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

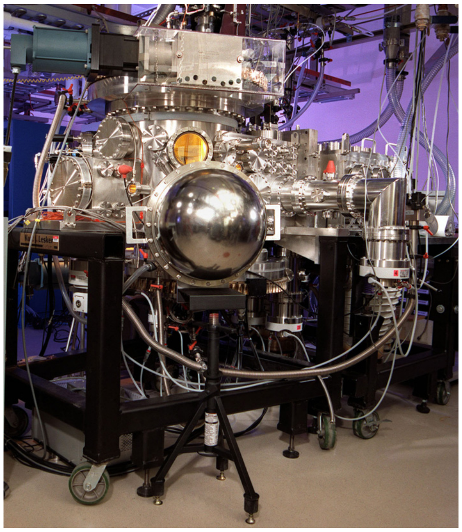

Figure 1. State-of-the-art molecular beam surface-scattering and kinetics instrument.

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.

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 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.

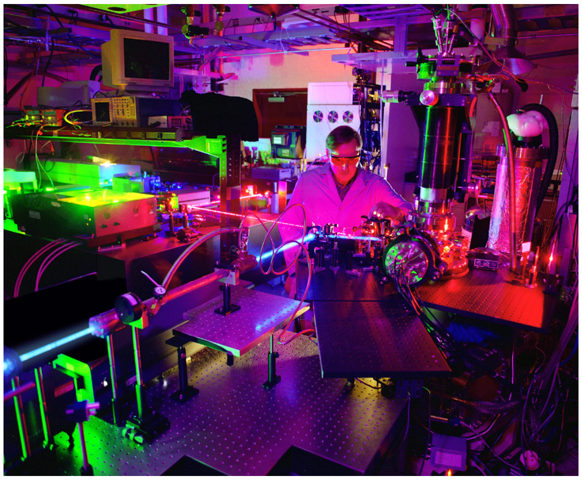

Figure 3. Laser desorption experiments investigate the effects of electronic excitation on crystalline materials.

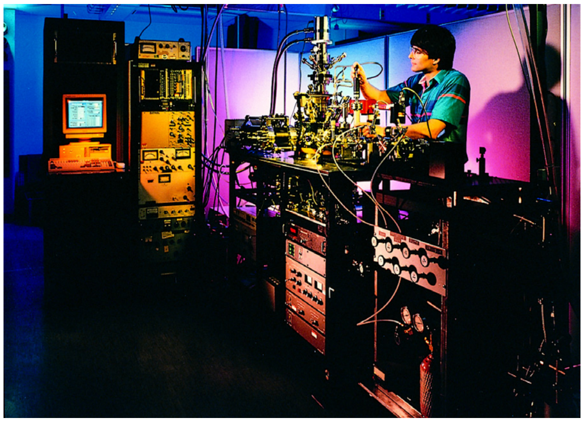

Figure 4. Electron-stimulated surface reaction apparatus is used to study non-thermal reactions that occur on surfaces or at interfaces.

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.

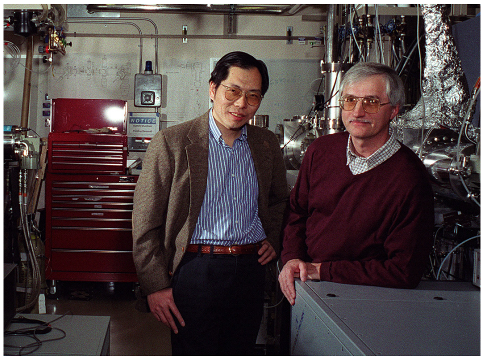

Figure 5. CPCS Facility users/collaborators L-S Wang, Washington State University Tri-Cities, Richland, Washington, and AA Boldyrev, Utah State University, Logan, Utah, are combining experimental and theoretical approaches to understand the unique properties and characteristics of metal clusters. Their 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 W.R. Wiley Environmental Molecular Sciences Laboratory 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 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.

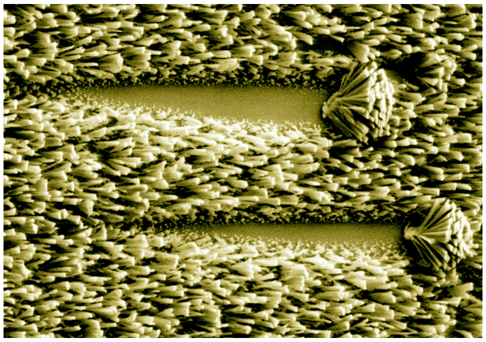

Figure 6. Nanostructures could be used to control and enhance chemical reactivity. Researchers at the CPCS Facility are trying to determine how molecules enter pores, are captured, and eventually released.

Ultra-Sensitive and Environmental 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.

Characterization of particulate matter in the atmosphere represents a unique challenge. Several approaches 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. One approach uses new mass spectrometric techniques for aerosol analysis. This instrumentation is built around a laser desorption/ionization mass spectrometer with an asymmetric ion trap for simultaneous positive/negative ion detection. It provides real-time sampling and analysis of aerosol particles in a field-deployable unit that is more compact and less expensive than current instruments.

In conjunction with this instrumentation, new devices are being developed and deployed to collect and preserve field samples for future automated analysis of individual particles in the laboratory. These same samples enable characterization of the chemical reactivity of native aerosols that can be used for comparison in laboratory studies of the formation and reactivity of model aerosol species. These studies are complemented by fundamental studies of the gas-phase chemistry of aerosol precursor molecules.

Upgrades

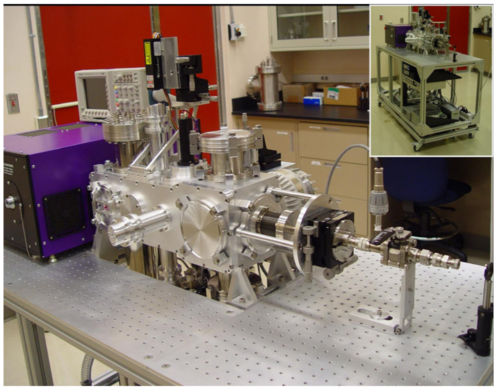

Figure 8. Second generation of single-particle laser ablation time-of-flight mass spectrometer.

Second Generation of Single-Particle Laser Ablation Time-of-Flight Mass Spectrometer (SPLAT II). Construction of the SPLAT II instrument was completed during FY 2005. In its basic form, SPLAT II can measure the size and chemical composition of individual aerosol particles down to 50 nm with extremely high sensitivity and unprecedented precision. The mass spectral signatures are generated in two steps: 1) a pulsed CO_2 heats the particle and evaporates the semi-volatile fraction and 2) a time-delayed excimer laser pulse ionizes the resultant plume.

Combining SPLAT II with differential mobility analyzers and the EMSL aerosol flow reactor enables unparalleled detailed studies of chemical and microphysical transformations of individual size-selected aerosol particles in real time. It allows monitoring simultaneously changes in size with sub-monolayer precision, shape, density, fractal dimension, and mass spectral signature of each individual particle.

Future Directions

In addition to its core research, the CPCS Facility is expanding its interests into the following major new areas: 1) detecting and monitoring trace atmospheric species, including gaseous and particulate matter, and 2) studying biological processes important in the environment and health, including live cell imaging to observe reaction dynamics of functioning biological systems in real time, single-molecule spectroscopy to understand protein-protein interactions and DNA damage and repair, and novel instrumentation for studying cellular responses to low-dose radiation. The CPCS Facility supports:

Biogeochemistry Grand Challenge, which involves studying how organisms exchange energy and electron flux with mineral matter in soils, sediments, and subsurface materials. The CPCS Facility-supported research used surface-enhanced Raman spectroscopy to characterize electron transfer across cell membranes associated with bioremediation.

Membrane Biology Grand Challenge, which involves understanding the network of genes and proteins that govern the structure and function of membranes and their components responsible for photosynthesis and nitrogen fixation in cyanobacteria (blue-green algae). CPCS Facility capabilities support will focus on 1) the use of Raman spectroscopy and imaging of, for example, the time-dependent compositions and distributions of the photosynthetic system proteins, and 2) detecting molecular interactions in the bacterial membrane using advanced fluorescence resonance energy transfer technology.

Atmospheric Aerosol Chemistry Science Theme, which involves understanding aerosol climate effects, improving our ability to characterize atmospheric aerosols, and reducing uncertainties associated with aerosols in air quality and climate predictions. The CPCS Facility-supported research focuses on 1) the next generation of *in situ*/*ex situ* aerosol characterization techniques capable of monitoring atmospheric aging (processing) of aerosols, including improved organic speciation and 2) numerically efficient computation of aerosol processing effects exploiting high-performance computing facilities.

Biological Interactions and Interfaces Science Theme, which is designed to provide an improved molecular-scale understanding of biological interactions and interfacing. The key role of the CPCS Facility involves improving resolution and visualization for tracking key biomolecules across membrane interfaces.

Interfacial Science Theme, which involves development, characterization, and modeling of tailored surface interfaces, nano-oxide catalysis, and oxidation reactions to advance our understanding of interfacial phenomena. The CPCS Facility provides major support to the DOE Office of Basic Energy Science programs in interfacial science.

Trace Environmental Detection and Monitoring Science Theme, which involves real-time, *in situ* detection and monitoring of chemical and biological species/agents in the environment to characterize the impacts of airborne pollutants, biomarkers, and chemical agents using optical and mass spectrometry detection methods. CPCS Facility instruments support, among others, the PNNL National Security Directorate programs in this area.

Imaging Individual Proteins and Living Cells, which involves advanced fluorescence techniques available in the CPCS Facility.

Mid-Infrared Versus Far-Infrared (THz) Relative Intensities of Room-Temperature *Bacillus* Spores

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This research evaluates potential spectroscopic techniques that may be used for rapid and accurate detection of biological spores and other possible bioterrorism agents.

Recently, interest has surged in the far-infrared or terahertz (THz) spectral region. An advantage of working at these wavelengths, located between the infrared and millimeter-wave regions, is that many synthetic materials are transparent, and although there are interferences from rotational transitions of water vapor, the transitions are relatively few at the very long wavelengths (i.e., <50 cm^{-1}). Work in the THz domain recently warranted great interest with emphases placed on both sensor development (such as those focusing primarily on technologies using pulsed laser sources and gated detectors) and on signature recognition—THz spectral signatures have been reported for explosives, nucleotides, DNA/RNA samples, organic materials, a few gas-phase samples, and pharmaceuticals whose coatings are transparent in the THz region, thus allowing for mapping within a tablet.

We recently reported identification and discrimination of bacterial spores using mid-infrared technologies (Johnson et al. 2005). Certain gram-positive bacteria have the ability to form spores, a dormant state that is highly resistant to both chemical and thermal extremes. Using both transmissive and photoacoustic infrared methods, we extended the mid-infrared studies for identifying vegetative bacteria to include bacterial spores. Applying established chemometric methods to our spectra, the data could be reduced to distinguish spores from unknown materials, and also to distinguish between spores of similar *Bacillus* species and strains.

The work described in this highlight compares the relative signal strengths of the mid-infrared to the far-infrared signatures of spores, thus probing the possibility of using THz signatures for clinical, analytical, or forensic applications.

Typical results for bacterial spore absorbance spectra are shown in Figure 1 for *B. subtilis 49760* and *B. thuringiensis subsp. kurstaki.* The data above 1900 cm^{-1} revealed little information other than the well-characterized C–H stretches, and are not discussed here. The strongest bands are the protein Amide I and Amide II bands near 1657 and 1541 cm^{-1}, respectively, with nucleic acid and lipid skeletal modes seen at lower frequency. Of greater interest is the lack of spectral signatures seen in the long wavelength regions (wavenumbers <600 cm^{-1}). Each of the mid- and far-infrared spectra was recorded for the same sample on the same substrate. With the exception of a weak 431 cm^{-1} band, no far-infrared signatures were found that are clearly associated with the sample. Although an exact spore count for the sample is not easily ascertained, an estimated spore count was between 10^8 and 10^{10}.

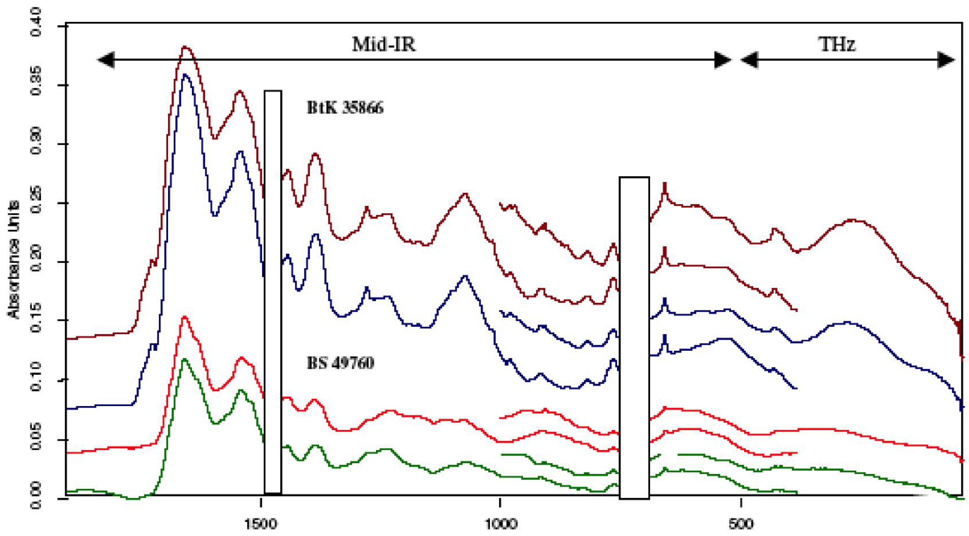

Figure 1. Composite mid-infrared and THz spectra of *B. thuringiensis ssp. kurstaki and B. subtilis 49760* from 1800 to 30 cm^{-1}. Those regions where the polyethylene substrate does not transmit have been blocked out for clarity. Spectra were recorded at 2 cm^{-1} resolution. Spectra have been vertically offset for clarity with the THz 3 spectrum of a sample plotted directly atop the mid-infrared spectrum of the same sample.

The present data demonstrate that any THz signatures associated with the room-temperature spectra of bacterial spores are comparatively weak. Averaged over 30 spectra and comprising five *Bacillus* species, any THz signatures are 28.5 times weaker (based on p-p noise) than the 1657 cm^{-1} Amide I band. The lack of THz peaks makes conjecture as to their (non-) origin difficult. Others researchers have reported DNA/RNA/nucleotide THz signals, but a spore is a complex containing thousands of chemical species. Smearing of large molecule signatures may play a role, as may masking by spore-bound water molecules. It may be that the transition dipole moments for such large amplitude motions are fundamentally weak. We anticipate that cooling the samples (e.g., to 77 or 10 K) would increase the intensity by narrowing the linewidths of the THz bands as has been shown (10 to 110 cm^{-1}) not only for short peptides, but also for long-chain retinal and DNA nucleotides. However, for many applications (e.g., first responders), time is critical and precludes using cryogenic methods. Although other species may show stronger signatures, particularly at low temperatures, the results of this research may suggest a limited utility of the THz domain for room-temperature detection of spores.

Citation

Johnson TJ, NB Valentine, and SW Sharpe. 2005. “Mid-Infrared Versus Far-Infrared (THz) Relative Intensities of Room-Temperature *Bacillus* Spores.” *Chemical Review Letters* 403(1-3):152-157.

Monte Carlo Simulation of the Spatial Distribution of Energy Deposition for an Electron Microbeam

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This research compares experimental measurements with Monte Carlo models that are used to understand the effects of radiation on biological cells.

Most human exposures to ionizing radiation involve high-energy photons that generate secondary electrons with a broad energy spectrum. These energetic electrons cause a number of lower-energy interactions, distributing energy, for instance, by ionization and excitation in the surrounding medium. Recent experiments with a low-linear energy transfer (LET) microbeam probe suggest that the amount of energy and quality of radiation absorbed by hit cells can also affect neighboring bystander cells. Demonstration of these "bystander effects" induced by low-LET radiation has proven to be more difficult than with high-LET particles. The current study compares experimental spatial distributions of energy deposition for an electron track in air obtained with EMSL's electron microbeam with computed results obtained from Monte Carlo simulation of electron track structures in water, taking into account the relative density of air and water. EMSL's electron microbeam in-air data provide a rare opportunity to test Monte Carlo electron-track simulation codes by comparison with experiments. If agreement is obtained with these physical measurements of electron microbeam characteristics, then we have greater confidence in the predictions of the track-structure simulations for application of the instrument as a single-cell irradiator.

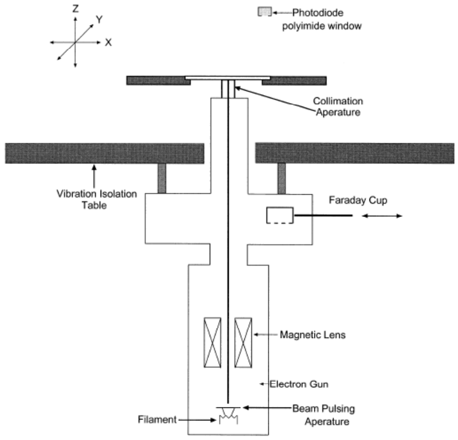

Figure 1. Schematic of the EMSL electron microbeam system.

Figure 1 is a schematic drawing of the electron microbeam apparatus, as configured for this study. To obtain detailed dosimetry for the electron microbeam, a photodiode was used to measure and characterize the spatial distribution of the microbeam in air, with electron microbeam energies ranging from 25 to 80 keV.

Figure 2 shows a comparison of experimental and computed beam spread, in terms of the full width at half maximum (FWHM) value, as a function of the penetration distance, z, for a microbeam energy of 30 keV. Overall, the agreement between the results of the microbeam in-air experiment and the Monte Carlo simulation of electron tracks in water, scaled by the relative density of the medium, is good. At low

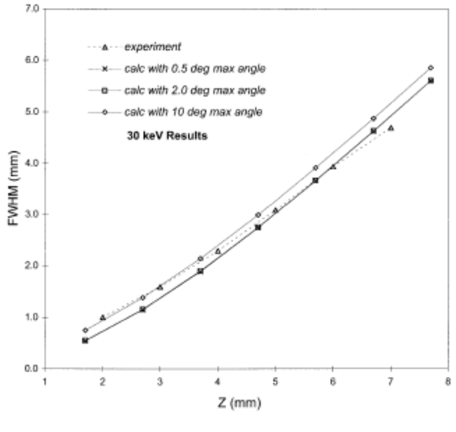

Figure 2. Comparison of experimental and computed values of the FWHM for the energy deposition of a 30-keV microbeam source for a range of penetration distances.

penetration, the experimental values of FWHM are slightly greater than predicted by the simulation, and the discrepancy increases for the higher microbeam energies where the beam diameter is smaller. Electron beam scattering within the collimator, which is not included in the simulation model, could be the cause of differences between the simulation and experimental data.

Dosimetry calculations characterizing the spatial variation of the energy deposited by the slowing and stopping of energetic electrons were conducted and compared with experimental measurements. The computations involve event-by-event, detailed Monte Carlo simulations of low-energy electrons interacting in water vapor. Simulations of electron tracks with starting energies of 30 to 80 keV are used to determine energy deposition distributions in thin cylindrical rings as a function of penetration and radial distance from a beam source. Overall, the experimental measurements of the spatial distribution of an electron microbeam in air show general agreement with the density-scaled simulation results for water vapor at these energies, yielding increased confidence in the predictions of Monte Carlo track-structure simulations for applications of the microbeam as a single-cell irradiator. While further experiments would be required to understand and resolve the differences in the observed and computed integrated signal results, the observed level of agreement supports the validity of our dosimetry computation based on a Monte Carlo simulation method. Details of this research were published in Lynch et al. 2005.

Citation

Lynch DJ, WE Wilson, MT Batdorf, MB Sowa Resat, GA Kimmel, and JH Miller. 2005. "Monte Carlo Simulation of the Spatial Distribution of Energy Deposition for an Electron Microbeam." *Radiation Research* 163(4):468-472.

n-Alkanes on MgO(100): I. Coverage-Dependent Desorption Kinetics of *n*-Butane; II. Chain Length Dependence of Kinetic Desorption Parameters for Small *n*-Alkanes

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The interactions of an adsorbate with a substrate will determine whether a molecule will react or not. Understanding these complex interactions at a fundamental level may eventually lead to our ability to control the reactivity and selectivity of gas/surface reactions. This research describes a detailed method for modeling the desorption kinetics of alkanes interacting with an MgO substrate.

The interactions of an adsorbate with a substrate, be it a metal, an oxide, or an ice, determine the ultimate fate of that molecule (i.e., whether the molecule scatters, traps, adsorbs, or reacts). Understanding these complex interactions at a fundamental level may eventually lead to our ability to control the reactivity and selectivity of gas/surface reactions. For example, during the last decade much progress has been made in understanding supported metal catalysts at the nanometer scale because of research on model catalyst systems. By studying these model systems, improvements in the efficiency and cleanliness of industrial chemical reactions can be made. Understanding the effect that the nanometer-scale confinement of matter has on catalytic properties is one of the current scientific challenges. Detailed analysis at the nanoscale allows us to probe the atomic-scale interactions of the adsorbed metals and their oxide supports, with each other and with other adsorbed species.

Alkane adsorption on oxide surfaces is of significant interest because of the wide use of oxides in heterogeneous catalysts as support materials and as active catalysts. For example, MgO catalysts are used for the oxidative coupling of methane to form C_2 hydrocarbons or for methane oxidation to produce formaldehyde. The MgO(100) surface is one of the most thoroughly studied of all single-crystal oxide surfaces from both experimental and theoretical approaches and has also received significant attention as a support in model catalyst studies. Therefore, the adsorption and desorption kinetics of alkane molecules on MgO and other oxide surfaces is of fundamental interest.

We used molecular beam scattering and temperature-programmed desorption (TPD) at low temperatures to study the adsorption and dissociation of hydrocarbons (e.g., methane, ethane, propane) on MgO(100) thin films. Highly collimated molecular beams of the small alkane molecules are impinged on the sample and the adsorption dynamics and desorption kinetics are studied. Figures 1 and 2 show the coverage-dependent desorption energy and desorption prefactor for a series of normal (straight-chain) alkanes adsorbed on MgO(100). These values are extracted from a TPD analysis technique that allows the coverage-dependent desorption energy to be accurately determined by mathematical inversion of a TPD spectrum, assuming only that the prefactor is coverage-independent. A variational method is used to determine the prefactor that minimizes the difference between a set of simulated TPD spectra and corresponding experimental data. The data in Figure 1 show that desorption energy increases linearly with chain length. The data in Figure 2 show that the prefactor for desorption increases dramatically with chain length.

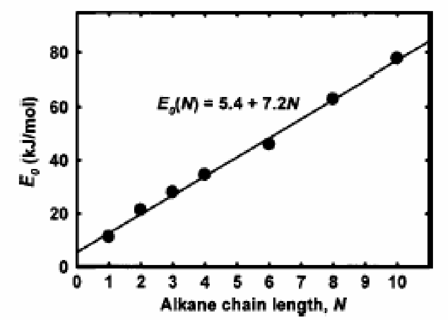

Figure 1. Desorption energy for a series of normal chain alkanes.

The observed increase can be physically justified by considering the increase in rotational entropy available to the molecules in the gas-like transition state for desorption. The dashed lines are predictions using various models to calculate the entropic change between a molecule adsorbed on the surface and one in the gas phase.

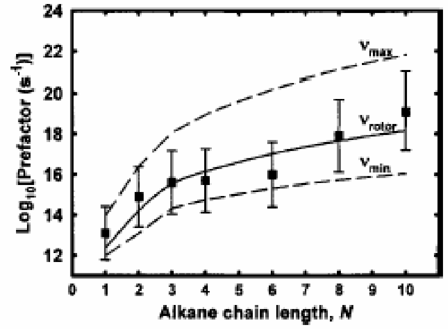

Figure 2. Desorption prefactors for a series of normal chain alkanes.

We have demonstrated the use of an optimization-inversion method for analysis of these TPD data that allows accurate determination of coverage-dependent desorption-kinetics parameters. Using these analysis results, we demonstrated that we are able to accurately simulate the TPD experiments over a wide range of initial coverage and heating rates. These measurements will advance our specific understanding of the catalytic activity of this important combustion catalyst and our general understanding of particle-size effects in hydro-carbon catalysis. Tait and co-workers (2005a, b) published the details of this work in 2005.

Citations

Tait SL, Z Dohnalek, CT Campbell, and BD Kay. 2005a. "*n*-Alkanes on MgO(100). I. Coverage-Dependent Desorption Kinetics of *n*-butane." *Journal of Chemical Physics* 122(16):Article No. 164707.

Tait SL, Z Dohnalek, CT Campbell, and BD Kay. 2005b. "*n*-Alkanes on MgO(100). II. Chain Length Dependence of Kinetic Desorption Parameters for Small *n*-Alkanes." *Journal of Chemical Physics* 122(16):Article No. 164708.

Heterogeneous Chemistry of Individual Mineral Dust Particles with Nitric Acid: A Combined CCSEM/EDX, ESEM, and ICP-MS Study

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The chemistry of individual mineral dust may play an important role in climate forcing and atmospheric chemistry, and may need to be explicitly accounted for in climate models.

It has been reported that 50 percent of global emissions of tropospheric aerosol particles consists of mineral dust particles injected into the atmosphere, mainly from desert and arid regions. Mineral dust tends to originate from very specific geographic areas and then is transported over very long distances, influencing climate and chemistry of the atmosphere on regional and global scales. Climatic effects of mineral dust include reflection and absorption of incoming solar radiation and impacts on cloud formation, cloud properties, and precipitation. Heterogeneous chemistry of mineral dust modifies both the gas-to-particle partitioning in the atmosphere and physicochemical properties of individual particles. An individual mineral dust aerosol may include a wide variety of individual minerals having different physical and chemical properties. Therefore, quantification of its global impacts requires information on dust-emission sources and its transport, particle size, and compositional data, and a description of the processes that govern changes in particle properties as they evolve in the atmosphere. Dust mineralogy and its emission inventory, transport, and dry and wet removal have been included in a number of recent global and regional climate models. However, the atmospheric chemistry of dust is oversimplified in current models, in which mineral dust is often considered as a single-entity aerosol with a single kinetic parameter for reaction with a particular trace gas.

Particle hygroscopicity is a key property of atmospheric aerosol that is important in its impact on climate and the overall atmospheric environment. The ability of dust particles to serve as cloud condensation nuclei, their optical properties, and their heterogeneous chemistry are all coupled to the hygroscopic properties of mineral dust, which is typically considered a largely nonsoluble material. Indeed, mineral dust aerosol consists mainly of different nonsoluble soil minerals such as quartz, calcite, gypsum, and clays. However, as mineral dust is processed or ages in the atmosphere, some of the particles may become substantially hygroscopic because of the presence of surface coatings. From a practical perspective, it is very difficult to assess the detailed mineralogy of mineral dust, its size- and composition-resolved heterogeneous chemistry, and its cloud formation abilities. An important first step may be the identification of the components of mineral dust that have the greatest atmospheric reactivity and impact on the Earth's chemistry and climate.

Towards this goal, we studied the heterogeneous chemistry of mineral dust with nitric acid. Our goal was to identify and characterize particles of greatest reactivity and determine changes in their physicochemical properties. We used computer-controlled scanning electron microscopy with energy-dispersive x-ray (CCSEM/EDX) analysis to follow heterogeneous chemistry of calcium-containing particles within a diverse mixture of mineral dust particles extracted from authentic sand samples collected in the following desert areas: the China loess region (upper basin of the Huang River), the Sahara Desert, and coastal and inland Saudi Arabia. We used state of-the-art environmental scanning electron microscopy to probe the hygroscopic behavior of mineral dust particles reacted with nitric acid.

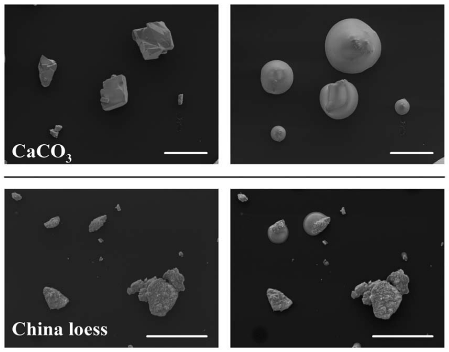

Figure 1. Secondary electron images of $CaCO_3$ and China loess particles (left) before and (right) after reaction with gaseous HNO_3 in the presence of water vapor.

The secondary electron images shown in Figure 1 demonstrate morphology changes observed for individual $CaCO_3$ and China loess particles following exposure to HNO_3 vapor. Particle images prior to reaction are shown on the left, and images after the exposure are shown on the right. Figure 1 (top) shows that the crystalline solid particles of calcium carbonate become enlarged and spherical in shape because a deliquesced calcium nitrate product is formed. Figure 1 (bottom) demonstrates that a few of the China loess particles reacted with HNO_3 under the same conditions also show similar morphology changes. Manual EDX analysis and x-ray mapping of particles that showed a crystalline-to-liquid transformation, as evidenced by a change in morphology, confirmed the presence of $CaCO_3$ in the original particles and consecutive formation of $Ca(NO_3)_2$ after reaction.

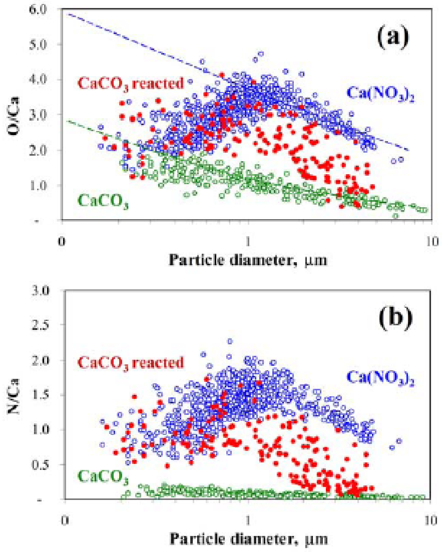

Figure 2. Elemental ratios of (a) oxygen/calcium and (b) nitrogen/calcium measured by CCSEM/EDX analysis, plotted as a function of particle size for $CaCO_3$ particles (green symbols) and $Ca(NO_3)_2$ particles (blue symbols). Data for $CaCO_3$ particles reacted with HNO_3 in the presence of water vapor (red symbols) are also included in the plots.

Figure 2 shows the elemental composition of a few hundred individual $CaCO_3$ and $Ca(NO_3)_2$ particles as a function of particle size determined by CCSEM/EDX. The elemental compositions of individual particles are expressed in terms of atomic ratios of oxygen/calcium and nitrogen/calcium. The red symbols in Figure 2 depict the oxygen/calcium and nitrogen/calcium elemental ratios for $CaCO_3$ particles exposed to HNO_3. The data show that submicron $CaCO_3$ particles appear to react completely. Larger particles (1 to 2.5 µm) show lesser reaction extent, and finally, very large particles (>2.5 μm) remain either almost or completely unaffected by the reaction. The data obtained from this focused laboratory study suggest that a portion of each of the four mineral dust aerosol samples from specific source regions may exhibit substantial reactivity with gas-phase HNO_3, leading to formation of hygroscopic $Ca(NO_3)_2$-containing particles. Therefore, in the atmosphere, once $Ca(NO_3)_2$ particles are formed, they remain in the aqueous phase and never dry out, even over desert areas. These liquid particles may change the optical properties of mineral dust, serve as effective cloud condensation nuclei, and modify clouds as well. In addition, these modified particles may open up the possibility of new multiphase reaction chemistry. It follows that a significant fraction of the dust from these specific locations will change their physical and chemical properties when transported over polluted areas. These changes may have an important impact on climate forcing and atmospheric chemistry.

This research is discussed in further detail in Laskin et al. 2005.

Citation

Laskin A, TW Wietsma, BJ Krueger, and VH Grassian. 2005. "Heterogeneous Chemistry of Individual Mineral Dust Particles with Nitric Acid: A Combined CCSEM/EDX, ESEM, and ICP-MS Study." *Journal of Geophysical Research D: Atmospheres* 110(D10):D10208.

Probing Inhomogeneous Vibrational Reorganization Energy Barriers of Interfacial Electron Transfer

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Understanding the dynamics of electron transfer may lead to improved nanoparticle catalysts for energy and environmental applications.

Interfacial electron-transfer processes in dye-sensitized semiconductor systems often involve complex and inhomogeneous dynamics. The complexity and inhomogeneity come from the spatial heterogeneities of the surfaces and the inhomogeneous vibronic coupling between the adsorbed molecules and the nanoscale rough surfaces of the substrates. Recently, there has been much interest in the use of TiO_2 particles as photo-oxidation catalysts. To better use these particles, a fundamental understanding of the electron-transfer process is needed. However, our current knowledge of the spatial and temporal inhomogeneities of interfacial electron-transfer dynamics is inadequate to characterize the heterogeneous local environments of nanoparticles and the nanoscale roughness on the surfaces of the substrates. Interfacial electron-transfer dynamics can vary spatially and temporally and can involve both static and dynamic inhomogeneities. Presumably, the inhomogeneity and fluctuations of the local driving force, the vibrational reorganization energy, the solvent reorganization energy, the electronic and Franck-Condon couplings, and the electron trapping and scattering at the interfaces and in the bulk of the semiconductor substrates could all contribute to the complexity and inhomogeneity in interfacial electron-transfer dynamics.

In this study, we used both resonance Raman microscopy and atomic force microscopy (AFM) to characterize the vibrational reorganization energy barriers of the interfacial electron transfer in a dye-sensitization system, namely alizarin adsorbed on TiO_2 nanoparticles. Figure 1 shows a representative experiment where we simultaneously obtained a resonance Raman spectrum and an AFM image. We observed that the Raman peak intensity and peak-to-peak intensity ratio are different among different submicrometer-scale spots at the TiO_2 nanoparticle layer. We then focused on revealing inhomogeneous vibrational reorganization energy barriers for interfacial electron transfer, using a time-dependent wave packet propagation analysis of resonance Raman spectra to obtain mode-specific vibrational reorganization energies upon the charge-transfer reactions for individual spots under a 250-nm spatial resolution. Although the spatial

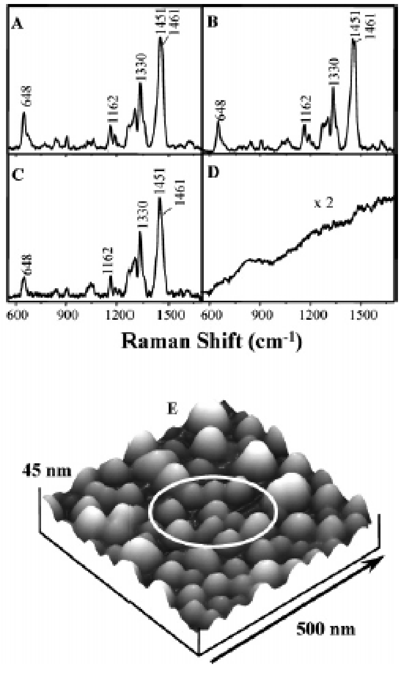

Figure 1. Resonance Raman and AFM characterization of alizarin/TiO_2 interfacial electron transfer.

resolution of our Raman spectroscopy was not at nanoscale, our results present a significant step forward in characterizing site-specific vibrational reorganization energy and shed light on inhomogeneous interfacial electron-transfer dynamics in terms of inhomogeneous Franck-Condon barriers.

Applying microscopic AFM-Raman characterization and analysis, we revealed that for alizarin/TiO_2 interfaces, the vibrational reorganization energy barriers of interfacial electron transfer are inhomogeneous at a sub-mesoscale (250 nm). We found that 1) the total vibrational reorganization energy was inhomogeneous from site to site, 2) the alizarin/TiO_2 bridging normal modes were the primary contributor to the total vibrational reorganization energy and its inhomogeneity, 3) the mode-specific analyses indicated that the energy distributions were inhomogeneous for bridging normal modes and less inhomogeneous or homogeneous for non-bridging normal modes, especially for modes far away from the alizarin-TiO_2 coupling hydroxyl modes, and 4) the vibrational reorganization energy inhomogeneity was closely associated with the local environmental heterogeneity of the alizarin/TiO_2 interface. It is most likely that the vibrational reorganization energy inhomogeneities contributed to the inhomogeneous dynamics of the interfacial electron-transfer processes. However, it is still a challenge to identify a detailed mechanism of the contribution of the inhomogeneity to both forward and backward electron-transfer processes in the alizarin/TiO_2 system. Although the topographic and spectroscopic detection limits reported here have not yet reached single molecules, single semiconductor nanoparticles, or even nanoscale-specific sites, our results demonstrated that correlated AFM-confocal Raman microscopy is a promising approach for a quantitative understanding of inhomogeneous interfacial charge transfers.

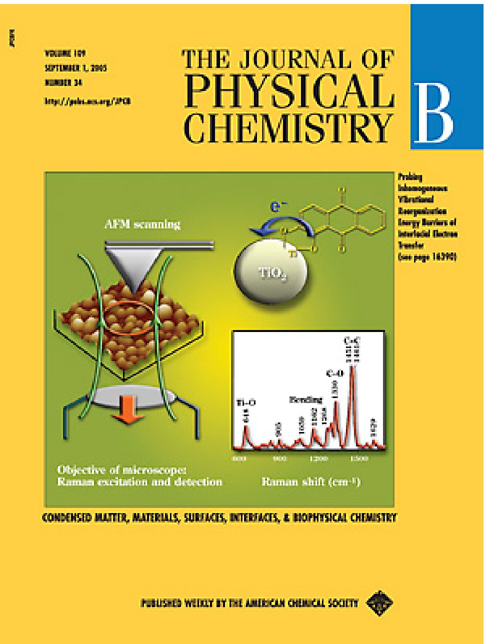

Figure 2. Cover of the September 1, 2005, issue of *Journal of Physical Chemistry B*.

This research was featured on the September 1, 2005, cover of the *Journal of Physical Chemistry B* (Figure 2).

Citation

Pan D, D Hu, and HP Lu. 2005. "Probing Inhomogeneous Vibrational Reorganization Energy Barriers of Interfacial Electron Transfer." *Journal of Physical Chemistry B* 109(34):16390-16395.

Crystalline Ice Growth on Pt(111): Observation of a Hydrophobic Water Monolayer

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Understanding the dynamics and morphology of crystalline ice formation is important in atmospheric science. In the seeding of clouds, for example, the water-particle interaction is a critical factor for the nucleation of ice crystals.

Water-surface interactions are ubiquitous in nature and play an important role in many technological applications such as catalysis and corrosion. To understand these interactions, numerous prior experiments have been done on thin water films grown on single-crystal metals such as Ru(0001) and Pt(111), which are considered to be good templates for the epitaxial growth of crystalline ice (CI). However, despite years of effort, our understanding of fundamental aspects of water-surface interactions, and even the structure of bulk water, remains incomplete.

Water adsorbs molecularly on Pt(111). At temperatures above 60 K, the adsorbed water monomers become mobile and form hydrogen-bonded clusters as the coverage increases. For typical water fluxes, CI films result for growth temperatures above 125 to 135 K. For multilayers of CI, the equilibrium structure has the lattice constant of bulk ice and is incommensurate with the substrate. Multilayer CI films desorb with zero-order desorption kinetics. Based on these and other observations, the prevailing view has been that multilayer films of water wet Pt(111).

In this work, we investigated the growth of CI films on Pt(111) using temperature-programmed desorption (TPD) of both water and krypton adsorbed on the water films. As expected, the water monolayer wets the Pt(111) surface. Figure 1 shows a typical series of TPD spectra for crystalline D_2O on Pt(111). The multilayer ice films desorb with zero-order kinetics, resulting in the low-temperature peak that shifts to higher temperature with increasing coverage. The water monolayer desorbs at higher temperature (about 170 K). Water TPD spectra similar to these have been obtained on a variety of metal surfaces and presented as evidence for the wetting growth of the multilayer water films on these metals.

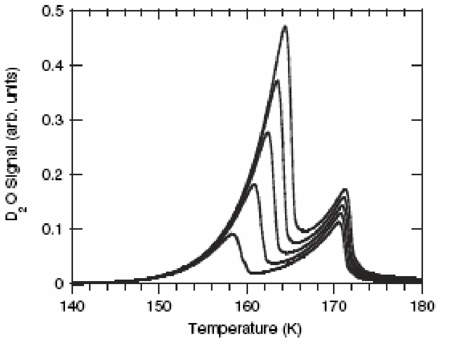

Figure 1. D_2O TPD spectra for 2, 3, 4, 5, and 6 ML CI films. The spectra exhibit zero-order desorption from the CI multilayers (i.e., the leading edges of the low-temperature peaks are aligned), and the monolayer desorbs at higher temperature. These characteristics are typically believed to indicate that the water films wet the substrate.

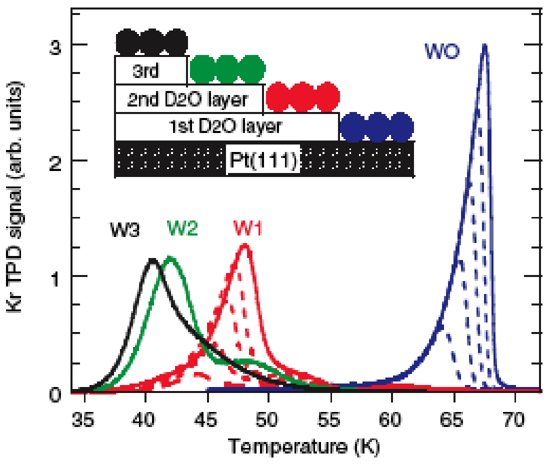

Figure 2. TPD spectra for 1 ML of krypton on various coverages of D_2O deposited on Pt(111) at 100 K where the films kinetically wet the surface. The solid blue, red, green, and black lines are the spectra for 0, 1, 2, and 3 ML of D_2O, respectively.

Figure 2 displays the TPD of krypton layers deposited on top of various water films deposited at low temperatures. The krypton desorption temperature is sensitive to the height of the desorbing atom above a metal surface. This approach can also be used to determine the height distribution of a thin water film grown on a metal substrate: the solid blue, red, green, and black lines in Figure 2 with peaks labeled W0, W1, W2, and W3 show the TPD spectra of 1 ML of krypton adsorbed on clean Pt(111) and 1, 2, and 3 ML of water deposited at 100 K, respectively. Clearly, adsorption of krypton on 1 ML of water can be easily distinguished from two or more layers of water or from the bare Pt(111). Hence, as we show below, TPD of physisorbed krypton can be used to probe the growth of water films on Pt(111).

Using the experimental techniques described above, we investigated the growth of crystalline water films on Pt(111). We find that the water monolayer wets Pt(111) at all temperatures investigated (20 to 155 K). At low temperatures (T <120 K), additional water layers kinetically wet the monolayer surface. However, for coverages greater than 1 ML, the additional water molecules form ice crystallites that do not wet the water monolayer, which remains exposed even for total coverages as large as 45 ML. CI films grown at higher temperatures (T >135 K) do not wet the water monolayer. The structure of the water monolayer on Pt(111), which has no dangling OH bonds or lone-pair electrons, is key to understanding the nonwetting growth of CI films. The fully coordinated water monolayer results in a hydrophobic surface on which water diffusion is facile. At high temperatures where large-scale rearrangement of the films is kinetically accessible, the low surface energy of the hydrophobic water monolayer relative to the CI surface thermodynamically favors the formation of nonwetting, three-dimensional ice crystallites. The hydrophobic character of the water monolayer is further supported by the observation that kinetically wetted, amorphous films dewet upon heating, exposing the water monolayer. We have also obtained results similar to the D_2O data presented here for H_2O on two different Pt(111) crystals, and for H_2O films grown on a thin epitaxial Pd(111) film deposited on Pt(111).

These results help clarify several reports in the literature and increase our fundamental understanding of ice structure. The absence of layer-by-layer growth can be the result of thermodynamics (i.e., nonwetting or incomplete wetting of the substrate) or can arise from kinetic limitations. It is now clear that the nonwetting growth of three-dimensional ice crystallites on the water monolyayer is thermodynamically favored. The PNNL researchers involved in this work are the first to observe this effect (Kimmel et al. 2005). For the novel hydrophobic property to show itself, the water-substrate bond has to be strong enough to form a stable monolayer. Weaker bonding results in a "classic" hydrophobic state, in which the water merely balls up immediately; in other words, not even a first monolayer of ice forms. This research should be of interest to those who, for example, study the seeding of clouds.

Citation

Kimmel GA, NG Petrik, Z Dohnalek, and BD Kay. 2005. "Crystalline Ice Growth on Pt(111): Observation of a Hydrophobic Water Monolayer." *Physical Review Letters* 95(16): Article No. 166102.

User Projects

Low-Coordinated Oxygen Sites on MgO Surfaces
Vienna University of Technology, Wien, Austria
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Study of Martensitic Transformations in Shape-Memory Alloys by Real-Time Measurement of Surface Work Function Change
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Properties of Ice and Liquid Interfaces
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Characterization of Quantum Cascade Lasers
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Photoreflectivity in Ge/Si Thin films
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Energetic Processes: Reaction in Thin Organic Films
University of Colorado, Boulder, Colorado
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Mechanisms of Fragmentation of Post-Translationally Modified Peptides
University of Melbourne, Melbourne, Victoria, Australia
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Theoretical Studies of Kinetic Processes in Nanoscale Ice Films

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University of Washington, Seattle, Washington
H Jonsson

Thrust 4: Surface-Enhanced Raman-AFM and Antibody Force Microscopy

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Laser Ablation/Ionization Characterization of Solids

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Probing the Electronic Structure of Metal Clusters

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Photoelectron Emission Microscopy (PEEM) Study of Cu Nanoparticles on TiO_2(110)

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Atomically Resolved Studies of Adsorbates on TiO_2(110)

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Development of 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

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Infrared and Coherent Anti-Stokes Raman Scattering (CARS) Spectroscopy of Cyclopropane

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High-Resolution Infrared Spectroscopy of Methyl Phosphonic Difluoride

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Vibration-Rotation Spectroscopy of Sulfur Trioxide

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Photoelectron Spectroscopy of Group VI Transition Metal Oxygen Clusters

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Measurement of the Two-Photon Absorption Cross-Section of Natural Dyes

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Investigation of Hydrogen Tunneling in Tropolone

Texas Technical University, Lubbock, Texas
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Kinetics in Ices with Complex Compositions

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Single-Particle Laboratory Studies of Heterogeneous Reactions of Trace Atmospheric Gases with Particles Present in the Troposphere

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Resonant Surface Excitation of Potassium Salts by Selective Laser Desorption

Mary Baldwin College, Staunton, Virginia
MT Perozzo

Jet Spectrum of Nitromethane

University of Akron, Akron, Ohio
DS Perry

High-Resolution Infrared Spectroscopy of Boron Trifluoride

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Spectroscopic Infrared Properties of Hydrogen Cyanide

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

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High-Resolution Infrared Spectroscopy of Metyl Nitrite

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

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Laboratory Studies of Atmospheric Processing of Sea Salt

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

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High-Resolution, Matrix-Assisted Laser Desorption/Ionization Imaging of Biological Samples

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High-Resolution Infrared Spectroscopy of Isotopically Substituted Butadienes

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NC Craig

High-Resolution Infrared Spectroscopy of Acetaldehyde

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

Investigation of the Electronic Structure of Fe-S Clusters

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

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

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Theoretical Models of the Adsorption and Desorption Dynamics in Compressed Monolayers

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Chalmers/Goteborgs University, Goteborg, Sweden
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Adiabatic Following Spectroscopy Using Quantum Cascade Lasers

University of Strathclyde, Glasgow, United Kingdom
G Duxbury

Synthesis and Analysis of Organic Hydroperoxide by Proton Transfer Reaction-Mass Spectrometry (PTR-MS)

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W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington
ML Alexander
National Center for Atmospheric Research, Boulder, Colorado
TG Karl

Microscopic Studies of Hydration and Corrosion in Nuclear Materials Disposition

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

Mexico City Municipal Area Air Pollution Study, 2003

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Surface-Induced Dissociation of Peptides Using Fourier Transform Ion Cyclotron Resonance (FTICR) Mass Spectrometry

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Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia
FM Fernandez
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K Kuppannan, VH Wysocki, KA Herrmann

High-Resolution Infrared Spectroscopy of Nitrogen Dioxide and Water

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MA Smith
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TA Blake

High-Resolution Infrared Spectroscopy of Methane

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Ultrasonic Catalysis of Chemical Reactions

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Electron-Induced, Low-Dose Hypersensitivity

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Electron-Induced Genomic Instability

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Triplet Decay Pathways of the Electrically Conducting Polymer Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]

Central Washington University, Ellensburg, Washington
DM Laman, SW Miller

LASER-Induced Neutral Metal Atom Desorption from Magnesium Oxide and Lithium Fluoride Probed Via Opti-Spectroscopies

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CN Afonso

Single-Molecule Dymanics of Protein DNA Interactions

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H Lu, R Liu

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

Weizmann Institute, Rehovot, Israel
Y Rudich

Fluorescence Imaging of Cellular Protein Dynamics

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Brigham Young University, Provo, Utah
GM Carr
Prairie View A and M University, Prairie View, Texas
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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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ML Alexander
Sacramento City College, Sacramento, California
MV White

Inelastic Electron Scattering Cross-Section Measurements in Liquid Water

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Dynamics Studies of Surface-Induced Dissociation of Polyatomic Ions

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Fluorescence Microscopy of Cells and Particles

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Development of Data Analysis and Visualization Software SpectraMiner

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State University of New York at Stonybrook, Stonybrook, New York
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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

Colorado State University, Fort Collins, Colorado
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Second Harmonic Generation from Organic Water/Air Interfaces

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AT Maccarone, GB Ellison

Surface-Induced Dissociation of Polyatomic Ions

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Single-Molecule Approach for Understanding Epidermal Growth Factor Receptor (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 the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) 1205 for Quantum Efficiency Studies on Semiconductor Quantum Dots

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Single-Molecule Electron Transfer Dynamics

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H Lu, D Pan, D Hu

Site-Specific Spectroscopy and Optical Imaging

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H Lu, D Pan

Atomic Force Microscopy- (AFM)-Enhanced Fluorescence Lifetime Imaging Microscopy (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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A Variable-Energy Electron Mibrobeam

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

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Y Fu, L Wang

Development of Multi-Functional Microscopy for Cancer and Acquired Immune Deficiency Syndrome (AIDS) Research

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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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Selective Immobilization of Biological Molecules on Single-Walled Carbon Nanotube (SWCNT) Surfaces

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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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Image Acquisition and Analysis of Fluorescent Biological Samples

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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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Charge Separation Kinetics in the Cr_2O_3/Fe_2O_3 System

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

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Development of Cell-Permeable Dyes for *In Vivo* Live Cell Imaging

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Analysis of Lipid Nanoparticle Interaction with Cell Membranes

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