Chemistry and Physics of Complex Systems Facility

The Chemistry and Physics of Complex Systems (CPCS) Facility supports the U.S. Department of Energy (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 national laboratories is their approach to problem solving. Significant scientific issues are addressed using focused and multidisciplinary investigative teams with each team member bringing a particular skill and capability to bear on the problem. This approach accelerates progress. The same approach—involving groups of scientists within the program as well as collaborators from throughout Pacific Northwest National Laboratory and the external scientific community—is inherent in how the CPCS Facility is managed.

The CPCS Facility and its staff have particular capabilities and expertise that support user research involving preparation and spectroscopic analysis of molecular clusters; high-resolution imaging of biological samples and studies of cellular processes, including DNA damage and repair and low-dose radiation processes; ultra-fast and non-linear optical spectroscopies; ultrahigh-resolution spectroscopy for measurements of electronic and geometric structures and dynamics; surface and interface structure; chemical reaction dynamics and kinetics; ion-molecule traps and storage technology; and specialized chambers, instruments, and models for studying chemical reactivity and analyzing 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 non-thermal (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 responses to environmental stresses. One focus is on structures and processes of molecular and nanoscale 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
- ultra-sensitive and environmental analysis.

Another central feature is the development of innovative experimental methods with broad applications to research in the natural sciences. Two examples of innovative methods developed in the CPCS Facility include 1) detecting and monitoring trace atmospheric species, including gaseous and particulate matter, and 2) studying biological processes important in the environment and health, including imaging of live cells to observe the reaction dynamics of functioning biological systems in real time, advancing our understanding of protein-protein interactions and DNA damage and repair using single-molecule spectroscopy, and studying cellular responses to low-dose radiation using novel instrumentation.

Capabilities

The capabilities of the CPCS Facility support research in five general areas, which are described below.

Reaction Mechanisms at Solid, Liquid, and Gas Interfaces. Research in this area focuses on developing fundamental molecular information about processes occurring at the interfaces between environmentally important liquids, solids, and gases. For example, a common element in environmental restoration is the need to understand molecular processes 1) in aqueous solutions and at the interface between aqueous and organic solutions and 2) at the interface between aqueous solutions and environmentally important solid materials. Examples of instruments that enable this research are shown in Figures 1 and 2.

Molecular processes occurring at liquid-liquid interfaces also play an important role in the subsurface transport of contaminants such as organic solvents (e.g., chlorinated hydrocarbons) released into soil and groundwater. Processes at the gas-liquid interface are critical in atmospheric transport processes.

Model systems such as amorphous solid water permit detailed studies of solvation and the effects of solvation on chemical reactivity. These studies provide information about intermolecular interactions that lay the foundation for accurate modeling of solution processes. Studies provide information about factors that control the rates of reactions in solution. This

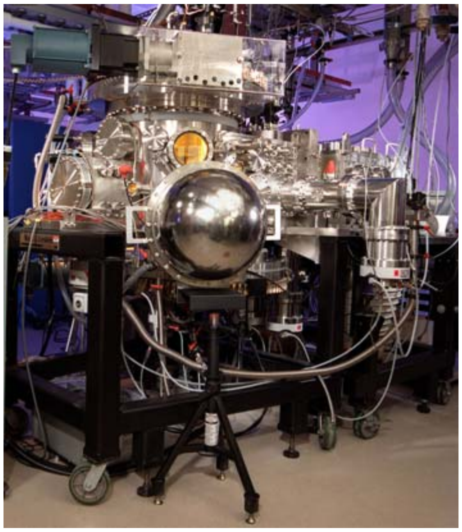

Figure 1. State-of-the-art molecular beam surface-scattering and kinetics instrument.

Figure 2. Combined instrument that allows fluorescent optical microscopes and magnetic resonance microscopes to focus on the same samples at the same time.

information is essential to both predicting the fate of contaminants in aqueous environments and influencing the selectivity of ligands for specific ions important in developing separations agents for waste treatment processes.

It is also crucial to understand molecular processes at the interface between aqueous solutions and environmentally important materials, such as aerosol particles, minerals, and glasses. This addresses fundamental science questions about contaminant fate and transport and waste immobilization. Because most environmental materials are in an oxidized form, we emphasize the structure and chemistry of oxide materials, especially naturally occurring oxides of silicon, aluminum, and iron. The adsorption of species on and their incorporation in soil minerals affect their transport through soil. Mineral interfaces can enhance or retard reactivity as well as transform contaminants. Knowledge of molecular processes at solid-liquid interfaces is also important to understanding the stability of glasses proposed for encapsulating high-level radioactive wastes that must be stored for long periods of time. Over the long half-lives of radionuclides, water can degrade these waste-encapsulating glasses, thus leading to higher-than-expected releases of radionuclides.

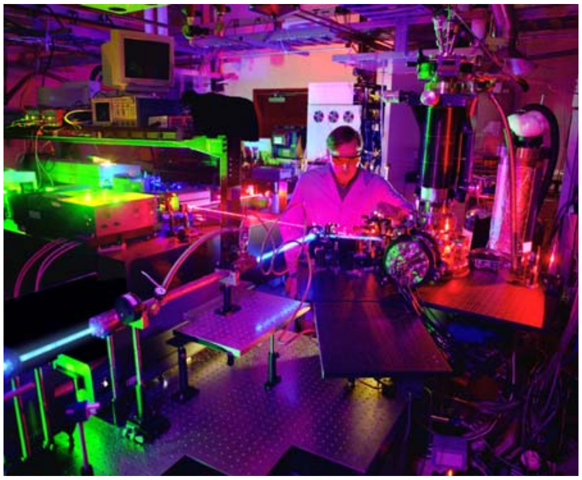

Figure 3. Laser desorption experiments investigate the effects of electronic excitation on crystalline materials.

High-Energy Processes at Environmental Interfaces. Research in this area focuses on obtaining a mechanistic understanding of chemical transformations resulting from electronic excitation in condensed-phase materials relevant to the DOE environmental cleanup mission. Examples of capabilities that enable this research are shown in Figures 3 and 4. Energetic processes are important in the degradation of mixed wastes because of the radiolytic decay-driven chemistry that occurs in the solid and liquid phases of stored radioactive waste and in final waste storage forms. Reactions occurring at interfaces are of particular interest for characterizing material composition and response to electronic excitation. We use pulsed femtosecond and nanosecond laser sources to study laser-solid interactions in a combined

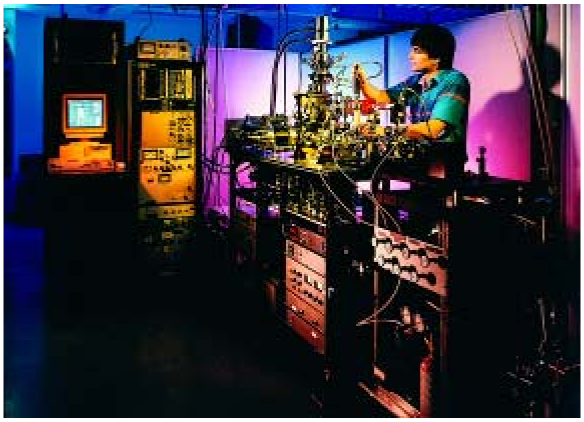

Figure 4. Electron-stimulated surface reaction apparatus is used to study non-thermal reactions that occur on surfaces or at interfaces.

experimental and theoretical program. Our goal is to continue development of models for excited-state reactions by measuring ultra-fast dynamic processes and by demonstrating laser control of solid-state chemistry.

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. A major experimental and theoretical effort is devoted to understanding surface and interface properties using cluster models to study structure and bonding. Small and controllable cluster systems provide atomic-level models that enable us to understand bulk surfaces and defect sites. They are also an excellent testing ground to benchmark theories intended for large and real-world systems. A productive collaboration in this area is illustrated in Figure 5.

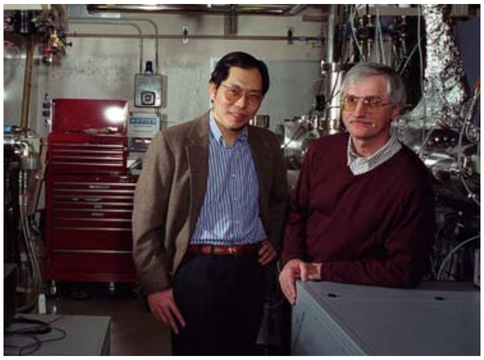

Figure 5. CPCS Facility users/collaborators L-S Wang, Washington State University Tri-Cities, Richland, Washington, and AA Boldyrev, Utah State University, Logan, Utah, are combining experimental and theoretical approaches to understand the unique properties and characteristics of metal clusters. Their research is at the forefront of cluster science.

Single-Molecule Spectroscopy and Biomolecular Sciences. This research emphasizes single-molecule spectroscopy and high-resolution biological imaging techniques for studying biological systems. Recent advances in fluorescence microscopy, at both the EMSL and elsewhere, make it possible to detect single molecules at room temperature and to conduct spectroscopic measurements to monitor their dynamic processes. We have demonstrated fluorescence imaging of single molecules by two-photon excitation with a femtosecond laser. This approach has several advantages—the excitation volume is small, the penetration is deep, and photo-damage is reduced for biological samples—thus offering the opportunity of viewing chemical reactions in a living cell in real time. Structures are known for many proteins that perform vital cell functions, including DNA damage repair, reaction catalysis, and cell signaling. Nanoscale-structure materials will affect their properties; Figure 6 provides an example. However, how they perform these functions is generally not understood. Single-molecule and single-cell measurements provide real-time data on the molecular motions involved during these functions and how the timing of these reactions is

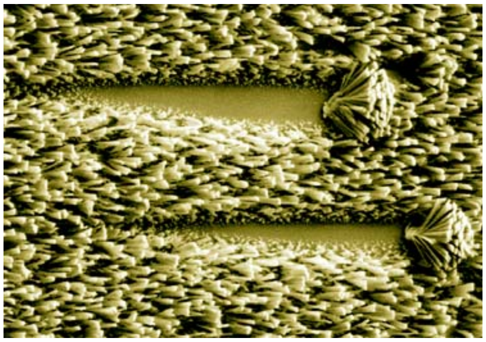

Figure 6. Nanostructures could be used to control and enhance chemical reactivity. Researchers at the CPCS Facility are trying to determine how molecules enter pores, are captured, and eventually released.

correlated with other cellular biological activities. These data are likely to produce new information that is otherwise hidden, and will open up exciting possibilities for probing cellular processes.

Ultra-Sensitive Trace Gas Analysis. Research in this area focuses on developing a suite of instrumentation for fast, accurate, highly sensitive, and discriminatory real-time analyses of chemical and biological natural or human-made agents. Such instruments are ideally suited for identifying and quantifying many gases and pollutants, trace isotopic species, metabolic products in the breath, and chemical precursors and products from industrial processes. Some of these techniques can be developed for remote probing over long optical paths for remote interrogation of trace absorption features. Our infrared methods are supported by a state-of-the-art, high-resolution infrared spectroscopy laboratory that also is used for studies of the structures and dynamics of molecular species important in contaminant chemistry, photochemistry, and atmospheric processes. The high-resolution infrared spectroscopy laboratory is shown in Figure 7.

Figure 7. The high-resolution infrared spectroscopy laboratory is used by numerous users and U.S. government agencies to obtain high-resolution infrared spectra for applications in remote sensing, atmospheric science, space and planetary research, and infrared databases.

Analyses of Environmental Aerosols Characterization of particulate matter in the atmosphere represents a unique challenge. Several approaches for both bulk and single particle analyses are employed that, in combination, are designed to understand the evolving inventory of atmospheric particulate matter and how particulates are changed by reactions with gas-phase species, photochemistry, and condensation and evaporation processes.

CPCS Facility capabilities relevant to aerosol characterization and aerosol chemistry research include single-particle mass spectrometry that provides real-time sampling and analysis of aerosol particles in laboratory and field studies, a variety of electron microscopy and microanalysis techniques for in-depth analysis of individual particles, and high resolution mass spectrometry for analysis of high molecular weight organic species (oligomers) in bulk aerosol samples. Figure 8 shows a unique, high-precision time-of-flight

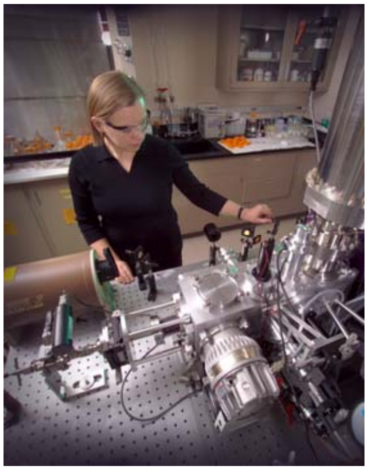

Figure 8. The second-generation single particle laser ablation time-of-flight mass spectrometer offers users the versatility of laboratory studies and field campaigns.

spectrometer used to study fundamental processes that govern the chemistry and physics of particles on the nano and micro scales.

Figure 9. EMSL staff have studied aerosols and aerosol transformations in many locations, such as Mexico City.

In conjunction with these analytical techniques, an array of special devices is being developed and deployed to collect and preserve aerosol samples for later analysis of in the laboratory. For example, in 2006 CPCS Facility researchers took part in a four-week field study in Mexico City (Figure 9), with the goal to characterize aerosol formation and changes in aerosol composition, size distribution, light scattering coefficient, absorption coefficient, optical depth, soot-specific absorption, and radiative fluxes at selected vertical and horizontal locations in the outflow downwind of Mexico City.

Together these analytical and sampling approaches and sampling techniques provide information over a broad range of particle types, chemistry, size, and morphology, leading to a more comprehensive understanding of the relationship between particles composition and their climate-related effects. In field studies, information is also correlated with meteorology data to understand possible sources and transport patterns of aerosols.

Instrument Upgrades

In 2006, the CPCS Facility made several upgrades and procurements:

- **Vacuum and turbo pump replacements.** Six systems were purchased and delivered, with four in use by September 2006.
- **Environmental scanning electron microscope.** Two systems were procured, with one received in September 2006.
- **Laser development and documentation.**
- **Fourier transform ion cyclotron resonance data acquisition system.** This new system was procured to replace an older system no longer serviced by its vendor. This instrument will support structural and thermodynamic studies of molecules. Full operation of this instrument is expected in early Fiscal Year 2007.
- **Zeiss Incubator and QuadView System.** This new system will be used for cell growth control and protein imaging. It is expected to be operational in early Fiscal Year 2007.
- **Photo-emission electron microscope cooling and sample transport mechanism.** This system will be used for studying catalytic and photocatalytic processes. It is expected to be operational in early Fiscal Year 2007.
- **High-sensitivity interface for proton transfer reaction mass spectrometer.** This system will extend detection limits for volatile organic compounds and allow real-time measurement of trace organic gases collected from atmospheric samples. It is expected to be operational in early Fiscal Year 2007.
- **High-resolution time-of-flight mass spectrometer and light-scattering module.** This system will be used for rapid single-particle measurements of complex organic species in particulates. It is expected to be delivered in mid-Fiscal Year 2007 and operational soon after.
- **High-resolution mass spectrometer LTQ-Orbitrap and support instrumentation.** This system will be used for chemical characterization of organic aerosols. This system is expected to be fully operational in mid-Fiscal Year 2007.

Future Directions

The CPCS Facility plans to support approximately 90 users and 8 distinctive users in Fiscal Year 2007. To provide the most effective support to projects and programs at EMSL, it is necessary to keep pace with state-of-the-art capabilities in characterizing the fundamental interactions among solids, liquids, and gases on a particle to the molecular level to understand the basic chemistry and physics of complex environmental and engineered systems. This will be done by:

- **Extending experimental characterization and description** of chemical reactions to encompass the effects of condensed media and interfaces.
- **Describing interfacial chemical processes** relevant to improved energy technologies, and understanding and mitigating the environmental impacts of energy use.
- **Creating state-of-the-art research and analytical methods** for characterizing complex materials of the types found in catalysts, natural and contaminated human-made systems.
- **Studying reaction mechanisms** at liquid interfaces, high-energy processes at interfaces, models of the condensed phase, and single molecule/particle kinetics and dynamics.

Gold Apes Hydrogen. The Structure and Bonding in the Planar $B_7Au_2^-$ and B_7Au_2 Clusters

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Clusters are groups of a small number of atoms that often have chemical and physical properties that are different than the corresponding bulk materials. Understanding the underlying physical and structural reasons for these unique properties may allow for improved materials for electronics, sensors, and catalysis.

Pure boron clusters have received limited experimental attention in the literature during the past couple of decades. A major breakthrough has resulted from a series of recent joint experimental and theoretical studies that have established that all small boron clusters are planar or quasi-planar. These studies have shown that photoelectron spectroscopy in conjunction with accurate *ab initio* calculations is a powerful approach to elucidate the complex structures of atomic clusters. Furthermore, the theoretical analysis has yielded detailed information about the chemical bonding in the clusters and allowed the planarity of the boron clusters to be understood on the basis of π and σ aromaticity/antiaromaticity.

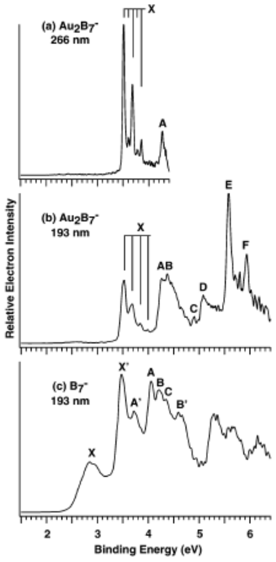

Figure 1. Photoelectron spectra of B_7Au_2 (a) 266 nm, (b) 193 nm, and of B_7^- (c).

The $B_7Au_2^-$ anions were produced using a laser vaporization cluster source and the photoelectron spectra obtained using a magnetic bottle-type photoelectron spectrometer. The photoelectron spectra of $B_7Au_2^-$ at 266- and 193-nm photon energies are shown in Figure 1 and are compared with that of B_7^-. The photoelectron spectra of $B_7Au_2^-$ are substantially simpler and better resolved than those of B_7^-, despite its larger size. Most surprisingly, despite the addition of two heavy atoms, the ground-state transition (X) of $B_7Au_2^-$ is completely vibrationally resolved at 266 nm (Figure 1a) with the excitation of two vibrational modes, a low-frequency mode of 790 cm^{-1}, and a high-frequency mode of 1380 cm^{-1}. The vibrationally resolved ground-state transition yielded an accurate electron affinity of 3.52 eV for B_7Au_2.

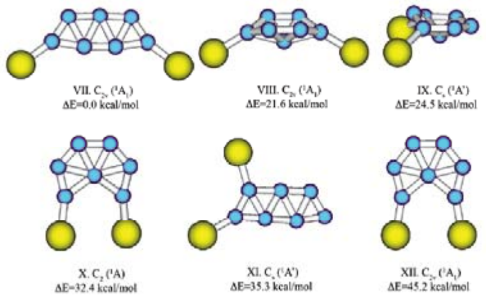

Figure 2. Global minima and low lying isomers of B_7Au_2.

Interestingly, the electron affinity of B_7Au_2 is very close to that of the elongated planar C_2V isomer for B_7 (3.44) corresponding to feature X′ in the spectrum of B_7^- (Figure 1c). Clearly, only one dominant isomer was present in the spectra of $B_7Au_2^-$. The observed $B_7Au_2^-$ cluster is likely to correspond to this isomer of B_7^- by adding two gold atoms to its two terminal B atoms similar to the ground-state structure of $B_7H_2^-$, as we expected.

To prove our hypothesis and confirm the observed $B_7Au_2^-$ structure, we performed quantum chemical calculations for a variety of $B_7Au_2^-$ structures. Figure 2 shows the global minimum and low-lying isomers of $B_7Au_2^-$. The good agreement between the experimental and theoretical vertical detachment energies confirmed the theoretical prediction of the global minimum structure VII for $B_7Au_2^-$, which is the same as that of $B_7H_2^-$.

The similarity in stability, structure, and bonding in the global minima of $B_7Au_2^-$ and $B_7H_2^-$ is analogous to the previous discovery of the gold/hydrogen analogy in silicon-gold clusters. Similar to the silicon-gold bond, which is highly covalent, we found that the boron-gold bonds in $B_7Au_2^-$ are also highly covalent with very little charge transfer from gold to boron. This is again due to the close electronegativity of boron and gold as a result of the strong relativistic effects in gold. This study demonstrates that the gold/hydrogen analogy may be a more general phenomenon and may exist in many species involving gold. The gold/hydrogen analogy will not only extend our understanding of the chemistry of gold, but will also be highly valuable in predicting the structures and bonding of many gold alloy clusters.

This exciting research appears in a recent issue of *The Journal of Chemistry A* and is featured on the cover (Figure 3).

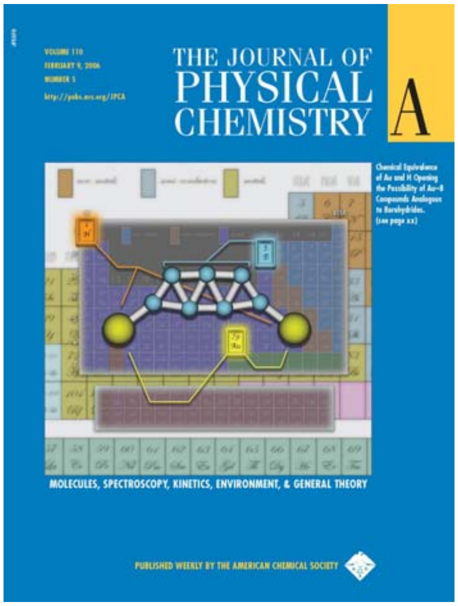

Figure 3. Cover of the February 9, 2006, issue of *The Journal of Physical Chemistry A*.

Citation

Zhai HJ, LS Wang, DY Zubarev, and AI Boldyrev. 2006. "Gold Apes Hydrogen. The Structure and Bonding in the Planar B_7Au_2- and B_7Au_2 Clusters." *Journal of Physical Chemistry A* 110(5):1689-1693.

Evidence of Hollow Gold Cages

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In this work, the researchers have found that some gold atom clusters form structures with hollow cages. The existence of these cages may allow for the insertion of other atoms to create new materials with unique properties for a wide range of applications.

The detection of carbon-free hollow cages has attracted much interest since the discovery and synthesis of the buckyball, C_{60}, and the higher fullerenes. Although "free-standing" inorganic cages have been synthesized, bare elemental metal cages have not been observed in nature or detected in the laboratory. Among metals, gold has unique properties, including strong relativistic effects and aurophilic attraction. Recently, a fullerene-like hollow cage with 32 gold atoms was predicted to be highly stable. However, photoelectron spectroscopy (PES) combined with theoretical calculations shows that at this relatively large size the overwhelming population of low-lying clusters for Au_{32} near room temperature appears to consist of only compact structures because of the entropic factor. Other, larger gold clusters with cage-like local minimum structures also have been suggested, but none have been observed experimentally. Conversely, it has been established from both ion-mobility and PES experiments that the most stable anion gold clusters (Au_n) in the size range n = 5–13 possess planar structures and that a structural transition from planar to three-dimensional structures occurs at n = 14. Beyond n = 14, previous global-minimum searches based on empirical potential functions of gold or semi-empirical tight-binding models of gold suggest that all low-lying isomers of gold clusters assume space-filling compact structures. Among the larger gold clusters, Au_{20} is the most interesting; it has

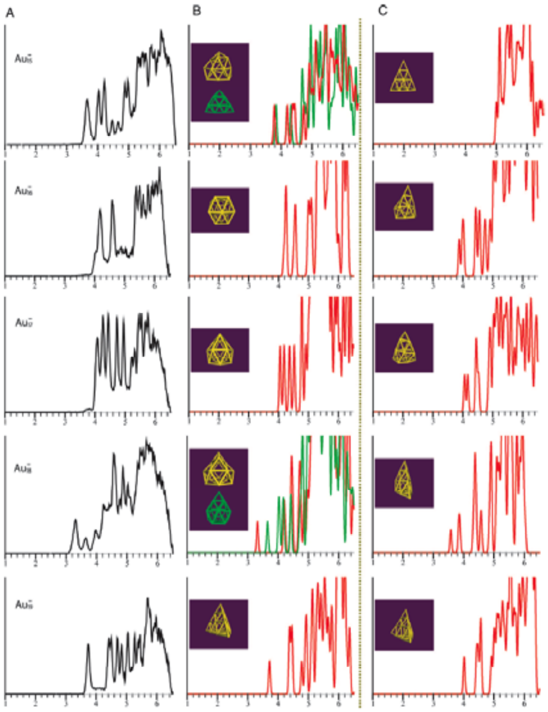

Figure 1. Experimental photoelectron spectra of Au_n^- (n = 15–19) compared with those simulated theoretically. (A) Experimental spectra measured at 193 nm (6.4 eV). (B) The simulated spectra for one (or two) lowest-lying isomer. (C) The simulated spectra for the non-hollow-cage candidate isomer.

been found to possess a pyramidal structure with tetrahedral symmetry just as carved out of the bulk face-centered cubic crystal.

To elucidate the structural transition from the planar Au at n = 13 to the pyramidal Au_{20}, we carried out a joint experimental PES and theoretical study on Au_n^- for n = 15–19. The measured spectra are shown in Figure 1A with numerous well-resolved features in the lower binding energy part, which are used to compare with theoretically simulated spectra (Figures 1B and 1C) with the candidate lowest-energy clusters.

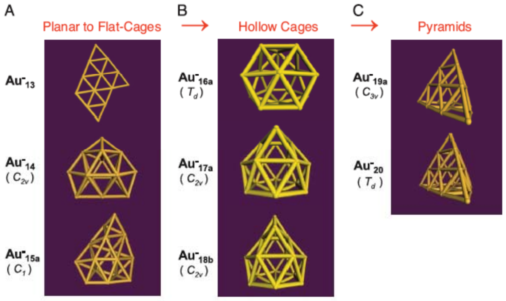

Figure 2. Structural evolution of mid-sized gold anion clusters from Au_{13} to Au_{20}. (A) The two-dimensional planar to three-dimensional flat-cage structural transitions (11). (B) The hollow gold cages with diameters 5.5 Å. (C) The pyramid-like clusters, which resemble bulk gold.

Remarkably, we observed that all but a total of three candidate lowest-energy isomers of Au_{16}^- , Au_{17}^-, and Au_{18}^- are "hollow cages" with an empty interior space. The interior space (typically with length scale 5.5 Å) of these hollow cages can easily host a foreign atom. Among the five candidate lowest-energy structures of Au_{15}^-, three are flat-cage structures, whereas the other two are pyramid-like structures. Previous studies have shown that in stable gold clusters, gold atoms tend to have a maximum coordination number of six (e.g., in the two-dimensional planar structures of Au_9 to Au_{13} and in the pyramidal structure of Au_{20}). Hence, it is understandable that both the flat-cage and pyramid-like structures are energetically competitive for the gold clusters within the size range Au_{14} to Au_{20}. Conversely, it is quite surprising that the hollow-cage structures dominate the low-lying population of Au_{16}^- to Au_{18}^- clusters. Specifically, at Au_{16}, only one of the five candidate lowest-energy structures has a flat-cage structure whose interior length scale can be 5 Å. The structural transition from hollow-cage to pyramid-like structure appears to occur at Au_{19}. To illustrate the structural evolution of gold clusters from two-dimensional planar to three-dimensional flat-cage, hollow-cage, and pyramid-like structures, we show in Figure 2 those candidate lowest-energy clusters that can provide a reasonable match to the experimental photoelectron spectra (Figures 1A and B). Our first-principles global search provides the electronic energy based evidence that the overwhelming majority of the low-lying clusters of Au_{16}^- to Au_{18}^- exhibit hollow-cage structures. These clusters and their larger neighbors are stable at room temperature; the size of the hollow should allow for other atoms to be trapped inside. The interior doping of these hollow clusters may dramatically change the cluster properties and thereby allow for the tailoring of the clusters for specific applications. This work was featured on the

Figure 3. May 23, 2006, issue of the *Proceedings of the National Academy of Science.*

cover of the May 23, 2006, issue of the *Proceedings of the National Academy of Science* (Figure 3) Bulusu et al. 2006).

Citation

Bulusu S, X Li, LS Wang, and XC Zeng. 2006. "Evidence of Hollow Golden Cages." *Proceedings of the National Academy of Science* 103(22):8326-8330.

Imaging Adsorbate O-H Bond Cleavage: Methanol on TiO_2(110)

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The wide-ranging importance of titanium oxide (TiO_2) in heterogeneous catalysis, photocatalysis, sensor applications, and hydrogen production using solar cells has made this surface one of the most extensively studied. Despite this extensive research attention, the interactions of well-characterized TiO_2 surfaces with simple molecules that participate in a number of catalytic reactions on TiO_2 are not well understood. This study focused on further developing our understanding these fundamental reaction mechanisms with the intent of further exploiting the properties of this technologically important material.

The thermal and photocatalytic oxidation of simple alcohols has been extensively studied on TiO_2 surfaces as a prototype for the catalytic oxidation of organic contaminants. Among them, methanol (CH_3OH), which is one of the simplest organic molecules, is often adopted as a probe. Experiments have shown that both molecular and dissociative adsorption take place on defective rutile TiO_2(110) surfaces. Methanol dissociation occurs primarily on bridge-bonded oxygen vacancy (BBOV) defect sites with some evidence for CH_3OH dissociation at non-defect sites as well. First-principle calculations show that on a stoichiometric surface, the dissociative adsorption of CH_3OH can occur via both O-H and C-O bond scission and that it is slightly favored over molecular adsorption. However, the atomic level understanding of these systems is still missing.

Scanning tunneling microcopy (STM) is an ideal analytical tool that allows researchers to track adsorbates on different surface sites. In this study, we employed *in situ* STM to follow the adsorption and dissociation of CH_3OH on BBOVs of TiO_2(110). Experiments were performed in an ultrahigh vacuum variable-temperature STM chamber. Figure 1 shows a set of STM images obtained from the same TiO_2(110) area before and after dosing with CH_3OH at 300 K. Figure 1a represents a clean surface before CH_3OH adsorption. The bright rows on Figure 1a are identified as the fivefold coordinated Ti^{4+} ions; the dark rows are the bridge-bonded oxygen (BBO) ions. The bright spots between the Ti^{4+} rows are assigned to BBOVs, believed to act as the primary dissociation centers for the alcohols. Statistically, the number density of BBOVs on this surface is about 8% with respect to the number of Ti^{4+}. The magnified images (insets in Figure 1) highlight the position of six BBOV sites (marked by yellow circles in Figure 1a) to illustrate the processes observed during CH_3OH adsorption.

The surface after an 80-s methanol dose is shown in Figure 1b. The CH_3OH adsorption-induced features appear as bright features on the BBOVs. The spatial location of adsorption sites becomes apparent from comparison of the magnified areas in the insets of panels "a" and "b" in Figure 1. The pattern of the bright features (marked with blue circles on the of panel b inset) is the same as the BBOV pattern on the clean surface (yellow circles on the panel a inset), indicating that CH_3OH preferentially adsorbed on the BBOVs. Comparing line profiles along the [001] direction shows that the bright features are 0.8 Å higher than BBOVs and that the CH_3OH-induced bright features have their maxima located on the original BBOV sites, but are asymmetric. This finding suggests that these features originate from two different chemical species present on neighboring BBO sites, in accord with the previously observed formation of hydroxyl and methoxy species resulting from the dissociative adsorption of CH_3OH. This process is shown schematically in Figure 1f.

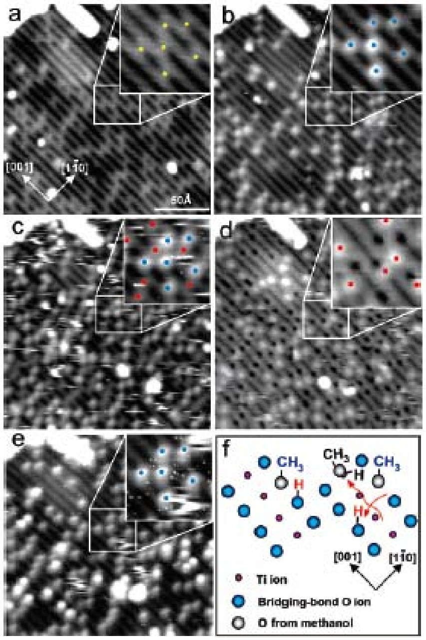

Figure 1. STM images of same area before and after adsorption of CH_3OH on $TiO_2(110)$ at 300 K: (a) bare surface; (b) after 80-s exposure to CH_3OH ; (c) after 110-s exposure to CH_3OH ; (d) taken on (c) after spontaneous tip change; (e) after high bias sweep of (c); (f) schematic of the adsorption process.

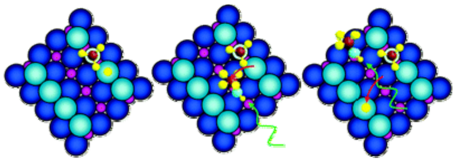

Figure 2. A schematic for methanol-assisted hydroxyl migration on $TiO_2(110)$.

We conclude that CH_3OH dissociates on BBOVs via O-H bond scission. In the case of C-O bond scission, the hydroxyl rather than the methoxy group would appear on the original BBOV sites. At high coverage levels (Figure 1c), all the hydroxyl groups appear to be spatially separated from the methoxy groups (bright/gray; 1:1) as they migrated away from their original geminate sites. We propose that diffusing CH_3OH molecules assist hydroxyl migration, most likely through proton "hopping." At CH_3OH coverage below the BBOV coverage, the CH_3OH molecules diffusing on Ti^{4+} rows dissociate after encountering an empty BBOV. At CH_3OH coverage exceeding the BBOV coverage, excess CH_3OH is mobile and leads to the observed dramatic increase in hydroxyl migration. Figure 2 shows a schematic model for CH_3OH-assisted hydroxyl migration on $TiO_2(110)$. Repeated imaging of the same area provides additional evidence for the high mobility of hydroxyls at high CH_3OH coverage. We believe this mobility is facilitated by molecular CH_3OH diffusing along the Ti^{4+} rows: as much as 40% of the hydroxyls changed position in two consecutive images (3 min).

In summary, we present the first atomically resolved images of dissociative methanol adsorption on BBO vacancies of $TiO_2(110)$. Imaging of the same area before and after adsorption allowed us to establish that the dissociation proceeds via O-H bond scission. At CH_3OH coverage below the BBO vacancy coverage, the methoxy and hydroxyls occupy primarily neighboring BBO sites. At higher levels of coverage, facile hydroxyl migration assisted by mobile, Ti^{4+}-bound CH_3OH molecules is observed.

This research is described in more detail in Zhang et al. 2006.

Citation

Zhang ZR, O Bondarchuk, JM White, BD Kay, and Z Dohnalek. 2006. "Imaging Adsorbate O-H Bond Cleavage: Methanol on $TiO_2(110)$." *Journal of the American Chemical Society* 128(13):4198-4199.

Pb_{12}^{2-}: Plumbaspherene

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In this work, the research team discovered a new class of endohedreal lead-cage compounds that they have named "plumbaspherenes." The existence of these new cage compounds may allow for the insertion of other atoms inside of these cages to create new materials with unique properties for a wide range of applications.

During recent photoelectron spectroscopy (PES) experiments aimed at understanding the semiconductor-to-metal transition in tin clusters, we found the spectra of Sn_{12}^- to be remarkably simple and totally different from the corresponding Ge_{12}^- cluster. This observation led to the discovery of a C_{5V} cage structure for Sn_{12}^-, which is only slightly distorted from the icosahedral (Ih) symmetry as a result of the Jahn-Teller effect. However, adding an electron to Sn_{12}^- resulted in a highly stable and closed-shell I_h Sn_{12}^{2-} cage cluster. Because of the large 5p-5s energy separation, the I_h Sn_{12}^{2-} cage was found to be bound primarily by the $5p^2$ electrons, which form four radial π bonds and nine in-sphere σ bonds, with the $5s^2$ electrons behaving like lone pairs. The Sn_{12}^{2-} cage was shown to be iso-electronic to the well-known $B_{12}H_{12}^{2-}$ molecule with the $5s^2$ lone pairs replacing the localized B-H bonds, and was named "stannaspherene" for its π-bonding characteristics and high symmetry.

In this highlight, we report both experimental and theoretical evidence that the corresponding Pb_{12}^{2-} cluster also exists as a highly stable I_h cage that has an even larger interior volume than stannaspherene and can host most transition metal atoms in the periodic table to form a new class of endohedral cage clusters.

Experimental evidence was obtained with a PES apparatus consisting of a laser vaporization supersonic cluster beam source and a magnetic bottle electron analyzer. Figure 1 shows the

PES spectra of Pb_x^- (x = 11-13) at 193 nm. Clearly, the Pb_{12}^- spectrum is special relative to those of its neighbors, showing only four bands (i.e., the X, A, B, and C bands), whereas much more complex spectral features are observed for Pb_{11}^- and Pb_{13}^-. This observation suggests that Pb_{12}^- should possess a relatively high symmetry structure. The current experimental data are better resolved spectra, have more accurate electron binding energies, and have more spectral features to cover the valence spectral range. As such, useful insights into these experimental results can be obtained from high-quality *ab initio* quantum mechanical calculations.

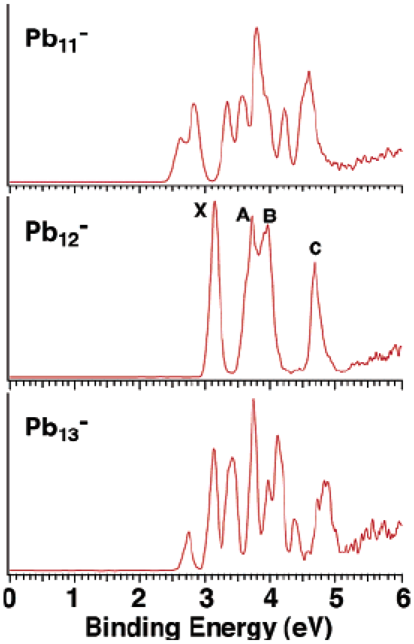
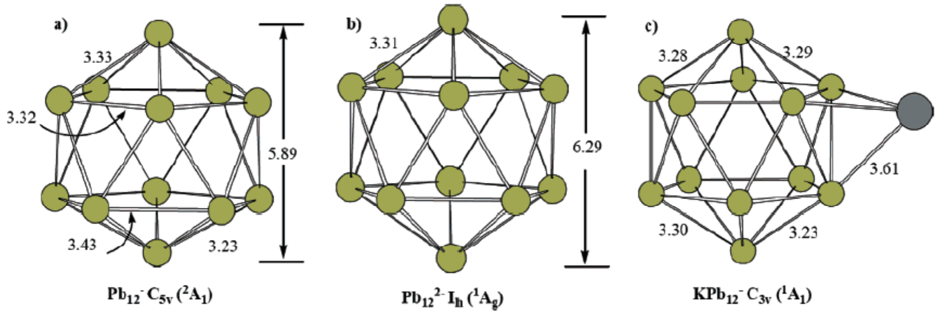


Figure 1. Photoelectron spectra of Pb_x^- (x = 11–13) at 193 nm. Note the relatively simple spectral pattern of Pb_{12}^- with respect to those of Pb_{11}^- and Pb_{13}^-.

Results of these calculations are shown in Figure 2. Geometry optimization for Pb_{12}^- from a high-symmetry icosahedral cage led to a Jahn-Teller distorted lower symmetry C_{5V} ($^2A_1$) species (Figure 2a) that is analogous to Sn_{12}^-. The computed first vertical detachment energy (3.08 eV) of the C_{5V} Pb_{12}^- is in excellent agreement with the experimental value of 3.14 eV. Whereas ion mobility experiments suggest that Pb_x^+ clusters possess compact near-spherical morphologies, several theoretical studies have given various structures for neutral Pb_{12}. However, we find that the doubly charged Pb_{12}^{2-} species is a highly stable and a perfect I_h cage with a closed electron shell (Figure 2b). Analogous to Sn_{12}^{2-}, which has been named stannaspherene for its π-bonding characteristics and its nearly spherical structure, we suggest the name "plumbaspherene" for the highly stable and robust Pb_{12}^{2-} cage. As such, we expect that the Pb_{12}^{2-} plumbaspherene should also be a stable species in solution and can be synthesized in the condensed phase. Plumbaspherene has a computed diameter of 6.29 Å, which is slightly larger than that of stannaspherene (6.07 Å). Thus, it is expected that Pb_{12}^{2-} can trap an atom inside its cage to form endohedral plumbaspherenes, M@Pb_{12}.



Pb_{12}^- C_{5v} ($^2A_1$) Pb_{12}^{2-} I_h (^1A_g) KPb_{12}^- C_{3v} ($^1A_1$)

Figure 2. Optimized structures: (a) Pb_{12}^-, (b) Pb_{12}^{2-}, and (c) KPb_{12}^-. The bond distances and cage diameters are in Å.

We expect that a whole new family of stable M@Pb_{12} endohedral clusters may exist, analogous to the endohedral fullerenes. The plumbaspherene cages may be able to host a variety of transition metal atoms, thus creating a new class of endohedral cage clusters. Varying the host metal inside an M@Pb_{12} cage may dramatically change the properties of the cluster, thereby allowing the clusters to be tailored for specific applications. This exciting work was featured on the cover of the August 31, 2006, issue of *The Journal of Physical Chemistry A* (Figure 3).

Figure 3. Plumbaspherence shown on the cover of the *Journal of Physical Chemistry A.*

Citation

Cui LF, X Huang, LM Wang, J Li, and LS Wang. 2006. "Pb_{12}^{2-}: Plumbaspherene." *Journal of Physical Chemistry A* 110(34):10169-10172.

User Projects

Low-coordinated Oxygen Sites on MgO Surfaces

O Diwald, E Knozinger, Vienna University of Technology, Wien, Austria

High-resolution Gas-phase UV- and IR-absorption Cross-sections of Naphthalene to Calibrate the First DOAS Detection of Naphthalene in Mexico City

MJ Molina, Massachusetts Institute of Technology, Cambridge, Massachusetts

RM Volkamer, University of California, San Diego, La Jolla, California

Study of Martensitic Transformations in Shape Memory Alloys by Real-time Measurement of Surface Work Function Change

M Cai, JT Dickinson, Washington State University, Pullman, Washington

AG Joly, G Xiong, WP Hess, Pacific Northwest National Laboratory, Richland, Washington

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

Properties of Ice and Liquid Interfaces (Kay's BES-Surface Kinetics, PNNL Scope #16248)

JP Cowin, HM Ali, Pacific Northwest National Laboratory, Richland, Washington

MJ Iedema, Environmental Molecular Sciences Laboratory, Richland, Washington

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Characterization of Quantum Cascade Lasers

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MA Mangan, Sandia National Laboratory, Albuquerque, New Mexico

Photoreflectivity in Ge/Si Thin Films

AG Joly, Pacific Northwest National Laboratory, Richland, Washington

D Brewe, Argonne National Laboratory, Argonne, Illinois

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

E Stern, University of Washington, Seattle, Washington

Energetic Processes: Reaction in Thin Organic Films

GB Ellison, University of Colorado, Boulder, Colorado

Mechanisms of Fragmentation of Post Translationally Modified Peptides

H Lioe, RA O'Hair, University of Melbourne, Melbourne, Victoria, Australia

J Laskin, Pacific Northwest National Laboratory, Richland, Washington

Theoretical Studies of Kinetic Processes in Nanoscale Ice Films

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HN Jonsson, University of Iceland, Reykjavík, Iceland

Thrust 4: Surface Enhanced Raman-AFM and Antibody Force Microscopy (LDRD: Cytochrome and Whole Cell Ineteractions with Iron Oxides)

HP Lu, Bowling Green State University, Bowling Green, Ohio

Laser Ablation/Ionization Characterization of Solids

JT Dickinson, Washington State University, Pullman, Washington

Probing the Electronic Structure of Metal Clusters

X Li, Washington State University, Richland, Washington

L Cui, Ln Wang, L Wang, H Zhai, J Yang, W Huang, Washington State University Tri-Cities, Richland, Washington

Energetics of Dissociation of Peptide Radical Cations

J Laskin, JH Futrell, Z Yang, Pacific Northwest National Laboratory, Richland, Washington

IK Chu, N Lam, The University of Hong Kong, Pokfulam, Hong Kong

Photoelectron Emission Microscopy (PEEM) Study of Cu Nanoparticles on TiO2(110)

WP Hess, Pacific Northwest National Laboratory, Richland, Washington

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

JM White, W Wei, University of Texas at Austin, Austin, Texas

Atomically Resolved Studies of Adsorbates on TiO_2(110)

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O Bondarchuk, JM White, S Li, Y Kim, University of Texas at Austin, Austin, Texas

Develop a Procedure for the Determination of the Calibration Parameters on the Host Side and Integrate Them into the Hardware to Facilitate Real Time Multiband Analysis

MB Sowa, KA Perrine, Pacific Northwest National Laboratory, Richland, Washington

AM Mayampurath, Utah State University, Logan, Utah

Infrared and CARS Spectroscopy of Cyclopropane

JW Nibler, Oregon State University, Corvallis, Oregon

J Kelly, Pacific Northwest National Laboratory, Richland, Washington

A Masiello, National Institute of Standards and Technology, Gaithersburg, Maryland

Aerosol and Organic Precursor Measurements at Ground-Based Sites during the Megacity Aerosol Experiment in Mexico City 2006 (MAX-Mex 2006)

JS Gaffney, University of Arkansas, Little Rock, Little Rock, Arkansas

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PW Lunn, RC Petty, DOE BER Climate Change Research ASP, Washington DC, Wash DC

R Gonzalez, Molina Center for Strategic Studies in Energy and the Environment, La Jolla, California

Aerosol Composition and Hydrocarbon Measurements from the DOE G-1 Aircraft during the Megacity Aerosol Experiment in Mexico City (Max-Mex)

Ln Kleinman, Brookhaven National Laboratory, Upton, New York

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High Resoulution Infrared Spectroscopy of Methyl Phosphonic Difluoride

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Chemical Ionization Mass Spectrometry of Organic Aerosols

PN Irving, Innovatek, Inc., Richland, Washington

VB Mikheev, Battelle Columbus, Columbus, Ohio

High Resolution Infrared Spectroscopy of Trans-Hexatriene

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High and Moderate Resolution Infrared Spectroscopy of Diiodomethane

TJ Johnson, Pacific Northwest National Laboratory, Richland, Washington

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Dynamic Changes in Molecular Interactions along the Circadian Rhythm

GN Orr, DJ Panther, Pacific Northwest National Laboratory, Richland, Washington

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T Ogawa, Shanghai Institute of Plant Physiology and Ecology, Shanghai, China

AFM Imaging of Photo System Protein in Photosynthetic Membranes

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HP Lu, Bowling Green State University, Bowling Green, Ohio

Reactive and Non-Reactive Deposition of Hyperthermal (1-100 eV) Peptide Ions Surfaces

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PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

Mechanisms of Organic Ions Release from Water Droplets

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High Resolution Infrared Spectroscopy of cis-cis and trans-trans Difluorobutadiene

NC Craig, Oberlin College, Oberlin, Ohio

High Resolution Infrared Spectroscopy of the 360 cm^{-1} Band of Acetonitrile

L Brown, Jet Propulsion Laboratory, Pasadena, California

Comparative Analysis of Growth and Morphology among Citric Acid Producing and Non-Producing Strains of *Aspergillus niger*

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Morphology and Composition of Encoded Segmented Metal Oxide Nanowires

A Kolmakov, Southern Illinois University, Carbondale, Illinois

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Y Lilach, Unknown, Richland, Washington

Environmental Effects of Aircraft Engine Exhaust Particles

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CW Spicer, MW Holdren, Battelle Columbus, Columbus, Ohio

Oxidation of Atmospheric Organic Particulate Matter

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Visualization of Gamma H_2AX Foci

MB Sowa, DL Springer, JS Peters, Pacific Northwest National Laboratory, Richland, Washington

WF Morgan, University of Maryland, Baltimore, Maryland

Chemical Characterization of Arrays of TiO_2 Nanocolumns

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B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

C Mullins, DW Flaherty, University of Texas at Austin, Austin, Texas

Measurement of Ambient Concentrations of Aerosols to Support the Analysis of MIRAGE Urban Plume Transport and Chemistry

BK Lamb, Washington State University, Pullman, Washington

Chemistry and Microphysics of the Small Particles

BJ Finlayson-Pitts, Y Yu, M Ezell, University of California, Irvine, Irvine, California

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K Mueller, State University of New York at Stony Brook, Stony Brook, New York

Y Han, Y Cai, Unknown, Richland, Washington

Nanoscale Insight into the Living Cell Membrane Responses to Ultrafine PM

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C Rodriguez, Washington State University Tri-Cities, Richland, Washington

FRET Screening of Protein-Protein Interactions in *Shewanella*

GN Orr, MF Romine, DJ Panther, B Hooker, HS Wiley, Pacific Northwest National Laboratory, Richland, Washington

Regulation of Cell Surface Ligand Dynamics

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SPLAT: Real-Time Characterization of Individual Exhaust Particles

A Zelenyuk, Pacific Northwest National Laboratory, Richland, Washington

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Aerosol Aging and Climate Change

JP Cowin, Y Liu, Pacific Northwest National Laboratory, Richland, Washington

MJ Iedema, A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

X Yang, Fudan University, Shanghai, China

In situ Probe of Oxidation at Environmental Interfaces

JP Cowin, Y Liu, Pacific Northwest National Laboratory, Richland, Washington

MJ Iedema, A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

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Optical and Hygroscopic Properties of Atmospheric Aerosols

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A Laskin, PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

L Alvarez-Aviles, University of Alaska Fairbanks, Fairbanks, Alaska

Use of SEM/EDX Analysis to Study the Oxidation of Aerosol by Hydroxyl Radical

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DJ Gaspar, Y Dessiaterik, JP Cowin, Pacific Northwest National Laboratory, Richland, Washington

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Transition Metal Oxide Clusters - Electronic Structure and Chemical Bonding Using Photoelectron Spectroscopy

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Spectral Library

SW Sharpe, TJ Johnson, RL Sams, DC Scott, RG Tonkyn, Pacific Northwest National Laboratory, Richland, Washington

TA Blake, Environmental Molecular Sciences Laboratory, Richland, Washington

Infrared Reflectance Spectroscopy of Soils

TA Blake, PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

Infrared Spectroscopy of Methyl Halides

TJ Johnson, Pacific Northwest National Laboratory, Richland, Washington

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Personal Samplers for Traffic-Related Particle Exposures in NYC

SR Chillrud, Columbia University, palisades, New York

JP Cowin, Pacific Northwest National Laboratory, Richland, Washington

MJ Iedema, TA Seim, Environmental Molecular Sciences Laboratory, Richland, Washington

Electronic Properties of the Metal and Thin Film Oxide Insulator Junction

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

PTR-ITMS: Next Generation Aircraft Instrumentation

SP Garland, University of California, Davis, Redding, California

CM Berkowitz, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, MK Newburn, Environmental Molecular Sciences Laboratory, Richland, Washington

Innovative Aerosol Collector

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

D Worsnop, J Jayne, Aerodyne Research Inc, Billarica, Massachusetts

Fundamental Investigations of Water Splitting on Model TiO_2

GA Kimmel, NG Petrik, Z Dohnalek, Pacific Northwest National Laboratory, Richland, Washington

CD Lane, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

The Non-Covalent Interaction of Some Aromatic Molecules with H_2O Studied with Photoelectron Energy Spectroscopy and Quantum Chemical Calculation

LN Wang, Washington State University Tri-Cities, Richland, Washington

G Wang, M Zhou, Fudan University, Shanghai, China

Development and Testing of a New Ion Trap Assembly

JA Lloyd, MV Johnston, University of Delaware, Newark, Delaware

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

TA Smith, Genesee Community College, Arlington, Virginia

Laboratory Studies of Gas-Particle Reaction Kinetics of Particulates Emitted from Aircraft

JP Cain, H Wang, University of Southern California, Los Angeles, California

A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

Exploratory Synthesis of Novel Cluster-Based Nanomaterials

TL Hubler, Pacific Northwest National Laboratory, Richland, Washington

LN Wang, Z Sun, Washington State University Tri-Cities, Richland, Washington

MF Bertino, University of Missouri, Rolla, Rolla, Missouri

Infrared Spectra of HCN at Low Temperatures

MA Smith, NASA Langley Research Center, Hampton, Virginia

Infrared Spectral Library of Bacterial Spores

TJ Johnson, NB Valentine, Pacific Northwest National Laboratory, Richland, Washington

Vibration-Rotation Spectroscopy of Sulfur Trioxide

JW Nibler, Oregon State University, Corvallis, Oregon

J Kelly, Pacific Northwest National Laboratory, Richland, Washington

A Masiello, AN Webber, National Institute of Standards and Technology, Arlington, Virginia

AG Maki, Private, Mill Creek, Washington

Soft-Landing of Complex Ions on Surfaces

JR Green, RG Cooks, W Peng, MP Goodwin, Purdue University, West Lafayette, Indiana

J Laskin, O Hadjar, P Wang, JH Futrell, Pacific Northwest National Laboratory, Richland, Washington

Z Zhu, PL Gassman, AS Lea, Environmental Molecular Sciences Laboratory, Richland, Washington

Chemistry of Aerosols in Mexico City: MILAGRO 2006 study.

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Chemical and Physical Properties of Biomass Burning Aerosol

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JL Hand, JL Collett, SM Kreidenweis, Colorado State University, Fort Collins, Colorado

A Laskin, CN Wang, Environmental Molecular Sciences Laboratory, Richland, Washington

Energy and Entropy Effects in Dissociation of Non-Covalent Complexes: A Combined Experimental and Theoretical Investigation

J Laskin, Z Yang, Pacific Northwest National Laboratory, Richland, Washington

Open Ocean Ship-Board Study of Atmospheric Aerosols at the Equatorial Pacific: Characterizing Iron in Marine Aerosol

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V Shutthanandan, Cn Wang, Z Zhu, A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

AM Johansen, LS Shank, Central Washington University, Ellensburg, Washington

JW Murray, University of Washington, Seattle, Washington

The Formation and Structure of Tropical Organic/Water Aerosols

GB Ellison, LA Cuadra-Rodriguez, University of Colorado, Boulder, Colorado

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ML Alexander, A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

Development of Novel Microchip CE-MS Platform for Organic Aerosol Characterization

X Yu, Y Lin, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, L Saraf, Environmental Molecular Sciences Laboratory, Richland, Washington

Integrated Experimental and Modeling Studies on Secondary Organic Aerosol Formation

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Characterization of Organic Aerosols throughout the Depth of an Urban Planetary Boundary Layer: Proposed Field Deployment of EMSL Mass Spectrometers

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Secondary Organic Aerosol Formation

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High Resolution Infrared and Coherent Raman Studies of Propellane

RW Kirkpatrick, JW Nibler, Oregon State University, Corvallis, Oregon

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Infrared Spectra of the Fundamental Bands of $^{34}SO_2$

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JH Flaud, University of Paris-7, Creteil CEDEX, France

High Resolution Spectra of Phosphine in the 1370-800 Wavenumber Region

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Excitation of Surface Excitons in the Nanoscale Calcium Oxide Surface

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

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Study of Martensitic Transformations in Shape Memory Alloys by Real-time Measurement of Surface Work Function Change

M Cai, JT Dickinson, Washington State University, Pullman, Washington

G Xiong, WP Hess, Pacific Northwest National Laboratory, Richland, Washington

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Laser Desorption from Metal Oxides

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Nanoparticle Fluorescence

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Investigation of Hydrogen Tunneling in Tropolone

RL Redington, Texas Technical University, Lubbock, Texas

Jet Spectrum of Nitromethane

DS Perry, University of Akron, Akron, Ohio

High Resolution Infrared Spectroscopy of Boron Trifluoride

AG Maki, Private, Mill Creek, Washington

High Resolution Infrared Spectroscopy of Metyl Nitrite

LM Goss, Idaho State University, Pocatello, Idaho

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

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SL Tait, S Fain, CT Campbell, University of Washington, Seattle, Washington

Laboratory Studies of Atmospheric Processing of Sea Salt

BJ Finlayson-Pitts, JN Pitts, RC Hoffman, WH Robertson, University of California, Irvine, Irvine, California

Development of an Electrospray Photoelectron Spectroscopy Apparatus with a Low Temperature Ion Trap

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Development of an Electrospray Photoelectron Spectroscopy Apparatus with a Low Temperature Ion Trap

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High Resolution Infrared Spectroscopy of Isotopically Substituted Butadienes

NC Craig, Oberlin College, Oberlin, Ohio

High Resolution Infrared Spectroscopy of Acetaldehyde

JT Hougen, National Institute of Standards and Technology, Gaithersburg, Maryland

Investigation of the Electronic Structure of Fe-S Clusters

T Ichiye, Y Fu, Washington State University, Richland, Washington

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Investigation of Aromatic and Other Novel Gas Phase Atomic Clusters and Molecules

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Investigation of Aromatic and Other Novel Gas Phase Atomic Clusters and Molecules

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Computational Chemistry Modeling of Main-Group and Transition-Metal Cluster Systems

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Adiabatic Following Spectroscopy Using Quantum Cascade Lasers

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Synthesis and Analysis of Organic Hydroperoxide by PTR-MS

BT Jobson, Washington State University, Pullman, Washington

TL Hubler, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

TG Karl, NCAR, Boulder, Colorado

Microscopic Studies of Hydration and Corrosion in Nuclear Materials Disposition

SA Joyce, Los Alamos National Laboratory, Los Alamos, New Mexico

Mexico City Municipal Area Air Pollution Study, 2003

BT Jobson, Washington State University, Pullman, Washington

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Surface Induced Dissociation of Peptides using FTICR Mass Spectrometry

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FM Fernandez, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

K Kuppannan, VH Wysocki, KA Herrmann, University of Arizona, Tucson, Arizona

High-Resolution Infrared Spectroscopy of Nitrogen Dioxide and Water.

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TA Blake, Environmental Molecular Sciences Laboratory, Richland, Washington

High Resolution Infrared Spectroscopy of Methane

J Kelly, RL Sams, Pacific Northwest National Laboratory, Richland, Washington

L Brown, Jet Propulsion Laboratory, Pasadena, California

Ultrasonic Catalysis of Chemical Reactions

KM Judd, Pacific Northwest National Laboratory, Richland, Washington

AM Williams, Gonzaga University, Spokane, Washington

Single Molecule Dymanics of Protein DNA Interactions

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Using the Environmental Scanning Electron Microscope for Studying the Atmospheric Transformations of Organic and Inorganic Particles

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Soft-landing of Peptide Ions on Surfaces

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Real Time Trace Gas Measurements by Chemical Ionization Mass Spectrometry

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Inelastic Electron Scattering Cross Section Measurements in Liquid Water

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Development of Data Analysis and Visualization Software - SpectraMiner

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Computer Programming of Data Acquisition Board for Single Particle Laser Ablation Time-of-flight Mass Spectrometer (SPLAT-MS)

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Determination of the Mo...OX Bond Strengths in Oxomolybdenum Model Complexes

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Laser-Materials Interactions: Theory and Experiment

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Single Particle Analysis of Smoke Aerosols During the Summer 2002 Yosemite Aerosol Characterization Study

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Second Harmonic Generation from Organic Water/Air Interfaces

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Surface Induced Dissociation of Polyatomic Ions

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Single Molecule Approach for Understanding EGFR Molecular Interactions

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Electron Stimulated Reactions in Thin Water Films

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Condensed Phase Chemical Physics of Low Temperature Amorphous Solids and Gas Surface Interactions

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Use of Fluorimeter in EMSL 1205 for Quantum Efficiency Studies on Semiconductor Quantum Dots

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Single Molecule Electron Transfer Dynamics

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Site-specific Spectroscopy and Optical Imaging

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AFM-enhanced FLIM and Raman Imaging

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Protein-protein Interaction Dynamics

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Microbial Cell Analysis and Imaging

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Ion Channel Protein Dynamics in Lipid Bilayer

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Syntheses of Fe-S Cluster Complexes with Peptides as Terminal Ligands

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Development of Multi-Functional Microscopy (MFM) for Cancer and AIDS Research

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Investigation of 4Fe-4S Cluster Complexes with Peptides as the Terminal Ligand

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Atomically Resolved Studies of Transition Metal Oxides

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Chemical Characterization of Heterogeneous Inclusions in Soot Particles

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Temperature-Dependent Yield of Frenkel Pairs Generated by Valence Excitation in NaCl

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EMSL CAT in Analytical Mass Spectrometry

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Early Transition Metal Oxides as Catalysts

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High Resolution Infrared Spectroscopy of BF_2OH

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High Resolution Infrared Spectroscopy of Peroxynitric Acid

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Metal Sulfide Clusters in the Environment

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Photoelectron Spectroscopic Studies of Complex Anion Solvation in the Gas Phase

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Phosphorous Poisoning of Automotive Catalysts

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Ultra-Trace Molecular Detection Instrumentation Based on Aerosol Nucleation with Rapid Preconcentration and Separation

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