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Access to the instrumentation and expertise is obtained on a peer-reviewed proposal basis. Users are participants on accepted proposals. Staff members work with users to expedite access. The EMSL Quarterly Highlights Report documents research and activities of EMSL staff and users.

Research Highlights

Atmospheric Aerosol Chemistry

A New Mechanism for Ozonolysis of Unsaturated Organics on Solids: Phosphocholines on NaCl as a Model for Sea Salt Particles

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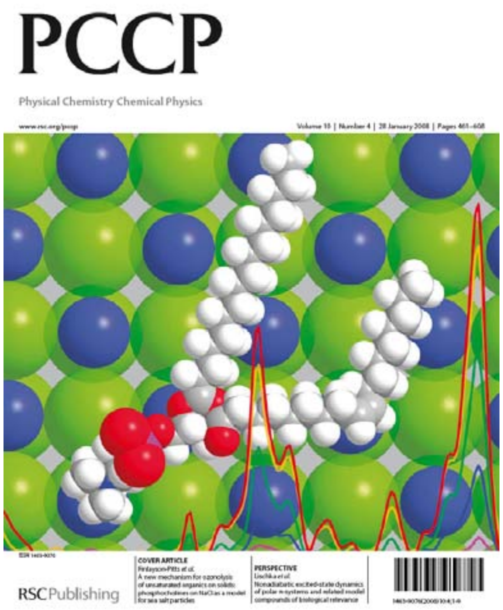
Distinguished EMSL user Barbara Finlayson-Pitts (University of California, Irvine) collaborated with EMSL researcher Scott Lea to determine the effect of ozone and ultraviolet light exposure on phospholipid coated salt crystals using Fourier transform infrared spectrometry, matrix-assisted laser desorption/ionization mass spectrometry, and Auger electron spectroscopy. They found a new mechanism for the ozonolysis of unsaturated organics on aerosols that may increase the understanding of chemistry, photochemistry, and toxicity of these aerosols in dry, polluted environments.

Sea salt particles are a major contributor to the global aerosol burden. They are formed by wave action, which carries along organic material with the sea salt. A major source of this organic layer is the decomposition of marine organisms, which have biomembranes that are a mixture of lipids, hydrophobic proteins, and carbohydrates. Phospholipids and fatty acids are common products of biomembrane disintegration. Previous work has indicated that fatty acid lipids in sea salt particles can be enhanced by factors of $(5\text{-}9)\times10^4$ compared to ocean surface water. An organic coating on sea salt particles is expected to modify the chemical and physical properties of the particles.

We report on the oxidation of an unsaturated phospholipid, 1-oleoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine (OPPC), adsorbed on NaCl (Figure 1) as a model for lipids on sea salt. The primary ozonide formed in the reaction has a sufficiently long lifetime that it can react with other species such as O_3 or H_2O. The reaction of OPPC/NaCl with ozone was studied in a flow apparatus equipped with a Fourier transform infrared spectrometer (DRIFTS). O_3 and relative humidity were controlled and measured in these experiments. In some experiments, the reacted mixture was photolyzed using a high pressure xenon arc lamp to probe for photochemically active products.

Figure 2 shows spectra for OPPC/NaCl during reaction with ozone. A new, strong absorption band is formed at ~1110 cm^{-1} that is characteristic of the peroxide C-O bond of the secondary ozonide ring (SOZ) known to be formed in ozone-alkene reactions. Bands at ~ 1751 cm^{-1} and ~ 1708 cm^{-1} are assigned to carboxylic acids and aldehydes, respectively. It is noteworthy that these bands are much smaller in intensity than the SOZ 1110 cm^{-1} band, despite the fact that their absorption coefficients are larger. This establishes that the SOZ is the major product.



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Physical Chemistry Chemical Physics

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COVER ARTICLE
Finlayson-Pitts et al.
A new mechanism for ozonolysis of unsaturated organics on solids: phosphocholines on NaCl as a model for sea salt particles

PERSPECTIVE
Lischka et al.
Nonadiabatic excited-state dynamics of polar π-systems and related model compounds of biological relevance

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Figure 1. *Model of OPPC adsorbed onto NaCl with corresponding DRIFTS spectra upon exposure to ozone superimposed.*

Figure 3 shows the spectra obtained when the reaction was carried out at 2, 10 and 25% RH. There is a dramatic decrease in the SOZ band at 1110 with increasing RH. Changes in SOZ were monitored at an RH of 10% and at O_3 concentrations of 7.0×10^{13} and 1.7×10^{12} molecule cm^{-3}. The relative decrease in SOZ on adding water vapor is more dramatic at the lower ozone concentration, suggesting that the Criegee intermediate (CI) which forms the SOZ can also react with water vapor in competition with SOZ formation. However, even at 10% RH, the water vapor concentration is large so that this reaction competes with other fates of the CI. It should be noted that in separate experiments, addition of water after the reaction had ceased did not change the SOZ peak, showing that it is not the SOZ itself that reacts with water vapor. After photolysis, the elemental composition measured using Auger spectroscopy is similar to that of unreacted OPPC/NaCl. This suggests that during photolysis, volatile products containing oxygen are generated.

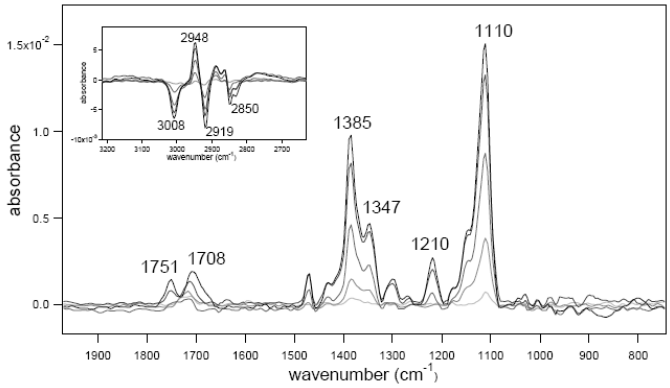

Figure 2. *DRIFTS spectra of OPPC/NaCl upon exposure to 5 × 10^{13} O_3 cm^{-3} at RH ~ 0%. at increasing ozone exposure times (light gray to black, respectively) of 1, 3, 10, 32 and 56 min.*

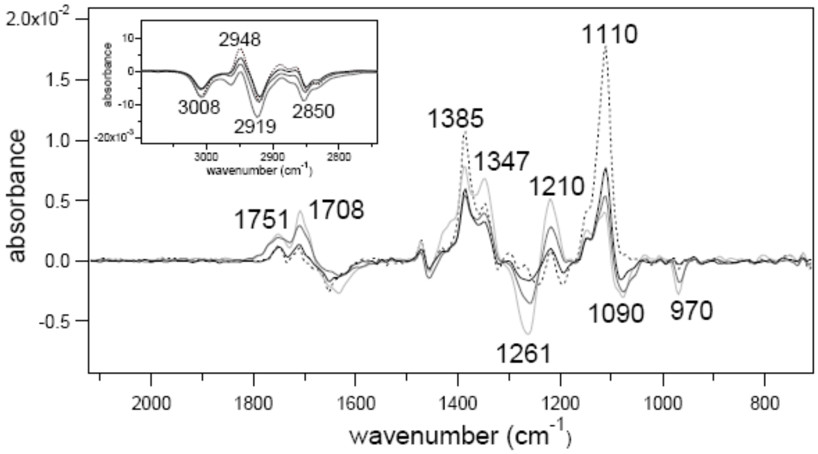

Figure 3. *DRIFTS spectra of OPPC/NaCl upon exposure to 5 × 1013 O3 cm-3 in the presence of water vapor at relative humidities of 2%, 10%, and 25% RH (black to light gray, respectively). The dashed line is the DRIFTS spectrum for a sample reacted with ozone at RH ~ 0%.*

These experiments show that the ozone-alkene chemistry on solids is quite different from that in the gas phase or in solution. In particular, the primary ozonide formed on addition of O_3 to the double bond is sufficiently stable, with a lifetime of ~100 ms that it can undergo further reactions with O_3 and with water vapor. The ozone reaction with OPPC is sufficiently fast that a lifetime of only 15 minutes is expected in the atmosphere at 100 ppb O_3. Even at typical concentrations of O_3 in remote regions, the OPPC lifetime will still only be on the order of an hour. It is clear from the data that the reaction with H_2O will under most circumstances be the major removal path for the POZ in the atmosphere.

There may be situations where formation of the SOZ represents a significant part of the reaction. For example, consider polluted, dry areas such as Mexico City with O_3 peaks of ~400 ppb. Under dry conditions with RH of ~20 %, the lifetime of the POZ is about 90 ms for reaction with O_3 and 5 ms for reaction with H_2O. While hydrolysis still dominates the removal of POZ, some SOZ would be formed. The health effects of SOZ are not known. However, given that it is an oxidant and that the organic side chains will increase its solubility in lipids and cell membranes, it has the potential to negatively impact health. This work was featured on the cover of *Physical Chemistry Chemical Physics* in January 2008.

Citation:

Karagulian F, AS Lea, and BJ Finlayson-Pitts. 2008. "A New Mechanism for Ozonolysis of Unsaturated Organics on Solids: Phosphocholines on NaCl as a Model for Sea Salt Particles." *Physical Chemistry Chemical Physics (PCCP)* 10(4):528-541.

Biological Interactions and Dynamics

Energetics and Dynamics of Electron Transfer and Proton Transfer in Dissociation of Metal^{III}(salen)-Peptide Complexes in the Gas Phase

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Peptides and proteins control nearly all of the chemical reactions in biological systems. This work studies the fundamental energetics and dynamics of model peptides in order to deepen the understanding of these biologically important molecules.

Electron transfer and proton transfer are the most fundamental processes in chemistry and biology. Electron transfer is particularly important in enzyme catalysis, photosynthesis, and respiration. Gas-phase decomposition of ternary complexes of transition metal ions with organic and peptide ligands provides a unique opportunity to explore the competition between these processes using relatively simple model systems. It can also be used for the formation of different types of odd-electron peptide ions for analytical applications focused on identification of peptides and proteins using mass spectrometry.

Here we present the first detailed study of the energetics and dynamics of dissociation of positively charged metal^{III}(salen)-peptide complexes in the gas phase using time and collision-energy-resolved surface-induced dissociation (SID) experiments combined with RRKM modeling. Several fragmentation pathways are commonly observed during collision-induced dissociation of the positively charged metal-salen complexes. These include proton transfer to the peptide molecule or to the ligand, reduction of the metal center followed by electron transfer from the peptide molecule and formation of the radical cation, dissociation of the complex into the [metal^{III}(salen)]$^+$ ion and neutral peptide molecule (D), and dissociative electron transfer resulting in formation of fragment ions of the corresponding peptide radical cation. We examine factors that affect the competition between proton-transfer and electron-transfer processes in gas-phase fragmentation of these model systems.

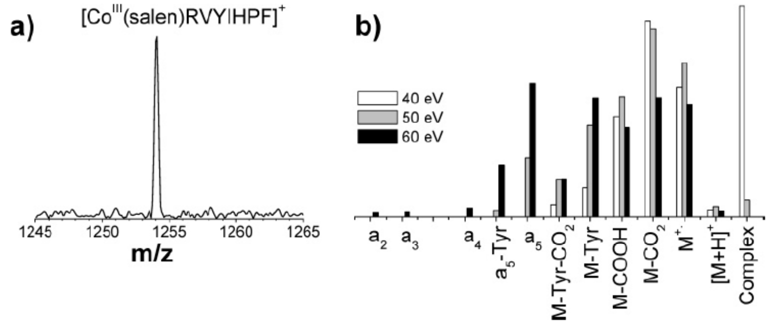

Figure 1. *(a) Mass selected Co^{III}(salen)RVYIHPF precursor ion and (b) fragment distribution for SID of Co^{III}(salen)RVYIHPF complex on the HSAM surface at three collision energies.*

Figure 1 shows a mass-selected [Co^{III}(salen)RVYIHPF]$^+$ precursor ion and its SID fragment distributions obtained at three collision energies. The four primary dissociation pathways are observed. Losses of

CO_2 and COOH• are characteristic dissociation pathways of peptide radical cations that have been previously observed for dissociation of both doubly-charged and singly-charged ternary complexes of transition metals with peptides. Formation of these ions requires electron transfer from the peptide to the metal core of the complex. In addition, electron transfer results in formation of the peptide radical cation, $M^{+\bullet}$, while the [M + H]+ ion is formed by proton transfer from the organic ligand to the peptide.

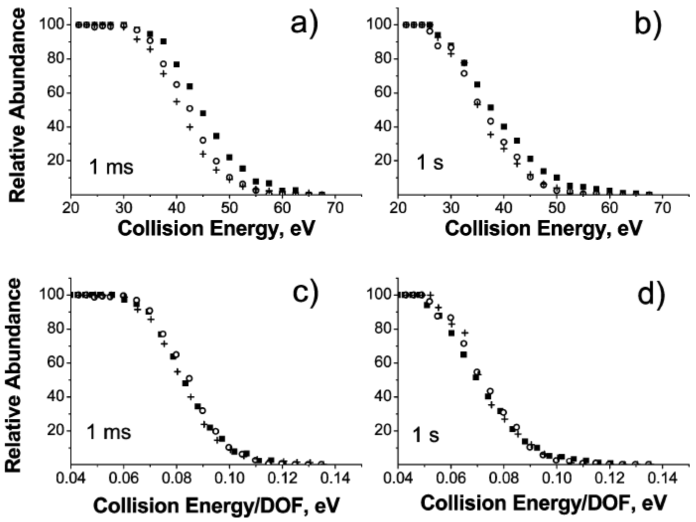

Figure 2. *SCs (Panels a and b) and SCs plotted as a function of collision energy scaled by the number of the vibrational degrees of freedom of the precursor ion (Panels c and d) for Co^{III}(salen)DRVYIHPF (square), Co^{III}(salen)RVYIHPF (O), and Co^{III}(salen)RVYIHDF (+), 1 ms (left panels) and 1 s (right panels).*

Time-resolved survival curves (SCs) were obtained by plotting the relative abundance of the intact precursor ion as a function of collision energy at different reaction delays. The SCs obtained at reaction delays of 1 ms and 1 s are shown for cobalt-salen complexes with three different peptides are displayed in Figure 2. The relative position of the SCs reflects the relative stability of different complexes toward fragmentation. The experimental SCs for [Co^{III}(salen)DRVYIHPF]$^{+}$ are slightly shifted toward higher collision energies for both 1 ms and 1 s reaction delays, while SCs obtained for cobalt-salen complexes of RVYIHPF and RVYIHDF show an almost perfect overlap. It should be noted that this trend follows the trend in the number of vibrational degrees of freedom (DOF) of the complexes (540 for DRVYIHPF, 501 for RVYIHPF, and 498 for RVYIHDF). The DOF effect can be eliminated by plotting the relative abundance of the precursor ion as a function of collision energy scaled by the number of DOF of the precursor ion. Perfect overlap between the SCs plotted versus the scaled collision energy clearly demonstrates that the observed shift in the position of the SCs shown results only from the DOF effect and suggests that both the energetics and dynamics of dissociation of all three cobalt-salen-peptide complexes are very similar.

This work represents the first detailed study of the factors that affect gas-phase fragmentation of ternary complexes of angiotensin analogues with trivalent metal-salen systems. Time- and collision-energy-resolved SID provide interesting insight on the competition between proton transfer, electron transfer, and loss of the neutral peptide ligand in these model systems. We found that both the fragmentation behavior and the stability of the complexes are similar for different peptide ligands examined in this study. In contrast, the observed fragmentation pathways, the mode of binding, and the energetics and dynamics of dissociation of these systems strongly depend on the electronic properties of the metal center. Interestingly, a very different kinetics of formation of the M$^{+\bullet}$ fragment ion from the cobalt-salen and iron-salen complexes was observed experimentally. We concluded that the electron-transfer process in the dissociation of the [Fe^{III}(salen)RVYIHPF]$^{+}$ ion requires substantial rearrangement of the complex. Details of this exciting research were recently published in the *Journal of the American Chemical Society*.

Citation:

Laskin J, Z Yang, and IK Chu. 2008. "Energetics and Dynamics of Electron Transfer and Proton Transfer in Dissociation of Metal^{III}(salen)-Peptide Complexes in the Gas Phase." *Journal of the American Chemical Society* 130(10): 3218-3230.

The Synergy between Molecular Theory and Solid-State NMR Spectroscopy

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Understanding DNA repair proteins is important to linking environmental impact to biological health effects.

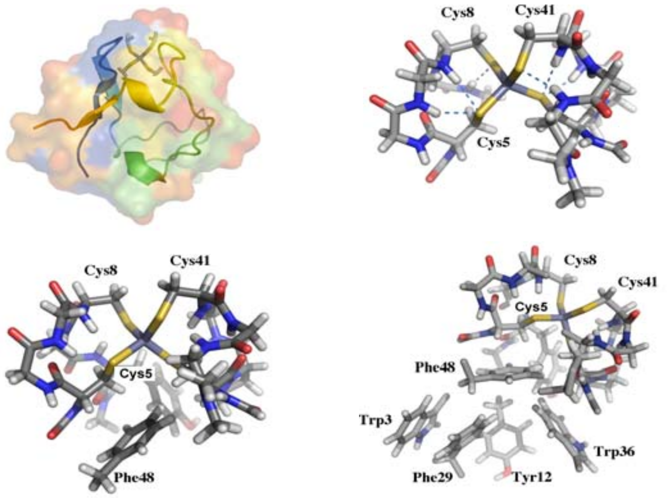

Figure 1. *Optimized quantum regions of Pf-rubredoxin, a zinc-containing DNA repair protein. Combined QM/MM calculations were performed on Pf-rubredoxin with increasing complexity in the quantum region. The research demonstrated sensitivity of the predicted NMR parameters to not only hydrogen bonding, but lone pair (LP)-π interactions. The research team achieved good agreement between theory and experimental values of both the electric field gradient and anisotropic shielding tensors.*

Research evaluating the local electronic environment of zinc that affects the structural or chemical function in proteins has been accelerated by the use of two key long-term capability investments at EMSL. The first is implementation of a NWChem module that provides *ab initio* quantum mechanical calculations using molecular mechanics (QM/MM) constraints; the NWChem code was developed at EMSL. The second is the successful development and implementation of low-temperature solid-state nuclear magnetic resonance (NMR) capabilities at high magnetic fields. The latter is designed to allow direct observation of NMR resonances of metals such as zinc and magnesium in metalloproteins that, under ambient conditions, would be arduous if not impossible to accomplish. Both the NWChem software development and the capability suite to perform low-temperature, solid-state NMR experiments at 18.8T were funded by the DOE Office of Biological and Environmental Research. A study employing the converged methodologies is summarized in a paper in press (Lipton et al. 2008), authored by EMSL staff (M. Valiev and W. A. De Jong) in collaboration with staff from Pacific Northwest National Laboratory's Biological Sciences Division (A. S. Lipton, R. W. Heck, and P. D. Ellis) and a Science Undergraduate Laboratory Internship student G. R. Staeheli. The publication discusses how QM/MM methods help elucidate the NMR spectra of zinc in a pivotal type of zinc metalloprotein, in which zinc is coordinated by four cysteines (Figure 1). In this case, the zinc plays an essential structural role. Based on knowledge gained from these investigations, the authors are now primed to investigate zinc sites (again fully coordinated by cysteine residues) where one of the cysteines has been activated by the zinc, allowing it to serve as a reactive center in DNA repair. This powerful combination of theory and experiment will be utilized to probe the means by which coordination geometry differentiates between a structural site and a reactive site, allowing a deeper understanding of DNA repair mechanisms.

Citation:

Lipton AS, RW Heck, M Valiev, WA De Jong, and PD Ellis. "A QM/MM Approach to Interpreting ^{67}Zn Solid-state NMR Data in Zinc Proteins." *Journal of the American Chemical Society* (in press).

Researchers Utilize Proteomics to Reveal a Core Proteome

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Researchers leveraged proteomics technology at EMSL to reveal the existence of a core proteome among 17 diverse bacteria. While many researchers make genomic comparisons among different bacteria and often report a set of common genes or core genome (Koonin 2003), the expression of this core genome as a core proteome is not generally verified. The verification of these genes as proteins has important implications to defining a set of basal proteins important to bacterial life that could aid in the construction of synthetic life-like systems, or synthetic biology. Ultimately, this research demonstrated the ability to use proteomic data in a comparative manner outside of conventional norms.

Enabled by a proteome database that encompassed ~967,000 experimentally determined unique peptides linked to specific protein information and publicly available genome sequences, the observation of proteins predicted from genomic comparisons among 17 environmental and pathogenic bacteria was investigated (Callister et al. 2008). Bacteria selected for this investigation included the metabolically diverse organisms *Rhodobacter sphaeroides*, *Shewanella oneidensis,* and *Synechocystis sp.* PCC6803, as well pathogens such as *Yersina pestis* and *Salmonella typhimurium*. Facilitated by successful collaborations that have made samples available for proteomic analysis, this investigation represents the gathering and evaluation of proteomic measurements made over the past six years.

Genomic comparisons among the 17 bacteria predicted the existence of a core genome composed of 144 genes (Figure 1). Proteins from 74% of these genes were observed within the database, with each protein identified by two unique peptides. The large percentage of the core genome being observed surprised researchers because of the somewhat diverse make-up of the bacteria selected, and the different number and variety of conditions used to culture the organisms. This observation has led to the hypothesis that although the number of genes making up a core genome may expand or contract depending on the number and diversity of organisms included, the percent of these genes being expressed as proteins in nature will be high.

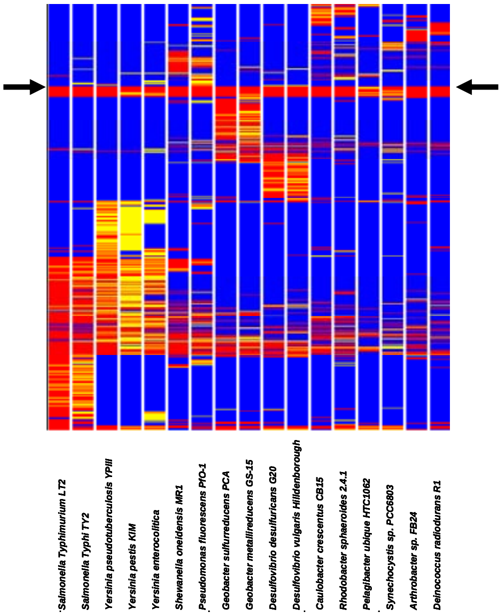

***Figure 1**. The core proteome is revealed for 17 bacteria. Genomic comparisons identified genes common to two or more bacteria (orange) resulting in a core genome of 144 genes. Proteomic measurements were used to verify the existence of these genes as proteins (red) resulting in the identification of a core proteome (arrow).*

A functional analysis revealed that a majority of core proteome proteins (~55%) have functions related to protein synthesis, not surprising as the ability of a bacterial cell to make proteins for cell maintenance and growth is a vital function. However, what was surprising to researchers was the observation of proteins (~7%) having very little or no functional characterization; for example, the observation of the iojap-like protein. This gene was predicted in our study as homologous across all 17 bacteria and is also found outside the bacterial domain as well. The product of this gene is a small protein so the number of detectable peptides is also potentially small relative to some of the larger ribosomal proteins we observed. Yet, little is known about this protein's function in the bacterial cell (Galperin and Koonin 2004). The observation of these relatively uncharacterized proteins emphasizes the need for a better understanding of basal bacterial functions.

Citations:

Callister SJ, LA McCue, JE Turse, ME Monroe, KJ Auberry, RD Smith, JN Adkins, and MS Lipton. 2008. "Comparative Bacterial Proteomics: Analysis of the Core Genome Concept." *PLoS ONE* 3(2):e1542.

Galperin MY, and EV Koonin. 2004. "'Conserved Hypothetical' Proteins: Prioritization of Targets for Experimental Study." *Nucleic Acids Research* 32(18):5452-5463.

Koonin EV. 2003. "Comparative Genomics, Minimal Gene-Sets and the Last Universal Common Ancestor." *Nature Reviews Microbiology* 1(2):127-136.

Geochemistry/Biogeochemistry and Subsurface Science

Understanding Uranium Complex Formation through Combined Modeling and Gas-Phase Experiments

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Using experimental analysis combined with EMSL's computational modeling capabilities, researchers obtained fundamental insight into the formation of uranium oxide complexes, knowledge that is essential for understanding the speciation of uranium in the subsurface and in Hanford waste tanks.

The production of radioactive materials has resulted in large amounts of waste and releases of radioactive constituents at DOE sites and in the environment. Gaining a comprehensive description and full understanding of contaminant mobility represents a major challenge to DOE's cleanup mission, as the transport and transformation of contaminants in the subsurface and across key groundwater-surface water interfaces is not well understood. In the dynamic realm of solution-phase actinide coordination chemistry, the formation and stability of complexes is controlled by coordination, geometry, oxidation state, and cooperative effects between different ligands. Probing these aspects provides fundamental insight that is leading to an understanding of the effect of electronic structure and bonding preferences that could eventually be exploited to manipulate actinide behavior.

Researchers from Idaho National Laboratory and Wichita State University have used infrared multiple photon dissociation experiments to probe the formation and reactivity of uranyl-ligand (UO_2^{2+}) complexes in the gas-phase, controlling the type of ligands, number of ligands, and oxidation state of the uranyl. Infrared spectra of the formed complexes and photo-fragmentation pathways were obtained from the experiments, but to obtain a complete understanding and interpretation of their observations, the researchers teamed up with computational chemists from EMSL and the Vrije Universiteit Amsterdam. Using EMSL's supercomputer and NWChem computational chemistry software, the researchers were able to obtain molecular structures, vibrational spectra, and reaction energetics that reproduced the experimental observations with reasonable accuracy, leading to a comprehensive interpretation of the results.

A comprehensive study of uranyl-nitrate complexes, readily present in Hanford Site waste tanks, was recently published in *Physical Chemistry Chemical Physics* (Groenwald et al. 2008a). The $[UO_2(NO_3)_3]^-$ was irradiated, but instead of losing a nitrate ligand, an NO_2 fragment dissociated from the complex. Infrared spectra did not provide the insight of the complex formed as either $[UO_2(NO_3)_2O]^-$ or, through a complex reaction mechanism, the superoxide $[UO_2NO_3NO_2O_2]^-$ could be formed (Figure 1). Comparing the results of computational modeling of different complex geometries and their associated infrared spectra with the experimental data revealed that the uranyl-nitrate complex dissociated to and from the $[UO_2(NO_3)_2O]^-$ complex.

An article published in the high-ranking *Journal of Physical Chemistry A* (Groenwald et al. 2008b) describes the formation of $[UO_2A(S)_n]^+$ complexes, where A was a hydroxide, methoxide, or acetate, while S (ranging from one to three ligands) was water, ammonia, acetone, or acetonitrile. Computational modeling showed that there is a clear correlation between the ligand dissociation energy and ability to donate electron density to the uranyl ion, and changes in the infrared asymmetric stretch of the uranyl. Generally, the computational results were found to be in good agreement with the experimental data. The only exception is the disagreement between theory and experiment for the free UO_2OH^+, which is still not fully explained. One possible cause could be anharmonicity, as the spectra are measured by pumping in energy and breaking the molecule. For this small a molecule, anharmonicity might become important, or excited states might be involved.

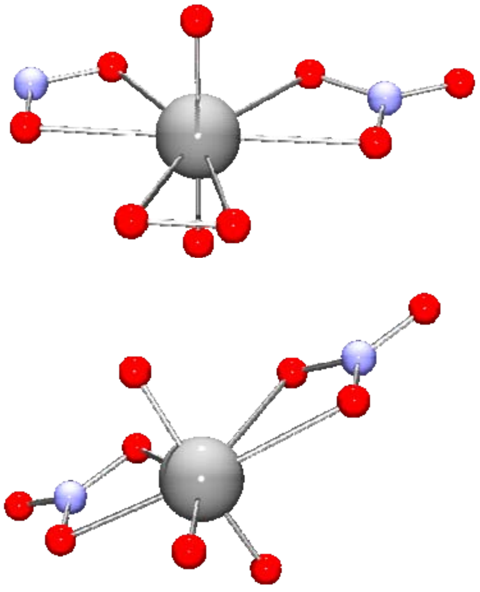

***Figure 1**. Possible uranyl nitrate complexes formed after photofragmentation. Top: $[UO_2(NO_3)_2O]^-$, Bottom: $[UO_2NO_3NO_2O_2]^-$.*

Citations:

Groenewold GS, J Oomens, WA de Jong, GL Gresham, ME McIlwain, and MJ Van Stipdonk. 2008a. “Vibrational Spectroscopy of Anionic Nitrate Complexes of UO_2^{2+} and Eu^{3+} Isolated in the Gas Phase.” *Physical Chemistry Chemical Physics (PCCP)* 10(8):1192-1202.

Groenewold GS, AK Gianotto, ME McIlwain, MJ Van Stipdonk, M Kullman, DT Moore, N Polfer, J Oomens, I Invante, L Visscher, B Siboulet, and WA de Jong. 2008b. “Infrared Spectroscopy of Discrete Uranyl Anion Complexes” *Journal of Physical Chemistry A* 112(3):508-521.

Science of Interfacial Phenomena

Alcohol Chemistry on Rutile TiO_2(110): The Influence of Alkyl Substituents on Reactivity and Selectivity

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TiO_2 is widely used as a catalyst and may provide a pathway for the use of solar radiation as a viable source of clean energy. This work is a detailed study of the reaction mechanisms for the dehydrogenation reaction of alcohols on TiO_2(110). This knowledge will increase our fundamental understanding of elementary surface reactions and may lead to improvements and new applications in heterogeneous catalysis.

Many reactions on solid surfaces (e.g., oxides) occur on defect sites. On prototypical rutile TiO_2(110) surfaces, there is direct scanning tunneling microscopy (STM) evidence that bridge bonded oxygen vacancies (BBOVs) are sites for dissociation of oxygen, water, and alcohols. In the surface science and catalysis literature involving alcohol, chemistry on TiO_2, dehydration to alkenes above 500 K is well established while dehydrogenation to aldehydes or ketones and reformation of the dosed alcohols are less well established. The chemical pathways leading to these products are typically described terms of paths requiring BBOVs. However, the inability to control surface order and BBOV concentration may account for reported variations in temperature-programmed desorption (TPD) profiles of alcohol dehydration, making it difficult to establish unambiguous connections between catalytic dehydration activity and the local surface structure of TiO_2(110).

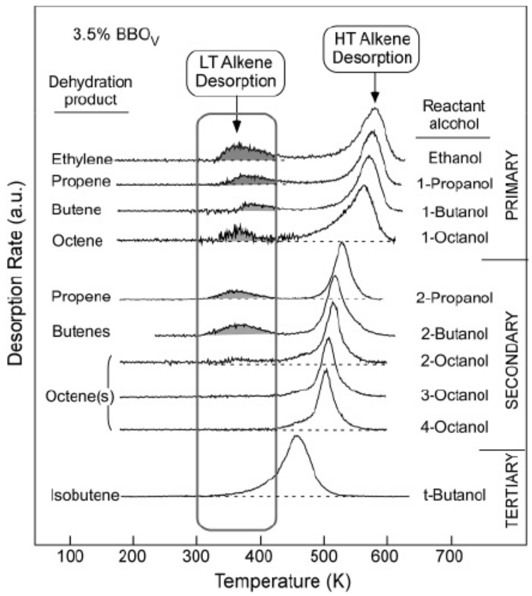

Figure 1. *TPD spectra of alkenes from 10 alcohols dosed on TiO_2^-(110) at 100 K grouped as primary, secondary, and tertiary. The net alkene desorption spectra (shown) were obtained by subtracting the fragmentation contributions of molecular alcohol. The 27 and 41 amu were used for ethylene and propene, respectively, and 56 amu was used for butenes and octenes. The alcohol dose was set to 1 ML, and all spectra were normalized to the HT alkene desorption peaks.*

As part of a research program to establish direct atomic-level descriptions by combining STM and reaction rate measurements for oxygenates on oxides, we have recently reported

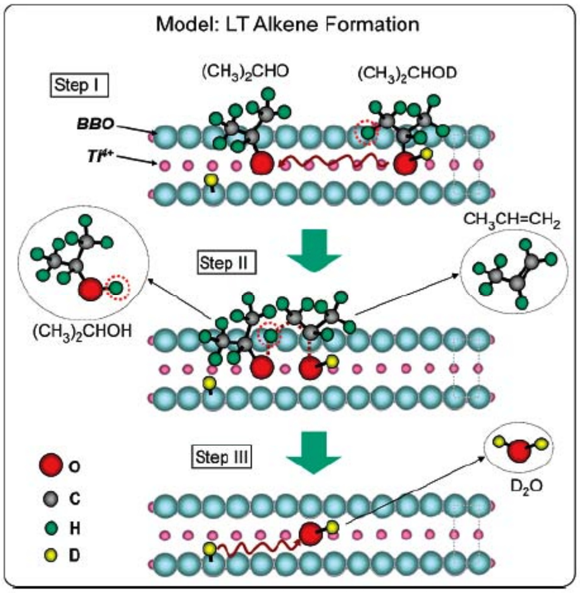

Figure 2. *Schematic of proposed LT dehydration mechanism. The key intermediate is a complex (Step II) formed by interaction of an oriented alkoxide with an oriented chemisorbed alcohol (Step I). There is a concerted rearrangement that involves beta-H, in the case shown on CH_3, coupling to the alkoxide oxygen and simultaneous cleavage of the C-O bond of the chemisorbed alcohol. Step III illustrates the final recombinative desorption of D_2O.*

on the ensemble average surface chemistry of three different isotopically labeled 2-propanols dosed at 100 K on TiO_2(110). For the first time, a low-temperature (LT) dehydrogenation path (300-450 K) was found to accompany the well-established high-temperature (HT) path ($T > 450$ K). While surface structure is one key, variations with the alcohol are also expected and have been reported; while dehydration typically dominates, dehydrogenation contributes more for primary alcohols. The present study was motivated by a desire to determine the detailed roles played by the alkyl substituents on the accessibility of the LT and HT channels and on the dehydration selectivity. The inductive and steric effects of alkyl substituents are the concepts commonly used to understand the trends in the reactivity of similar molecules in homogeneous organic chemistry (e.g., in liquids). Here, we show that similar concepts can be successfully applied to understand the heterogeneous reactions at gas-solid interfaces. In this work, we report the details of the LT and HT reaction paths for primary, secondary, and tertiary alcohols for 100 K doses on well-ordered TiO_2(110) with a reproducible, relatively small BBOV concentration (3.5%).

With the above picture in mind, Figure 1 displays the alkene TPD spectra for 1 ML of 10 different alcohols deposited on TiO_2(110). In the LT region, seven of the 10 (ethanol, 1- and 2-propanol, 1- and 2-butanol, and 1- and 2-octanol) exhibit intensity, whereas the other three (3- and 4-octanol, and *t*-butanol) do not. When the LT channel is present, the peak temperature shows no systematic variation with alcohol structure. On the other hand, the HT channel is observed for all 10 alcohols and varies systematically with two properties of the dosed alcohol. First, the HT peak positions group together; primary alcohols are systematically higher by 50-60 K than the secondary alcohols which are, in turn, higher by another 50-60 K than the tertiary alcohol. Within each grouping, the production rate maximum drops 10-20 K as the chain lengths increase. The HT shifts are explained in terms of inductive electronic effects of the alkyl groups; the latter are described empirically using the Taft parameters of organic reaction chemistry.

The variations in LT alkene production confirm effects related to the number of carbon atoms in the alkyl chains. For primary alcohols. the low-temperature channel is active for all chain lengths studied (up to C8). For *t*-butanol, there is no evidence for LT alkene production. For secondary alcohols, alkene production is observed, except if there is no CH_3 attached to the alpha carbon.

Based on a series of experiments, we have developed a mechanism for the LT reaction pathway. The LT dehydration pathway is attributed to the species bound to Ti^{4+} rows. Mobility of ROH along the Ti^{4+} rows is expected and was observed in STM below the temperature where this desorption commences. The mechanism, illustrated in Figure 2, involves a mobile and oriented, but undissociated, alcohol molecule that undergoes a 1D random walk along a given Ti^{4+} row (Step I). An encounter with 2-propoxy, also oriented, during this 1D random walk form a critical activated complex (Step II) that rearranges in the LT region to form propene and 2-propanol that desorb and a mobile OH group bound to Ti^{4+} (Step III), HO_{Ti}. Finally, in the OH groups, one on a BBO row, HO_{bb}, and the other mobile and on an adjacent Ti^{4+} row, HO_{Ti}, collide and form H_2O that desorbs leaving the O_{bb}. Thus, no net loss of lattice oxygen occurs during the reaction cycle.

The exact nature of the activated complex is not clear, but the experimental evidence suggests that it requires two oriented reactants with close proximity of their alpha and beta carbon atoms. Details of this exciting research were published in the *Journal of Physical Chemistry C.*

Citation:

Kim YK, BD Kay, JM White, and Z Dohnalek. 2007. “Alcohol Chemistry on Rutile $TiO_2(110)$: The Influence of Alkyl Substituents on Reactivity and Selectivity.” *Journal of Physical Chemistry C* 111(49):18236-18242.

Probing Reaction Pathways Using *in situ* ^{1}H NMR Spectroscopy

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Real-time observation of the reaction mechanisms for the generation of H_2 will help researchers identify potential hydrogen storage materials.

In collaboration with Professor Leon Shaw’s group from the University of Connecticut, Drs. Jian Zhi Hu, Ja Hun Kwak and Zhenguo Yang from PNNL used *in situ* variable temperature ^{1}H nuclear magnetic resonance (NMR) spectroscopy to observe the products produced during controlled conditions. The results gave direct evidence of the two-step reaction pathway for evolution of H_2 in the dehydrogenation reaction:

$$LiNH_2+LiH=Li_2NH+H_2. \qquad (1)$$

This Li-N-H system, first reported by Chen et al., has been extensively investigated as potential hydrogen storage material. It was shown that decomposition is rapid in the order of 25 milliseconds, and several studies have hinted that a two-step mechanism existed (see Equations 2 and 3).

$LiNH_2 = 1/2Li_2NH + 1/2NH_3$ (2)

$1/2NH_3 + 1/2LiH = 1/2\ LiNH_2 + 1/2H_2$. (3)

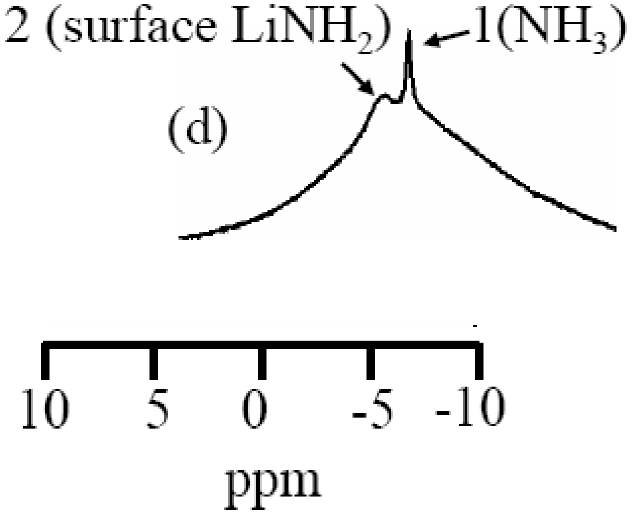

Figure 1. *^{1}H spectrum of $LiNH_2$ power acquired at 30°C, which highlights the molecules attributed to surface $LiNH_2$ and the NH_3 released at 30°C.*

Results from this *in-situ* experiment at EMSL resulted in definitive direct evidence for the two-step mechanism. The results were published online (http://dx.doi.org/10.1016/j.jpowsour.2008.03.034), and a paper is in press for publication in *Journal of Power Sources* (an ISI Top-5 journal in energy and fuels).

During the variable temperature *in-situ* NMR experiment performed on a powder sample of $LiNH_2$ that was prepared using high-energy ball milling, three separate peaks were identified in the subsequent ^{1}H spectra (Figure 1). These peaks verified the existence of bulk $LiNH_2$, surface $LiNH_2$, and gaseous NH_3. All assignments were assisted by understanding the connection of line width to molecular motion. In particular, fast motion on the NMR time scale leads to narrow lines and rigid slow motion to wide lines.

Changing the temperature conditions shows that NH_3 was released slowly at 30°C and the speed of ammonia release significantly increased at temperatures above 75°C.

The variable temperature *in-situ* NMR experiments (Figure 2) on a powder sample consisting of a mixture of $LiNH_2$ + LiH that was mechanically activated via high-energy ball milling reveals the observation of NH_3, indicating that reaction (3) is not very fast until temperatures above 150°C are reached and that the minimum temperature required activating (2) is lower than the temperature required to activate (3). The appearance of NH_3 peak in Figure 2(d) and the disappearance of the NH_3 peak in Figure 2(f) clearly confirm the two elementary reaction steps [i.e., NH_3 is generated first by $LiNH_2$ (see Equation (2) and then NH_3 reacts with LiH to release H_2 (Equation (3)].

The *in-situ* techniques developed here serve to illustrate the potential application of a relatively simple approach that will enable the real-time observation of mechanistic data and performance evaluation in future hydrogen storage material studies.

Citation:

Chen P, Z Xiong, J Luo, J Lin, and KL Tan. 2002. "Interaction of Hydrogen with Metal Nitrides and Imides." *Nature* 420(6913): 302-304.

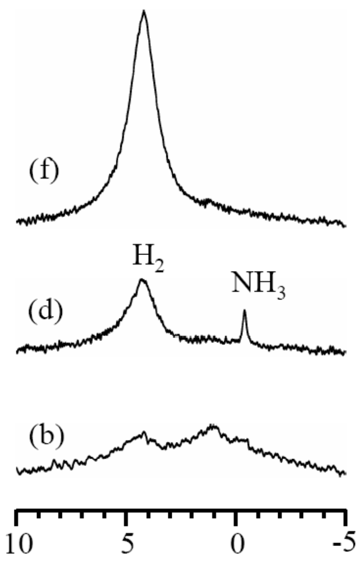

Figure 2. *Representative in situ ^1H NMR spectra of the $LiNH_2$ + LiH samples. Spectrum (f) was acquired when the temperature was ramped from 150°C to 180°C (no NH_3 peak observed). Trace Spectrum (d) was acquired when the temperature was ramped from approximately 40°C to 150°C. Both the NH_3 product from Equation 2 and the H_2 product from Equation 3 are observed. Spectrum (b) was acquired at room temperature.*

Conductivity of Oriented Samaria-Doped Ceria Thin Films Grown by Oxygen-Plasma-Assisted Molecular Beam Epitaxy

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(d) Pacific Northwest National Laboratory, Richland, Washington

Due to global demands for increased energy resources and sustainable and renewable alternative energy, technologies such as solid-oxide fuel cells (SOFCs) are becoming the significant focus of researchers across the globe. In an effort to make this technology economically and practically viable for everyday use, it is of paramount importance for researchers to understand the fundamental aspects that control the performance of an SOFC. The heart of the SOFC is the electrolyte material that transports oxygen ions from cathode to anode. High-quality, epitaxial thin films of doped cerium oxide (a potential material for SOFC electrolytes at low and intermediate temperatures) are an excellent resource that allows researchers to explore the fundamental mechanisms that control the ionic conduction in SOFC electrolytes.

With the increasing demand for energy efficiency and the realization that greenhouse gas emissions must be reduced, technologies such as solid-oxide fuel cells (SOFC) are gaining significant attention. The fundamental understanding of the actual mechanisms that govern the ionic conduction in SOFC electrolytes is still elusive. A major hurdle in overcoming this bottleneck stems from the lack of studies based on high-quality materials. Use of conventional powder-processed pellets with porosity and grain boundaries makes analysis more complicated. Oxygen-plasma-assisted molecular beam epitaxy capabilities housed at EMSL have allowed researchers to synthesize high-quality epitaxial thin films with controlled dopant levels and thickness. Among the various materials used for low- and intermediate-temperature SOFC electrolyte application, samaria (Sm_2O_3, samarium oxide) doped ceria (CeO_2, cerium oxide) (SDC) is expected to be the best possible material. Hence, high-quality epitaxial SDC films were grown on sapphire (0001) substrates.

The grown films were characterized using various *in-situ* and *ex-situ* techniques to understand their structure, crystalline quality, elemental distribution, and chemical composition (oxidation states of the cations). After establishing the optimum growth conditions, films with various amounts of dopant concentrations were grown (1 – 33 atom % samaria). Electrochemical impedance measurements were carried on these films using a four-probe van der Pauw method. The conductivity data obtained from these measurements were analyzed as a function of temperature and dopant concentration (Figure 1). Some of the salient features from this work are highlighted below:

- Ceria films with more than 10 atom% samaria were found to show polycrystalline features, while the films with less than 10 atom% samaria were found to be epitaxial, highly oriented films.
- Rutherford backscattering spectrometry and x-ray and electron diffraction measurements confirmed the high-quality, epitaxial nature of the films.

- 5 atom % samaria doping was found as an optimum concentration to obtain maximum conductance among various compositions.
- The reduction in the conductivity in films with high dopant concentration is attributed to the polycrystalline nature of the films. In the polycrystalline films, grain boundaries may act as scattering centers for the oxygen ions, hence the observed decrease in the overall conductivity.

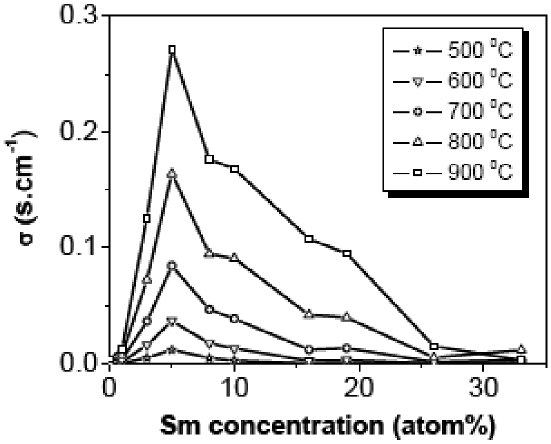


***Figure 1.** The conductivity of Ce1-xSMxO2*Δ films as a function of samaria concentration for the temperature range of 500-900°C.*

- The higher ionic conduction at lower temperatures in the highly oriented SDC films is attributed to the alignment of oxygen vacancies [generated to retain the electrical neutrality of the ceria ($Ce^{4+}O^{2-}$) crystal when doped with Sm^{3+}]. The aligned oxygen vacancies help efficiently transport oxygen ions across the electrolyte from cathode to anode.

Various ongoing user research programs at EMSL are focused on exploring the finer details behind these observations and are aimed at developing a comprehensive understanding of the fundamental mechanisms that control the performance of nanoscale doped-oxide materials as potential SOFC electrolyte materials. This research was published in *Electrochemical and Solid State Letters* (Yu et al. 2008).

Citation:

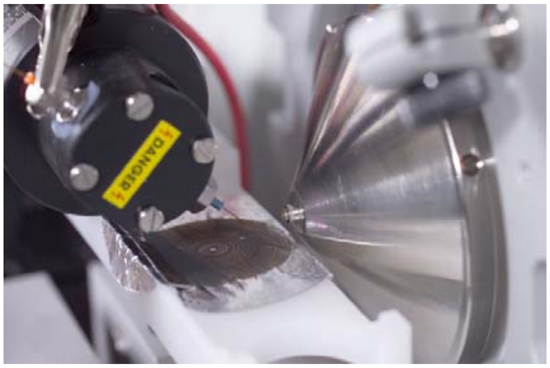
Yu ZQ, SV Kuchibhatla, LV Saraf, OA Marina, CM Wang, MH Engelhard, V Shutthanandan, P Nachimuthu, and S Thevuthasan. 2008. "Conductivity of Oriented Samaria-Doped Ceria Thin Films Grown by Oxygen-Plasma-Assisted Molecular Beam Epitaxy." *Electrochemical and Solid State Letters* 11(5):B76-B78.

Major Upgrades

Desorption ElectroSpray Ionization (DESI) – Linear Ion Trap Quadrupole Orbitrap™ Hybrid Mass Spectrometer. The major problem in understanding the formation mechanisms and effects of organic aerosols on climate change is the limited knowledge of the chemical composition of this type of particulate matter, which is poorly characterized and incomplete at best. Recent studies indicate that about 50-70% of organic aerosols are composed of large oligomeric and humic-like substances with molecular weights of 500 amu and higher. These high molecular weight compounds cannot be identified using traditional approaches for aerosol chemical analysis, which are best suited for analysis of low molecular weight organics.

High-resolution hybrid Linear Trap Quadrupole/Orbitrap™ Mass Spectrometer located in EMSL's Aerosol Chemistry Laboratory.

EMSL houses a novel, high-resolution hybrid Linear Trap Quadrupole/Orbitrap™ Mass Spectrometer dedicated to identification and chemical structure characterization of high molecular weight organic compounds in aerosol and cloud water samples. A desorption electrospray ionization (DESI) source is used to produce ions of large non-volatile organic molecules with minimal fragmentation. The DESI- Linear Trap Quadrupole/Orbitrap™ Mass Spectrometer is characterized by inherently high mass accuracy (0.1-5 ppm), high mass resolution (up to 100,000), and reliable high-sensitivity multiple-stage tandem mass spectrometry set up for analysis of ions with the mass-to-charge ratios in the range of 20-2000 amu. Accurate mass measurements using high-resolution mass spectrometry are crucial for unique identification of the elemental composition of the constituents of organic aerosols, while multiple stages of tandem mass spectrometry experiments are essential for structural characterization of complex molecules. In addition, the system is coupled with a high-performance liquid chromatography separation stage to enable better detection and confident, unequivocal identification of complex oligomeric constituents and humic-like substances in aerosols.



DESI interfaced with Linear Trap Quadrupole/Orbitrap™ Mass Spectrometer.

Applications of the DESI- Linear Trap Quadrupole/Orbitrap™ Mass Spectrometer in aerosol research are focused on the development of a new knowledge base for the fundamental understanding of the chemistry and composition of organic aerosols and their impact on the hygroscopic and CCN properties of particles, thereby addressing one of the major areas of uncertainty in atmospheric chemistry.

Recently, the system was used for:

- laboratory studies of the mechanisms of aerosol formation from ozonolysis of gas-phase precursors (Walser ML, Y Desyaterik, J Laskin, A Laskin, SA Nizkorodov. 2008. “High-Resolution Mass Spectrometric Analysis of Secondary Organic Aerosol Produced by Ozonation of Limonene.” Physical Chemistry Chemical Physics: *PCCP* 10(7):1009-1022)

- Molecular speciation of biomass burning aerosols
- Molecular speciation of non-refractory aerosols emitted from aircraft jet engines.

Awards and Recognition

EMSL user appointed to DOE's Basic Energy Sciences Advisory Committee. Bruce Kay, Pacific Northwest National Laboratory, recently accepted an appointment to DOE's Basic Energy Sciences (BES) Advisory Committee. This committee helps solve challenging scientific and technical issues for BES. As a part of the 25-member committee, composed of experts from academia, national laboratories, and other institutions, Kay will make recommendations on research and facilities priorities, appropriate balance among scientific disciplines, and collaboration among research institutes and industries. Undersecretary for DOE's Office of Science Dr. Raymond Orbach selected Kay for this assignment.

Visitors and Users

During the second quarter of Fiscal Year 2008, a total of 381 users benefited from EMSL capabilities and expertise. This total included 255 onsite users and 126 remote users.

Publications

Book Chapters

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Conferences and Presentations

During the second quarter of Fiscal Year 2008, EMSL staff presented on research performed at the user facility or attended conferences at the following meetings or locations:

- 48th Sanibel Symposium in St. Simons Island, Georgia
- American Meteorological Society Meeting, New Orleans, Louisiana
- American Physical Society March Meeting, New Orleans, Louisiana
- AirUCI Annual Workshop, Irvine, California
- DOE Atmospheric Sciences Program Meeting, Annapolis, Maryland
- IEEE Electrical Safety Workshop, Dallas, Texas
- Greener Nano 2008 Conference, Corvallis, Oregon
- Society of Toxicology Annual Meeting, Seattle, Washington.