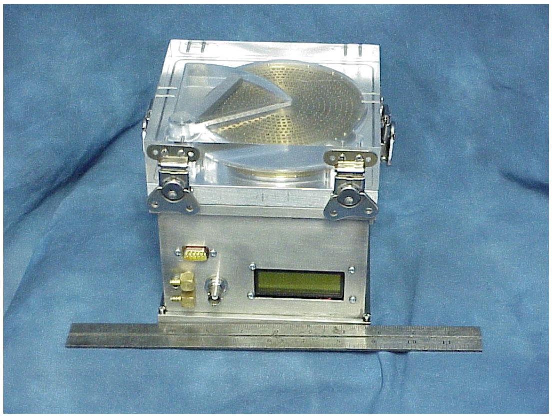

Figure 3. Time-resolved aerosol collector (TRAC). The device is packed inside an approximately 7″ cube, has a load of 560 samples and is operated from a pocket PC. The instrument runs off 12V, consumes 8W of power and is suitable for battery operation in remote areas.

Details and discussion on different aspects of the TRAC-CCSEM/EDX analytical approach can be found in the references listed below.

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Laskin, A, M J Iedema, and JP Cowin. Time-Resolved Aerosol Collector for CCSEM/EDX Single-Particle Analysis. *Aerosol Sci. Technol*, 37, 246-260 (2003).

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Up Conversion Luminescence of Mn^{2+} in ZnS:Mn^{2+} Nanoparticles

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Due to potential applications in lasers, laser cooling, optical communications, storage, displays, and imaging techniques, up-conversion luminescence has been extensively investigated. Up-conversion, often referred to as anti-Stokes luminescence, is a process where the luminescence emitted from the material is at higher energy than the excitation source and is well documented in rare earth compounds and a wide variety of nanoscale materials. Auger recombination, energy transfer, and two-photon absorption processes have been proposed to explain these observations in semiconductor quantum well structures and nanoparticles.

The average sizes of the particles used in this study as estimated from high-resolution transmission electron microscope and X-ray diffraction, are approximately 1, 3, 3.5, 4.5, and 10 nm. The 1 nm sized ZnS:Mn^{2+} nanoparticles are encapsulated in an ultrastable zeolite-Y (USY), while the 10 nm nanoparticles are naked particles without any capping. The 3, 3.5, and 4.5 nm particles are capped with methacrylic acid/citric acid.

Figure 1 shows the photoluminescence (excited at 300 nm) and up-conversion (excited at 767 nm) emission spectra of the ZnS:Mn^{2+} nanoparticles. For comparison, the up-conversion emission spectrum of bulk ZnS:Mn^{2+} is also shown. The broad emission is from the $^4T_1$ to $^6A_1$ transition of Mn^{2+}. To see the difference between the photoluminescence and the up-conversion emissions, the two spectra are normalized in each sample. Figure 1 clearly shows that for the bulk and the 1 nm sized ZnS:Mn^{2+} particles encapsulated in USY, the up-conversion emission spectra are almost identical with the photoluminescence emission spectra. However, for the 3, 3.5, 4.5, and 10 nm nanoparticles, the up-conversion emission maxima are redshifted by approximately 7.5, 9, 6, and 4 nm from their photoluminescence emission maxima.

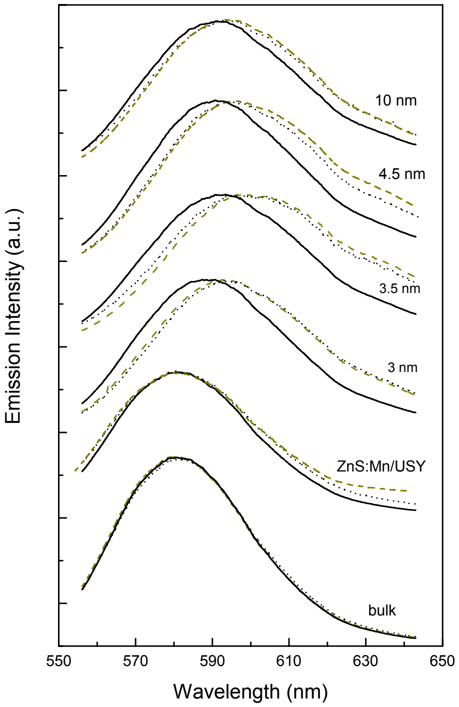

Figure 1. The photoluminescence spectra after excitation at 300 nm (solid lines), at 383.5 nm (dashed lines), and the up-conversion luminescence spectra resulting from 767 nm excitation (dotted lines) of bulk ZnS:Mn^{2+} and different sized nanoparticles.

Figure 2 shows the lifetime decay curves of the photoluminescence excited at 300 nm and upconversion luminescence excited at 767 nm. It is interesting to note that the up-conversion decay lifetimes are shorter than the corresponding photoluminescence decay lifetimes. Excitation power dependences show that the photoluminescence is due to a single photon excitation while the up-conversion luminescence intensity displays a quadratic dependence on excitation power, indicating a second order process.

Optical properties of semiconductor nanoparticles have been extensively studied in recent years. Due to quantum confinement, a large surface to-volume ratio, and the geometrical confinement of phonons, semiconductor nanoparticles behave differently than bulk materials and have some novel properties and effects. Mn^{2+} doped materials represent a class of phosphors that have already been used for many applications. Transition metal ion doped semiconductor nanoparticles may display unique and interesting properties worth studying for both basic research and application purposes. It is anticipated that the results of our research will contribute to the fundamental understanding of these complex systems. This collaborative user project has resulted in the publications listed below in the references section.

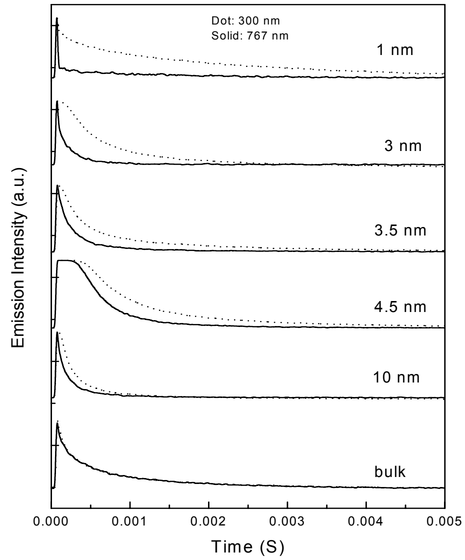

Figure 2. Lifetime decays of photoluminescence dot, excitation at 300 nm) and up-conversion (solid, excitation at 767 nm) luminescence of Mn^{2+} in ZnS:Mn^{2+} bulk and nanoparticles.

References

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Selective Laser Desorption of Ionic Surfaces: Resonant Surface Excitation of KBr

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Electronic excitation of solids creates bulk and surface defects, induces surface decomposition and particle emission, and leads to desorption of adsorbed species, electron emission, and other processes. Many of these processes, such as desorption induced by electronic transitions (DIET) and laser ablation, have numerous technological applications and have been studied in great detail. However, surface desorption of materials by electronic excitation is difficult to control. One of the main reasons is that available irradiation sources, such as ion and electron beams, X-rays, and lasers induce a variety of different processes inside a solid. Since the mechanisms of relaxation of electronically excited states in most cases are poorly understood, selectively inducing a particular surface desorption mechanism has been difficult.

In this work, we combine theoretical calculations with sensitive laser desorption experiments on cleaved KBr single crystals. We have achieved selective desorption of hyper-thermal Br atoms by using laser excitation in the Urbach tail of the bulk exciton absorption of KBr. In addition, we produce an extremely large excess of the Br($^2P_{3/2}$) ground state over the spin orbit excited Br($^2P_{1/2}$) state (Br*). We calculate transition energies for specific surface structures such as terraces, steps, and kinks and argue that surface specific emission of neutral halogen atoms is induced by resonant excitation of excitons on surface terraces at 6.4 eV. We note that the principles of resonant surface excitation are general and likely extend not only to other alkali halides but also to technologically important materials, such as oxides. Using this approach it may be possible to tailor surface excitation to control solid-state reaction in a variety of useful materials.

Figure 1 shows the normalized raw velocity profiles of Br following 6.4 and 7.9 eV excitation. A narrow hyper-thermal component peaking at 3.8 μs is observed in the arrival time data at 6.4 eV. The velocity distribution generated using 7.9 eV excitation is markedly different. There is a clear near-thermal component peaking near 16 μs. The 7.9 eV laser fluence is approximately ten times greater than that used at 6.4 eV to achieve the same detectable levels of Br emission. The emission yield shows a linear power

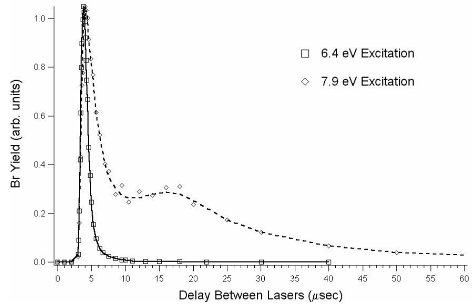

Figure 1. Velocity profiles of Br emission following 6.4 and 7.9 eV excitation. The 6.4 eV distribution (squares) display only the hyperthermal component while the 7.9 eV distribution (dots) display both hyperthermal and near-thermal components. Both curves have been normalized.

dependence of $P^{0.9\pm.2}$ indicating that the 6.4 eV photons are resonant with a surface excitation despite being below the first bulk exciton band at ~6.6 eV.

To estimate a possible shift of the surface excitation energy with respect to the bulk we have calculated the TD-DFT excitation energies for the three QM clusters K_6Br_6, K_9Br_9, and $K_{18}Br_{18}$. Each of these clusters is three-layers deep where the top layer is in the surface plane. The results demonstrate the hierarchy of excitation energies near the surface, which is mainly due to the difference in the electrostatic potential in different surface layers. The excitation in the surface layer has the lowest energy and is split by about 0.2 eV from higher energy excitations with the charge transfer from the sub-surface layers to the surface.

To model the surface exciton relaxation after excitation we consider the lowest triplet excited state, which can be calculated self-consistently, as in our previous calculations. This lowest surface excited state is initially strongly delocalized on the perfect surface, as is demonstrated by the spin density plot in Figure 2. The lowest energy relaxation path corresponds to a displacement of one of the surface Br ions out of the surface plane. This leads to an additional localization of the spin density around that ion and to a force displacing the ion outward and perpendicular to the surface plane. This collaborative user project has resulted in the publications listed below in the references section.

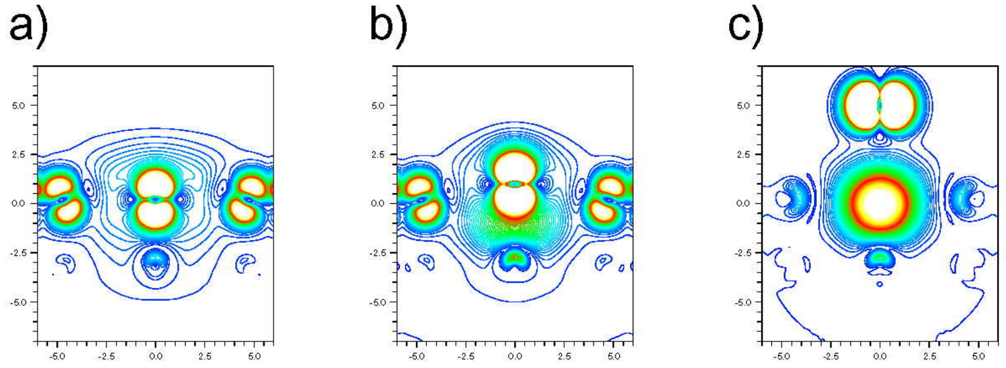

Figure 2. Spin density for the triplet surface exciton: (a) unrelaxed exciton, (b) initial stages of the relaxation (Br atoms is leaving the surface), and (c) Br atom is about 5 Å from the surface.

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Hess, WP, AG Joly, DP Gerrity, KM Beck, PV Sushko, and AL Shluger. Selective laser desorption of ionic surfaces: Resonant surface excitation of KBr. *Journal of Chemical Physics*, **115**, 9463-9472 (2001).

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Measurement of Absolute Infrared Absorption Cross Sections of Nitric Acid

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Nitric acid plays an important role in the NO_x chemistry of the earth's atmosphere. The ability to accurately quantify its concentration in field campaigns has become a major goal of atmospheric chemists. In the troposphere, gaseous HNO_3 dissolves in water to form a component of acid rain. In the lower stratosphere HNO_3 condenses with water to form polar stratospheric clouds. Throughout the atmosphere, gaseous HNO_3 is involved in the sequestration of the ozone destroying species NO_x.

Monitoring HNO_3 in the atmosphere is needed to verify models and establish trends. Since infrared spectroscopy is used as a monitoring technique, our team (Figure 1) attempted to determine the cross-sections of this molecule over a wide range of frequencies. Typical tropospheric concentrations are on the order of 100 ppt to 1 ppb in remote to rural areas. Fourier transform infrared spectroscopy or tunable infrared diode laser spectroscopy is often used to make these measurements. Consistent laboratory data relating observed infrared line strengths to concentration does not exist. In order to remedy this problem, we are attempting to quantify absolute infrared cross sections, line shift, and broadening parameters for anhydrous nitric acid.

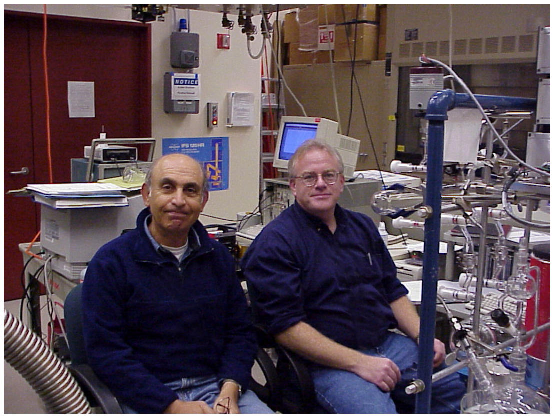

Figure 1. Visiting NASA Ames scientist Chuck Chackerian of NASA (left) and PNNL scientist Tom Blake record high resolution infrared spectra of HNO_3. The spectrometer is located in EMSL and is part of the high resolution infrared spectroscopy laboratory.

Nitric acid is a notoriously sticky molecule, and measuring its concentration in a sample cell is difficult. In this project great care was taken in the selection of cell and window materials. In addition, our experimental technique includes flowing the compound through the absorption cell. Using this approach, we have been able to measure absolute absorption cross sections for individual ro-vibrational transitions for several fundamental vibrational bands using our high resolution Fourier transform spectrometer (FTIR).

FTIR absorbance measurements of small aliquots of anhydrous nitric acid were used to determine the regional integrated cross sections at 278.2 K, 298.22 K, and 323.15 K. The spectra were recorded with pressure broadened samples in a 20 cm path length cell at spectral resolution of 0.112 cm^{-1}. A representative high resolution spectrum of the υ_2 band of anhydrous HNO_3 is shown in Figure 2. The spectral regions measured included the vibrational bands, υ_1 (~3575 cm^{-1}), υ_2 (~1710 cm^{-1}), υ_3, υ_4 (1335 cm^{-1}), υ_5, 2 υ_9 (~890 cm^{-1}), as well as regions of weaker absorption between 820 cm^{-1} and 5300 cm^{-1}. Complete analysis of the data is ongoing. An initial report of this work will appear in the reference below.

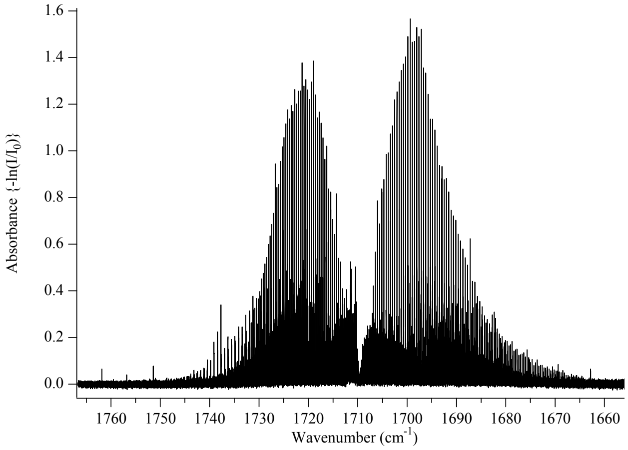

Figure 2. The υ_2 band of anhydrous HNO_3. The spectrum was recorded using the high resolution infrared spectrometer in the EMSL. The sample cell was constructed from gold-coated stainless steel and was capped with BaF_2 windows. Spectral resolution was 0.0025 cm^{-1}. Sixty-four scans were co-added.

References

Chackerian, C, SW Sharpe, and TA Blake. Anhydrous Nitric Acid Absolute Integrated Cross Sections: 820 to 5300 cm^{-1}. *Journal of Quantitative Spectroscopy and Radiative Transfer* (in press).

Revealing Function-Regulating Conformational Dynamics of an Ion Channel by Simultaneous Single-Molecule Fluorescence Imaging and Patch-Clamp Recording

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Ion channels control and regulate the ion current flux and therefore play a key role in regulating how cells respond to their changing environment. We have been developing a unique technique by combining our extensive imaging capabilities, a confocal scanning linear/non-linear optical microscope, with state-of-theart patch clamp technologies. Application of this unique instrumentation presents an unprecedented opportunity of seeking a mechanistic and dynamic understanding of ion channel functions and structures in living cells.

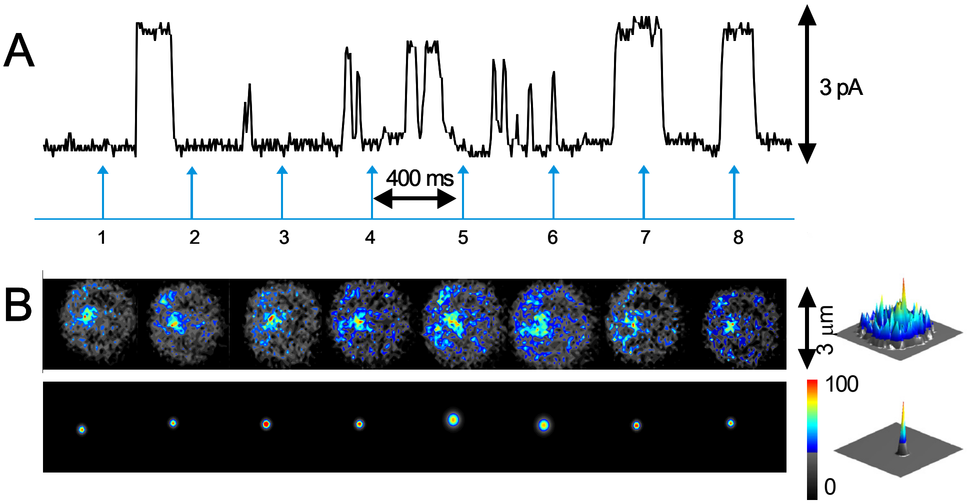

Figure 1. A) Upper trace: single channel current recorded at 100 mV from a TMR labeled single gramicidin channel incorporated in a lipid bilayer. Lower trace: time flags indicating the 5 ms of laser excitation and CCD camera exposure simultaneously acquired with the single channel recording. B) top panel: consecutive 3 μm x 3 μm fluorescence images of the pipette-tip taken simultaneously with the singlechannel current showed in A. TMR labeled gramicidin was excited with 514 nm for 5 ms. The images were taken every 400 ms and were numbered according to the time flags in A. Bottom panel: plot of the 2-D Gaussian fitting for the above image. Right insert: 3D plot of the first image (top) and 3-D plot of the 2-D Gaussian fitting (bottom).

Subtle conformational changes of ion channels control gating and selectivity. Structure-function studies of ion channels at the single molecule level are needed to identify such conformational changes within the membrane that govern their dynamic activity. We have used single-molecule fluorescence spectroscopy simultaneously with single-channel current recordings, to detect discrete structural changes simultaneously with fluctuations in channel activity of single gramicidin channels in a lipid bilayer membranes and single NMDA ion channel in a living cell (Figure 1). Single pair fluorescence resonant energy transfer (spFRET) imaging and single-molecule polarization imaging experiments and single-channel current correlation analysis revealed the correlation of multiconformational states with multiconductance levels of the channel. Our findings suggest that the inhomogeneous, dynamic conformational changes of the gramicidin channel underlie the correlation of the structural changes with the channel conductance.

Correlation function analysis of single channel currents supports the combined single channel fluorescence and conductance results by indicating multiple open/closed states and a dependence between the two states. From experimental evidence that has accumulated during the years, the multiple states may arise from intra-and inter-molecular conformational changes and geminate recombination.

We have also validated a novel technique and methodology of simultaneously probing ion-channel mode-specific conformational change and its correlated channel trajectory, combining two real-time single-molecule approaches. Ion channel structural dynamics and kinetics can now be studied site-specifically at the molecular level under physiologically relevant conditions. Refinements of this strategy will make it possible to study subtle conformational changes in the receptor-ligand complexes that control ligand-gated channel activity in intact excitable cells.

Pd Nanoclusters Supported on MgO(100): Effects of Cluster Size on Chemisorption

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Low-temperature methane combustion for applications in electric generator turbines is catalyzed by Pd nanoparticles to minimize NO_x pollution. The reaction depends on the dissociation of methane molecules on the Pd surface. Nanoscale Pd particles contain coordinatively unsaturated Pd atoms which may facilitate the dissociation of CH_4, thereby making this process more facile. Little is known about how metal particle size affects dissociation of small hydrocarbons, in spite of its obvious importance in a variety of catalytic processes.

Over the last decade, much progress has been made in understanding supported metal catalysts at the nanometer scale due to research on model catalyst systems. By studying these model systems, improvements in the efficiency and cleanliness of industrial chemical reactions can be made. Understanding the effect that the nanometer scale confinement of matter has on catalytic properties is one of the current scientific challenges. Detailed analysis at the nanoscale allows us to probe the atomic scale interactions of the adsorbed metals and their oxide supports, with each other and with other adsorbed species.

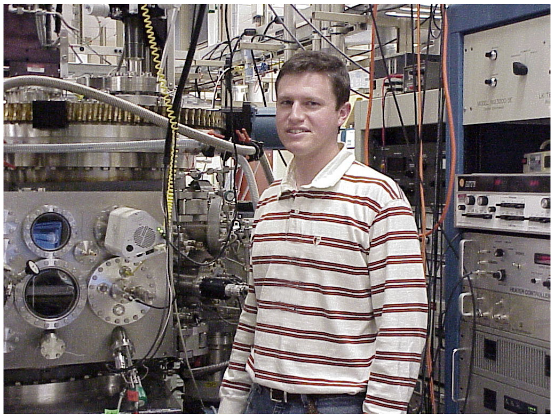

Figure 1. Graduate student Steven Tait from the University of Washington conducts research using the Molecular beam scattering instrument in Bruce Kay's laboratory within the EMSL. Steve was at EMSL from October 2002 until April of 2003.

As part of our initial approach to address this problem we have used molecular beam scattering and temperature programmed desorption at low temperatures to study the adsorption and dissociation of hydrocarbons (methane, ethane, propane, etc) on MgO(100) thin films. This work is being conducted in the molecular beam scattering laboratory within the EMSL (Figure 1).

Figure 2 shows a series of methane temperature programmed desorption (TPD) from an epitaxially grown MgO (100) thin film. Methane is deposited on the substrate at about 20 K, and each spectrum corresponds to a different coverage of methane on the MgO thin film. Analysis of these spectra coupled with the dynamic scattering measurements will reveal the quantitative details of the adsorption dynamics and desorption kinetics for hydrocarbon/catalytic surface interactions.

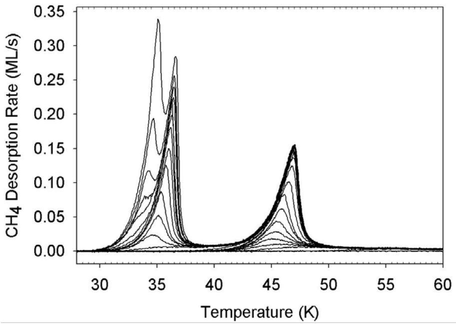

Figure 2. Temperature programmed desorption spectra of methane desorbing from an epitaxially grown MgO thin film. Each spectrum corresponds to a different methane coverage on the MgO film.

The data obtained above will provide an excellent baseline for studying the effects of Pd particle size on hydrocarbon/catalyst substrate interactions. Presently, we are studying the interactions of the same set of hydrocarbons with controlled Pd nanoclusters supported on MgO(100). Clusters of Pd are grown on the MgO thin film by vapor deposition at low temperatures and annealed to higher temperature in order to control the size of the Pd nanoparticles. The effects of the nanocluster particle size on the adsorption and dissociation of the hydrocarbons on these model catalysts is of primary interest.

Catalytically significant properties of metal particles can be very different for very small particle sizes. Previous studies of model catalyst systems at the nanometer scale have shown that nanoparticles have significantly different properties than larger particles of the same material. Complementary non-contact atomic force microscopy (ncAFM) measurements (being conducted at the University of Washington) will yield information about the morphology and number density of the Pd nanoclusters as a function of deposition temperature and coverage, under the same conditions as the TPD experiments conducted at PNNL.

The Transformation of Solid Atmospheric Particles into Liquid Droplets through Heterogeneous Chemistry: Laboratory Insights into the Processing of Calcium Containing Mineral Dust Aerosol in the Troposphere

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(c) Pacific Northwest National Laboratory

It has been reported that approximately 1000–3000 Tg of mineral aerosol are injected into the atmosphere as wind-blown soils annually. In the coming years, this value is predicted to increase because of the global expansion of arid regions. Fine mineral dust can be transported long distances in the atmosphere and thus have the potential to undergo a variety of heterogeneous reactions with atmospheric gases.

In principle, it is possible that the heterogeneous chemistry of atmospheric aerosols can change both the gas-phase chemical balance of the atmosphere and the physicochemical properties of individual particles. Changes in the properties of individual particles, such as size, shape, composition, and hygroscopicity, will alter aerosol optical properties and thus may have an impact on the Earth's climate. The ways in which mineral dust aerosols impact atmospheric processes such as climate forcing, heterogeneous atmospheric chemistry, and phase transitions of ammonium salts containing dust inclusions are just beginning to be understood. Calcium carbonate is a common component of mineral dust and may be a very reactive component of the aerosol present in the Earth's atmosphere.

This project studies the heterogeneous chemistry of individual calcium carbonate particles with nitric acid. Figure 1 shows a set SEM images of calcium carbonate after various exposure times to nitric acid at ~41% relative humidity. The image in Figure 1a is of calcium carbonate particles that have not yet been exposed to nitric acid. The four particles seen in the image are all larger than ~2 μm. The images show that the particles grow in size and become spherical in shape after only one hour of exposure to nitric acid vapor. Experiments at a lower relative humidity showed a slow change in morphology as the particles reacted with nitric acid.

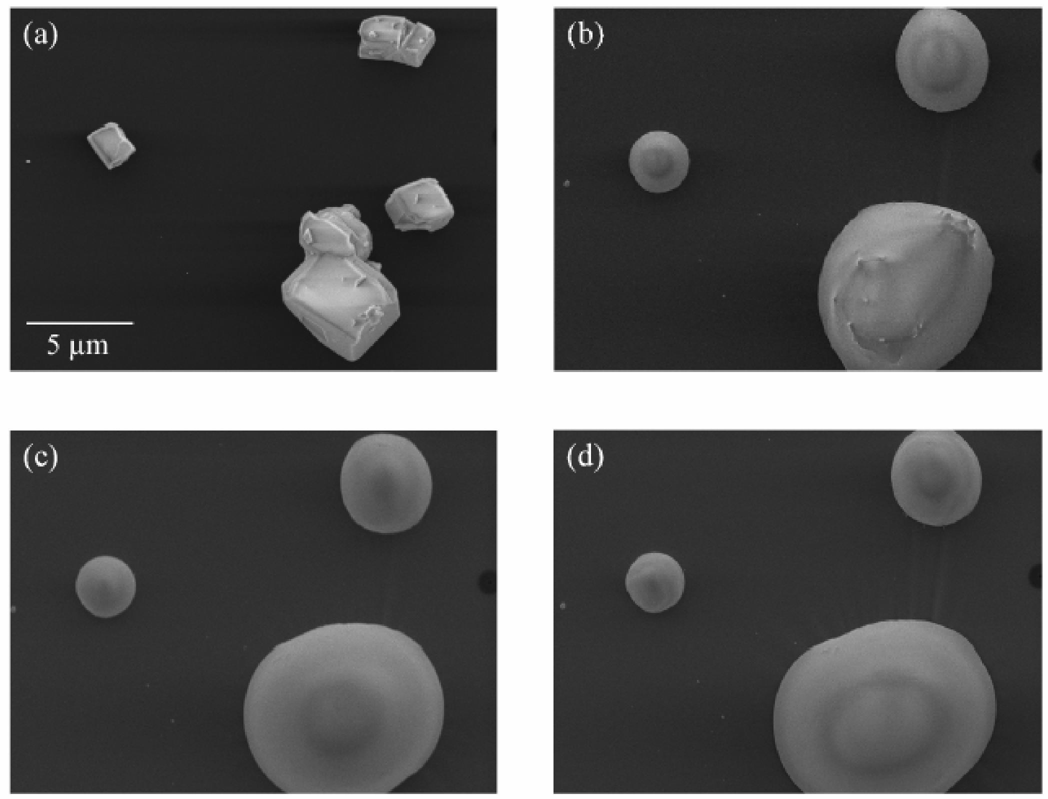

Figure 1. SEM images of calcium carbonate particles exposed to 20 μtorr of HNO_3 at 41 % Relative Humidiy: (a) before exposure, and after exposure for (b) 1 hour (c) 2 hours and (d) 4 hours.

The conversion of solid particles into liquid droplets through heterogeneous chemistry has important atmospheric implications in terms of the continued reactivity of the aerosol and the impact of the reacted aerosol on climate. As shown here, single particle analysis can be used to determine changes in particle morphology, relative reaction rates, and the extent of reaction. In this work we will continue to study the role of relative humidity on reaction rates. Listed below is a reference for the publication of these initial results.

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Krueger, BJ, VH Grassian, A Laskin, and JP Cowin. The Transformation of Solid Atmospheric Particles into Liquid Droplets through Heterogeneous Chemistry: Laboratory Insights into the Processing of Calcium Containing Mineral Dust Aerosol in the Troposphere. *Geophysical Research Letters* (in press 2003).

Strontium Migration and Co-Precipitation at Columbia Basin Basalt/Caliche Interfacial Regions

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Carbonate minerals are components in the soil and vadose zone of several DOE sites such as Hanford (Figure 1). Because they can form rapidly and are highly reactive, carbonates may be extremely effective in attenuating transport of toxic metals and radionuclides by several uptake mechanisms, including co-precipitation and adsorption. In contrast to the sorptive behavior shown by many hydroxide and clay minerals, sorptive uptake of dissolved metals onto calcite may result exclusively in co-precipitation. This has important implications for the long-term retention of contaminants, since metal species are incorporated into the bulk, rather than solely at the surface of the crystal, and bulk dissolution is necessary for their re-release to fluids.

Throughout the vadose zone of the Hanford Site, which is dominated by siliciclastic sediments, pedogenic calcification has resulted in the extensive occurrence of carbonate as coatings on grains, as disseminated particles, and as thick and extensive buried caliche layers (Figure 1). Where carbonate coatings exist, they are likely to be more important than the substrate grains in controlling uptake of contaminants. Release of highly alkaline tank waste into the vadose zone, combined with a generally low soil moisture content, is expected to promote periodic precipitation of calcium carbonate, and high-pH conditions should also favor sorption on existing calcite. Preliminary characterization of the caliche underlying a tank waste location at the Hanford Site indicates that $^{90}Sr^{2+}$ radionuclides are strongly associated with calcite.

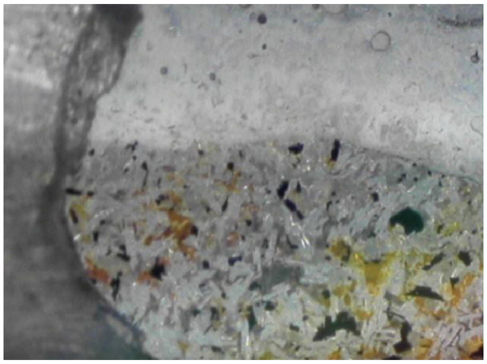

Figure 1. Thin sections (30 microns thick) were prepared from caliche-coated samples of "Hanford formation" basalt sediment. Microprobe imaging and analysis were conducted at sample areas where the basalt/caliche interface remained intact following mounting on high-purity silica slides. A wide-angle CCD image of the sample used in this study is pictured above. Caliche (top, white region) is seen to interface with basalt (bottom region).

In addition to the work being done at EMSL, companion synchrotron-based techniques micro x-ray fluorescence (sometimes called x-ray microprobe) and micro-XAS (x-ray absorption spectroscopy), which offer micron-scale element mapping combined with x-ray absorption spectroscopy are being conducted. These experiments are ideally suited for determining spatial heterogeneity of contaminants on natural samples with various levels of information about speciation. Naturally occurring strontium near the basalt/caliche interfacial region affords an opportunity to investigate how divalent metal leaching and co-precipitation may occur within the caliche layer.

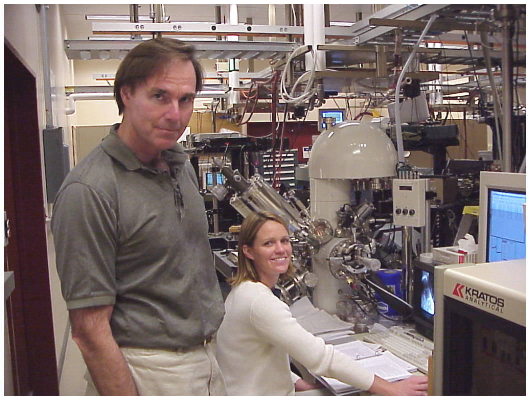

Figure 2. PNNL staff member Ken Beck and graduate student Sandra Withers-Kirby collect X-ray photoelectron spectra from caliche-coated samples of "Hanford formation" basalt sediment at EMSL.

Our primary focus is the heterogeneity of contaminant uptake and retention on natural caliche and coatings from Hanford Site samples (Figure 2). Carbonate minerals (particularly calcite) are important components in the soil. In contrast to the sorptive behavior shown by many oxide and clay minerals, sorptive uptake of Sr^{2+} onto calcite results in effective co-precipitation. Extensive mapping of natural strontium deposits near the basalt/caliche interface via x-ray microprobe indicates heterogeneous calcium and strontium concentrations: where there is calcium, there is strontium. This implies a co-precipitation mechanism for both natural and radioactive strontium migration and incorporation in caliche. Since metal species are incorporated into the bulk, rather than solely at the surface of the crystal, this has important implications for the long-term retention of contaminants intersubsurface. Uptake of incompatible divalent contaminant species by co-precipitation appears to be significant for calcite.

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The following publications discuss this research in more detail.

Elzinga, EJ, RJ Reeder, SH Withers, RE Peale, RA Mason, KM Beck, and WP Hess. EXAFS study of rare-earth element coordination in calcite. *Geochimica Et Cosmochimica Acta*, 66, 2875-2885 (2002).

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Observation of All-Metal Aromatic Molecules

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Aromatic compounds are named for their fragrance; the most famous example is probably benzene. Technically, however, aromaticity is a concept to describe a class of organic compounds with unusual stability. These compounds are planar molecules with a cyclical configuration having equal bond lengths linking atoms to each other. In the past, chemists have not considered aromaticity in purely metallic molecules, but this is going to change.

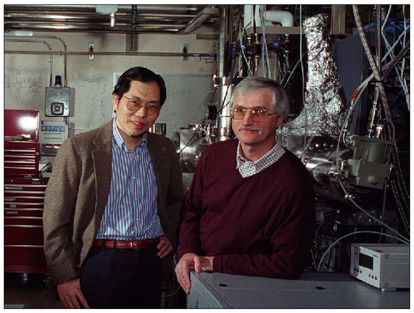

Figure 1. Professor Lai-Sheng Wang (L) from Washington State University and Pacific Northwest National Laboratory and Professor Alexander Boldyrev (R) from Utah State University.

A team of scientists, led by PNNL/EMSL scientist Lai-Sheng Wang (jointly associated with Washington State University) and collaborator Alexander I. Boldyrev (Utah State University) shown in Figure 1, has recently discovered experimental and theoretical evidence of aromaticity in all-metal systems. The discovery happened when Wang and his technical assistant Xi Li and postdoctoral associate Hai-Feng Zhang used a laser to blast an alloy of copper (or sodium) and aluminum. This caused the aluminum and copper atoms to enter a gaseous state and recombine to form new molecules. Using a photoelectron spectroscopy system (built by Wang and his team) at EMSL, Wang and his team collected and analyzed the data of the electron energy spectra of the newly formed bimetallic molecules. Combining the experimental observations with theoretical calculations by Boldyrev and his doctoral student Aleksey E. Kuznetsov, the team proved the existence of aromaticity in the all-metal molecules.

This important discovery was recently reported in *Science* (Li et al. 2000). *Science* called attention to this work in a "Perspectives" article by D. K. Seo and J. D. Corbet, "Aromatic Metal Clusters," same issue, 841-842, which comments that "Li et al.'s surprising aluminide clusters not only extend aromaticity into metallic elements but also bring to our attention other factors that govern structural patterns and the stability of solids." *Chemical and Engineering News*, Feb. 5, p. 8, covered this work in a "News of the Week" sidebar, "It's a Metallic Aromatic," and *Science News* reported this discovery in its Feb. 17 issue, "New all-metal molecules are organics." Recently *Chemical and Engineering News* wrote an in-depth article covering these exciting results, "Metalloaromatics" in C&EN September 24, 2001, p. 39-40. This work has also attracted the interest of other news sources since this advance may lead to the development of totally new classes of aromatic inorganic and metal compounds.

The National Science Foundation and the DOE Office of Biological and Environmental Research supported the EMSL portion of this work. Key PNNL/EMSL contributors include Xi Li, Hai-Feng Zhang and Lai-Sheng Wang (all jointly associated with Washington State University). External collaborators include Aleksey E. Kuznetsov and Alexander I. Boldyrev of Utah State University.

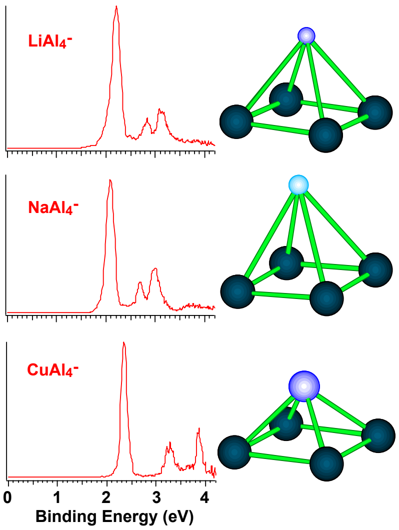

Figure 2. Comparison Between Experimental Results and Theoretical Predictions On the left is a set of PES spectra for LiAl$_4^-$, NaAl$_4^-$, and CuAl$_4^-$ and their calculated structures. These clusters were produced using the Gas Phase Cluster Instrument in Professor Wang's Laboratory in EMSL 1118. On the right are the results of Professor Boldyrev's calculations predicting square planar structures of Al$_4^{2-}$, Hg$_4^{6-}$ ad GeAl^{3-} and delocalized p orbitals, characteristic of aromatic molecules.

References

This collaborative User project has resulted in the following publications.

Li, X, AE Kuznetsov, HF Zhang, AI Boldyrev, and LS Wang. Observation of all-metal aromatic molecules. *Science*, **291**, 859-861 (2001a).

Li, X, HF Zhang, LS Wang, AE Kuznetsov, NA Cannon, and AI Boldyrev. Experimental and theoretical observations of aromaticity in heterocyclic XAl$_3^-$ (X = Si, Ge, Sn, Pb) systems. *Angewandte Chemie-International Edition*, **40**, 1867-1870 (2001b).

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Kuznetsov, AE, AI Boldyrev, X Li, and LS Wang. On the aromaticity of square planar Ga$_4^{2-}$ and In$_4^{2-}$ in gaseous NaGa$_4^-$ and NaIn$_4^-$ clusters. *Journal of the American Chemical Society*, **123**, 8825-8831 (2001).

Zhai, HJ, LS Wang, AE Kuznetsov, and AI Boldyrev. Probing the electronic structure and aromaticity of pentapnictogen cluster anions Pn(5)(-) (Pn = P, As, Sb, and Bi) using photoelectron spectroscopy and ab initio calculations. *Journal of Physical Chemistry B*, **106**, 5600-5606 (2002).

Laboratory Studies of Atmospheric Processing of Sea Salt

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(a) University of California, Irvine
(b) W.R. Wiley Environmental Molecular Sciences Laboratory
(c) Pacific Northwest National Laboratory

The field of atmospheric chemistry encompasses the chemical and physical processes which play key roles in the natural and polluted atmosphere, from urban to remote areas and from the lower to the upper atmosphere. Understanding these processes requires field measurements, the development, testing and application of models, and laboratory studies of kinetics and mechanisms (Figure 1).

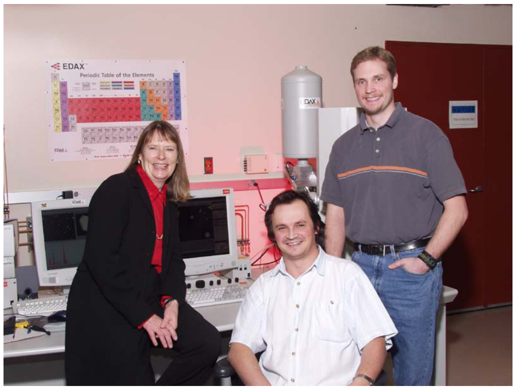

Figure 1. Barbara Finlayson-Pitts (left) worked with Alex Laskin (center) and Dan Gaspar (right) to understand the heterogeneous chemistry of sea salt at single particle level.

Heterogeneous chemistry of atmospheric aerosol affects both the gas-phase chemical balance of the atmosphere and the physico-chemical properties of individual particles. Changes in the properties of individual particles, such as size, shape, composition and hygroscopicity, will alter aerosol optical properties and thus may have an impact on the Earth's climate.

Sea salt particles overwhelmingly dominate the aerosol composition in the marine boundary layer in remote and coastal urban regions. The ways in which sea salt aerosol impact atmospheric processes such as climate forcing, heterogeneous atmospheric chemistry, cloud formation etc. are therefore off particular interest in atmospheric science.

Previous studies (Knipping et al. 2000) of the reaction of deliquesced NaCl particles with hydroxyl free radicals (a major atmospheric oxidant) showed that the Cl_2 generated was far greater than that expected from uptake of OH into the particles and oxidation of chloride ions in the bulk liquid. A reaction of OH with Cl^- at the air-water interface as a key part of the mechanism was proposed to explain that observation. However, direct measurements to detect the changes of the particle composition were not done in those experiments.

The project in the EMSL is to investigate experimentally the reaction mechanisms of the reactions of NaCl with O_3 and OH. This work uses the state of the art CCSEM/EDX and TOF-SIMS analytical techniques at the EMSL user faculty to search for the production of NaOH in individual particles, which presumably should be formed via the proposed air-water interface mechanism. Initial experiments have been completed and more experiments and analysis is ongoing.

The SEM images in Figure 2 are of NaCl particles prior and after exposure to OH radicals. Formation of the reaction product recrystallized on the particle surface can be easily seen. It is believed that additional experiments (currently underway) using CCSEM/EDX and TOF-SIMS techniques would allow us to determine elemental and molecular composition of the reaction product.

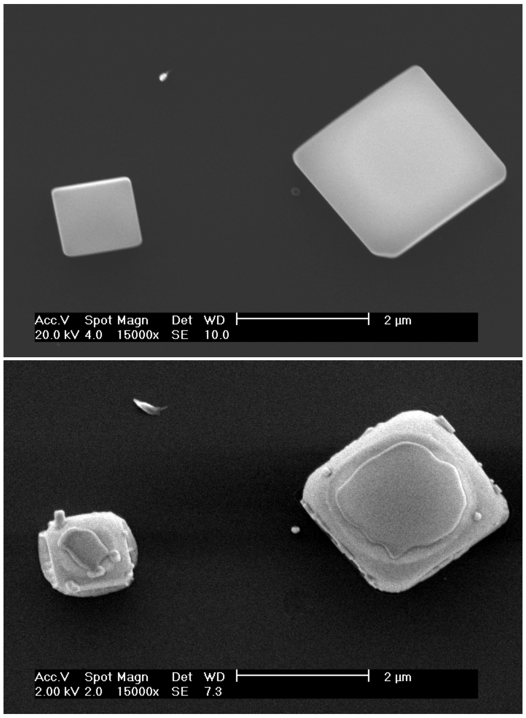

Figure 2. SEM images of NaCl particles exposed to ~10^{10} molecules/cm^{-3} OH at 80 % Relative Humidity: before exposure (upper panel) and after exposure (lower panel).

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Knipping, EM, MJ Lakin, KL Foster, P Jungwirth, DJ Tobias, RB Gerber, D Dabdub, and BJ Finlayson-Pitts. "Experiments and Simulations of Ion-Enhanced Interfacial Chemistry on Aqueous NaCl Aerosols." *Science*, 288, 301-306 (2000).

User Projects

Theoretical Studies of Kinetic Processes in Nanoscale Ice Films
H Jonsson
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B Kay, J Daschbach
Pacific Northwest National Laboratory

Vibration-Rotation Spectroscopy of Sulfur Trioxide
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National Science Foundation, Arlington, Virginia
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Oregon State University, Corvallis, Oregon
A Maki
NIST, Retired
S Sharpe, T Blake, R Sams
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Investigations of Microbial Spore Analysis Using Near-IR Laser Irradiation
D Wunschel, K Beck
Pacific Northwest National Laboratory

Aerosol Particle Generation, Collection and Analysis
V Mikheev, S Barlow
Pacific Northwest National Laboratory

Nanoparticle Fluorescence
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K Beck, A Joly
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Laser Induced Fluorescence Detection of C_2 and C_3 Vapor
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K Beck, A Joly
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Investigation of Electronic Structure of Fe-S Clusters
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S Colson
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Photoelectron Spectroscopy of Group VI Transition Metal Oxygen Clusters
T Waters
University of Melbourne, Australia
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An Electrochemical Investigation into the Origin of the Enhanced Reactivity of Clays in Contact with Iron Metal
B Balko
Lewis and Clark College, Portland, Oregon
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Measurement of the Two-photon Absorption Cross-section of Natural Dyes
J Woodford
Eastern Oregon University, La Grande, Oregon
K Beck, A Joly
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Investigation of Hydrogen Tunneling in Tropolone
R Redington
Texas Tech University, Lubbock, Texas
T Blake, R Sams
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Material Characterization of Fluid-Loaded Lycopodium Membrance
J Jones-Oliveira, S Barlow
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Kinetics in Ices with Complex Compositions
P Ayotte
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Resonant Surface Excitation of Potassium Salts by Selective Laser Desorption
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Fourier Transform Infrared Spectroscopy and Temperature Program Desorption (TPD) Studies of Amorphous Solid Water (ASW) as a Function of Dosing Temperature

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Jet Spectrum of Nitromethane

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Measurement of Absolute Infrared Absorption Cross Sections of Nitric Acid

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High Resolution Infrared Spectroscopy of Boron Trifluoride

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Study of Nd^3+ Surface Adsorption on Calcite

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Cellular Responses to Ionizing Radiation as Examined by FTIR

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Use of EMSL Scanning Microscopy Capabilities to Study Soil Mineral Weathering

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Spectroscopy Infrared Properties of Hydrogen Cyanide

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Evaluation of Municipal Incinerator Contribution to Spokane Particular Matter

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Scanning Mass Spectroscopy of Aerosols

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Photochemistry of Diluted Magnetic Semiconductor Quantum Dot: A Possible Photocatalyst for Water-Splitting

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High Resolution Infrared Spectroscopy of Methyl Nitrate

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Pd Nanoclusters Supported on MgO(100): Effects of Cluster Size on Chemisorption Properties

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Microscopic Characterization of Sampling Inlet Penetration Efficiency for DOE G-1 Research Aircraft

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Laboratory Studies of Atmospheric Processing of Sea Salt
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Development of an Electrospray Photoelectron Spectroscopy Apparatus with a Low Temperature Ion Trap
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High Resolution Matrix Assisted Laser Deorption/Ionization Imaging of Biological Samples
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High Resolution Infrared Spectroscopy of Isotopically Substituted Butadienes
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High Resolution Infrared Spectroscopy of Acetaldehyde
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Investigation of the Electronic Structure of Fe-S Clusters
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Investigation of Zwitterions in the Gas Phase
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Investigation of the Electronic Structure of Fe-S Clusters
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Investigation of Aromatic and Other Novel Gas Phase Atomic Clusters and Molecules
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Investigation of Gold, Boron, and Fe-S Clusters and Metal Complexes
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L-S Wang
Washington State University, Pullman, Washington

Absolute Infrared Absorption Cross Section of CF_3SF_5
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Single-Molecule Enzymatic Reaction Dynamics
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Theoretical Models of the Adsorption and Desorption Dynamics in Compressed Monolayers
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Laser Desorption From Alkali Halides
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Laser Control of Atomic Desorption
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Matrixed-Assisted Laser Desorption/Ionization
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Laser Ablation of Ionic Crystals
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Ultra-fast Processes in Sodium Chloride
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