Chemistry Department

Professor Jeffrey P. Fitzgerald
Chair

The 2005-2006 Academic year saw a return to normalcy for the Naval Academy's Chemistry Department following the move back into a renovated Michelson Hall. Faculty and students have made the most of the renovated laboratory spaces and new instrumentation. Twenty-five USNA Chemistry Department faculty members, an equal number of 1/C (senior) chemistry majors and six full-time postdoctoral associates were able to carry out research on almost fifty different research projects. These included thirty externally-funded efforts covering a wide range of chemical and biochemical projects, from the synthesis of new materials and pharmaceuticals, to simulations of atomic level processes such as friction or detonation, to detection of trace contaminants in the environment. Funding agencies included the Air Force Office of Scientific Research (AFOSR), the Air Force Research Laboratory (AFRL), the Army Research Office (ARO), the DOD High Performance Computing Modernization Program, the DOD Strategic Environmental Research and Development Program, a General Electric Fellowship (administered via the University of Michigan), the Kinnear Fellowship, the National Aeronautic and Space Administration (NASA), the National Institute of Health (NIH), the National Science Foundation (NSF), the Naval Academy Research Council (NARC), the Naval Research Laboratory (NRL), the Naval Surface Warfare Center (Indian Head), the Office of Naval Research (ONR), Walter Reed Army Institute for Research (WRAIR), the Crowley Bioscience Fellowship and the Research Corporation. The above efforts resulted in over twenty peer-reviewed publications, multiple conference proceedings, a book chapter, one patent and sixty-seven presentations, including several by midshipmen researchers at regional and national scientific society meetings.

Faculty members whose accomplishments are particularly noteworthy include Professor Judith Harrison who supports three full-time post-doctoral associates doing molecular dynamic simulations. This group produced two refereed journal articles, a book chapter and fifteen presentations. Equally prolific was Associate Professor Paul Trulove who supports two full-time post-doctoral research associates producing five refereed publications and six presentations, Associate Professor Daniel O'Sullivan who published two journal articles and made eight presentations and Professor Mark Elert who published two conference proceedings and made seven scientific presentations. Assistant Professors Brian Rehill and Virginia Smith had two and three peer-reviewed publications appear during the '05-'06 reporting period. Professors Cheek, Elert, Copper and Schroeder continued long and fruitful collaborations with NRL, which in the case of Professor Cheek, resulted in new U.S, patent.

New sources of funding include the NIH, the AFRL and the John and Aileen Crowley Bioscience Fund, a private donation intended to promote midshipmen education in the biosciences. Assistant Professor Tammy Domanski and Assistant Professor Jamie Schlessman were selected as Crowley Bioscience Fellows and Associate Professor Chris Kinter was selected as the Kinnear Fellow.

Sponsored Research

Determination of Water in $EMIBF_4$ by Infrared Spectroscopy

Researcher: Professor Graham T. Cheek
Sponsor: Naval Research Laboratory (NRL)

The determination of water in 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) was carried out using infrared (IR) spectroscopy. Samples were placed in quartz cells for IR transmission measurements in a Fourier-Transform infrared instrument. The quartz IR window is rather narrow, allowing investigation of only the water stretching modes in the 3500 – 3700 cm^{-1} range. Starting with vacuum-dried $EMIBF_4$, successive additions of

water were made to the ionic liquid. An increase in the absorbance peak at 3550 cm^{-1} was observed from 1 mM to 20 mM added water, and the integrated intensity of this peak was linear with added water concentration. These observations produced an estimated lower limit of detection for water of approximately 1 mM. An interesting aspect of this work is the appearance of another peak at 3650 cm^{-1} at added water concentrations above 20 – 25 mM. It is possible that the two peaks are due to the symmetric and antisymmetric stretching vibrations of water which is hydrogen-bonded to tetrafluoroborate anions in the ionic liquid.

UV Absorbance Detection of Colchicine and Related Alkaloids on a Capillary Electrophoresis Microchip

Researcher: Associate Professor Christine L. Copper
Sponsor: Chemical Dynamics and Diagnostics Branch, Chemistry Division, Chemical Sensing/Chemometrics Section, Naval Research Laboratory (NRL)

The separation and UV absorbance detection of four toxic alkaloids, colchicine, thiocolchicine, colchicoside, and thiocolchicoside, on a microchip-based capillary electrophoresis device are reported. To increase the sensitivity of UV absorbance detection, optical cells with extended pathlength are integrated into the separation channel during the microfabrication process. The absorbance values realized on the microchip using these optical cells were proportional to the increase in average depths according to the Beer-Lambert Law, resulting in sensitivity enhancements by as much as five times. Linearity of response was observed from 12.5 μM to 1.25mM of colchicine, with detection limits ranging from 4 μM-6 μM depending upon the specific alkaloid and the dimension of the optical cell. The extraction of colchicine from spiked milk samples was performed and an average recovery rate of 83% with a relative standard deviation of 3.8% was determined using the optimized conditions on the microchip.

Molecular Classification of *Staphylococcus aureus* Strains

Researcher: Assistant Professor Tammy L. Domanski
Sponsor: Crowley Bioscience Fellowship

Over a five month period, forty athletic facilities at USNA were swabbed, and one-quarter tested positive for *S. aureus*. Additionally, twenty-seven clinical samples that had been collected during the same period were obtained from the on-site Naval Medical Clinic. The *S. aureus* samples were characterized on the basis of antibiotic susceptibility and at the genomic level utilizing the multi-locus sequence typing methodology. Similarity was found between several of the environmental samples and those obtained from the clinic. There was more diversity and less resistance to multiple drugs among the environmental samples than those obtained from the clinic. In addition, the utility of using commercial kits and schemes designed for clinical samples proved limited and made definitive identification of several samples from surfaces as *S. aureus* difficult. An expanded epidemiological study of staphylococcal infections at the United States Naval Academy is being planned for the future.

Molecular Dynamics Simulations of Cubane Detonation

Researcher: Professor Mark L. Elert
Sponsor: Naval Research Laboratory (NRL), Chemistry Division

Cubane is a molecule composed of eight carbon atoms at the corners of a cube, with one hydrogen attached to each carbon. This novel material has long been regarded as a potential explosive because of the high strain energy of the molecule. However, experimental evidence of its detonation properties has been lacking. During the past two years, molecular dynamics simulations have been carried out to ascertain the detonation properties of this unique energetic material, using gradually more complex and realistic models of the cubane crystal structure.

Antimalarial Chalcones

Researcher: Assistant Professor Clare E. Gutteridge
Sponsor: Walter Reed Army Institute of Research (WRAIR)

The ongoing investigation of substituted chalcones was continued; the aim being to identify compounds with good *in vitro* antimalarial activity and then test these for *in vivo* activity. In previous years a computational model which provides a description of the structural requirements for active compounds in chalcones and related structures was developed. Additionally a variant on the chalcone structure was identified which is likely to posses

improved metabolic stability compared to the chalcones. Using these data, a series of novel compounds expected to be active antimalarials with good metabolic stability were designed along with a route to synthesize them. The synthetic work to the first analog is almost complete. What remains is purification of the final compound, which should be facilitated by the acquisition of a preparative HPLC in the near future.

MD Investigations of the Friction and Tribology of Solid Lubricants

Researchers: Dr. J. David Schall and Professor Judith A. Harrison
Sponsor: Air Force Office of Scientific Research (AFOSR)

Microelectromechanical systems (MEMS) represent an emerging technology. These systems have generated a great deal of interest because of their potential use as sensors and actuators. The devices are on the order of microns in size and it is possible to fabricate thousands of devices at one time for a cost of a few cents per device. Consequently, systems with MEMS-based technologies will be lighter, smaller, and be less expensive than systems utilizing non-MEMS-based technologies. Workers at Sandia National Labs predict that these devices will play a significant role in future technologies with a broad range of commercial and military applications. Possible future applications of MEMS-based devices include accelerometers for use in military systems such as stability control, attitude heading reference, and short-time flight navigation. The use of silicon-based MEMS devices in nanosatellites to form an interconnected aerospace surveillance system has been proposed by The Aerospace Corporation. Workers at Hughes Aircraft Company and collaborators have proposed a MEMS-based system to replace current rocket, missile, and space vehicle navigational systems.

Silicon-based MEMS devices suffer from two major problems. First, because these devices are so small, the fabrication process can leave critical components adhered to one another. This phenomenon, call stiction, renders the MEMS device inoperable. Second, the wear rate of silicon is such that MEMS composed of silicon cannot be used in applications were parts are in relative motion for extended periods of time. To overcome these problems, researchers at the University of California have suggested coating the silicon-based MEMS with carbon coatings. Researchers at the Raytheon Corporation have suggested constructing MEMS devices from diamond because it possesses superior friction and wear properties compared to silicon. We have extensive experience investigating the friction and wear of diamond, which should lend insight into the construction of diamond-based MEMS. In addition, we are currently debugging a molecular dynamics code that will be capable of examining the friction and wear properties of silicon-based MEMS devices coated with carbon films.

Classical molecular dynamics simulations have been used to conduct a systematic examination of the mechanical and tribological properties of amorphous carbon films doped with silicon and hydrogen. Preliminary results show that increasing the percentage of silicon in the films changes the mechanical properties of the film. This preliminary work also identified problems with the published potential energy functions for C-Si-H systems. We have begun the process of developing a new C-Si-H analytic function that will have the proper mechanical properties and will not have discontinuities in the derivatives of the function with respect to position. Once the new function is developed a detailed analysis of the effects of percent silicon and temperature on the mechanical and tribological properties of these films is planned.

Molecular Dynamics Investigations of the Tribology of Diamond Surfaces and Films

Researchers: Assistant Research Professor Kevin Van Workum,
Assistant Professor Paul T. Mikulski (Physics Department),
Midshipman 1/C Lawrence A. Herman, USN and Professor Judith A. Harrison
Sponsor: Office of Naval Research (ONR)

Friction and the related phenomenon of wear are two of the more costly problems facing industry today. Understanding and ultimately controlling friction and wear has long been recognized as being central to many areas of technology. For instance, combustion engines break down and cutting tools become dull usually because of friction induced wear. Despite the obvious importance of friction and the induced wear, much of the atomic-scale dynamics responsible for these phenomena remain elusive. If the atomic-scale origins of friction and wear were understood, this might ultimately lead to the design of materials with specific friction and wear properties.

Molecular dynamics (MD) simulations and a potential energy function developed at the Naval Academy are being used to investigate the atomic-scale origins of friction and wear in hydrocarbon systems. Using MD simulations has proven useful in examining atomic-scale friction and relating the results to experimental data. For example, tribochemical reactions and their atomic-scale mechanisms were cataloged. These reactions and their products were consistent with inferences drawn from macroscopic friction experiments on diamond.

Atomic force microscope (AFM) measurements have examined the friction of alkanethiol monolayers that differ in length by one methylene (-CH2-) unit. These monolayers are refered to as the odd and even monolayers. Some AFM measurements show that domains of odd and even monolayers have different friction. Other AFM measurements reveal no friction differences between the odd and even monolayers. Contact forces between the amorphous carbon tip and the monolayers were examined in detail. The simulations showed that when sliding in the direction of chain tilt, the even monolayer system exhibited lower friction at all but the lowest loads. Because friction can be defined as the sum of the forces opposing tip motion (resisting) and the forces pushing the tip along (pushing) , insight into friction can be gained by examining these contact forces separately. Detailed analysis revealed that structural differences in the conformation of the monolayer chains at the sliding interface yields a different distribution of contact forces in these two systems. This work was recently published in the American Chemical Society journal *Langmuir*.

Multi-functional Extreme Environment Surfaces: Nanotribology for Air and Space

Researcher: Dr. Guangtu Gao and Professor Judith A. Harrison (Co-PI)
Other MURI Co-PIs: NC State University: Jacqueline Krim (PI), D. W. Brenner (CoPI), Mohammed Zikry (CoPI), A. I. Kingon (CoPI), R. J. Nemanich (CoPI), Sandia National Labs: Michael T. Dugger (CoPI), University of California: Peter Taborek (CoPI), J. Rutledge, (CoPI), Naval Research Lab: Kathryn J. Wahl (CoPI), Wispry Corp: Art Morris (CoPI), Aerospace Corp: Steve Didziulis (CoPI), Wright Patterson AF Lab: Jeffrey S. Zabinski (CoPI)
Sponsor: Multi-University Research Initiative (MURI):
The Air Force Office of Scientific Research (AFOSR)

Tribological issues such as friction and wear are currently the limiting factors in the development and commercialization of a myriad of enabling technologies for advanced air and space applications, with surfaces and lubricants frequently being the weakest link in overall system reliability and performance. While no single lubricant/coating has been identified that can withstand the entire range of extreme environments encountered by these systems, multi-functional nanocomposite materials appear capable of withstanding such debilitating tribological conditions. Their widespread implementation will be inhibited, if not impossible, however without tribological design rules that are integrated from the onset with system design. This project brings together an unparalleled team of experts with wide ranging backgrounds but one common goal: Solution of Air Force/DoD and commercial tribological problems deemed paramount, while concomitantly training personnel and collaborating closely with Air Force researchers to carry forth these solutions in Department of Defense (DoD) and industrial settings.

The MURI team will (1) develop the scientific basis for tribological properties in terms of scale-dependent thermal, chemical, and mechanical processes that is critical for the engineering of advanced materials and coatings with tailor-made properties, and (2) from this basis introduce a new generation of coatings comprised of constituents that are optimally scaled and blended for life-cycle service in extreme environments associated with air, space and MEMS applications that would be of critical importance to the Air Force, DoD and industry. To accomplish these goals, our team will combine methods for synthesizing advanced materials, highly innovative and unique test-devices, and extensive multiscale modeling to identify and take advantage of critical physical mechanisms that underlie successful performance of structures for service in a widely varying range of extreme environments. This strong coupling between synthesis, testing, and modeling, which is a hallmark of our team, will provide unprecedented new insights and engineering capabilities that are not possible through individual efforts.

Our work over the last year has focused on the development of techniques to calculate elastic constants using molecular dynamics simulations as a function of temperature for angle-dependent potentials. We have derived these expressions and have submitted a paper to *The Journal of Chemical Physics*. In addition, we use the methods developed to calculate the elastic constants of diamond as function of temperature. This work will be published in the *Journal of Physics: Condensed Matter.*

Preparation of a Radioligand for Study of the AMPA Receptor by Positron Emission Tomography (PET)

Researcher: Associate Professor Christopher M. Kinter

Sponsor: PET Radiopharmaceutical Science Section Molecular Imaging Branch, Division of Intramural Research Programs, National Institute of Mental Health (NIMH), National Institutes of Health (NIH)

AMPA receptors are one of the three major ionotropic glutamate receptors. These receptors mediate normal synaptic transmission along excitory pathways and participate in the modification of synaptic connection during development and changes in the efficiency of synaptic transmission throughout life. The excessive or inappropriate stimulation of these receptors can lead to neuronal death or loss by a process known as excitotoxicity. Excitotoxicity has been implicated in the pathophysiology of a number of neurological disorders and neurodegenerative conditions. Positron Emission Tomography (PET) gives researchers the ability to noninvasively measure neurotransmitter receptor densities and metabolic change in human subjects by making use of compounds labeled with positron emitting isotopes (carbon-11, fluorine-18, oxygen-15) The development of novel compounds for the study of the AMPA receptor by positron emission tomography (PET) has the potential to aid in the development of AMPA receptor-based therapies and the development of new neuroprotective agents. Previous research realized the preparation of precursor compounds for radiolabelled synthesis of several target compounds for study of the AMPA receptor. Current work has focused on optimizing the synthetic route to the precursors and exploring the conditions required for introduction of the positron emitting isotope.

Block Copolymers through Noncovalent Interactions

Researcher: Assistant Professor Shirley Lin

Sponsor: Research Corporation

The goals of this project are to incorporate hydrogen-bonding interactions into the chain ends of two different polymers and to explore the self-assembly of mixtures of these polymers into noncovalent block copolymers. The effect of the noncovalent nature of the block copolymer juncture on the formation of a periodic 3-dimensional structure will be explored. Will the reversible nature of hydrogen bonding affect the self-organization of these noncovalent block copolymers through microphase separation? What value of K_{ass} between hydrogen bonding pairs is necessary for these morphologies to form?

The project will first attempt to quantify K_{ass} of various hydrogen-bonding motifs in the presence of polymers containing functional groups capable of disrupting hydrogen bonding. The synthesis of 2-ureidopyrimidinones has been undertaken. The next step is to use 1H NMR to evaluate the assembly of 2-ureidopyrimidinones in the presence of poly(4-vinylpyridine), poly(ethyleneoxide), and other polymers.

Solubilization of Nitroaromatic Compounds in Surfactant Solutions

Researcher: Assistant Professor Dianne J. Luning Prak

Sponsor: General Electric Fellowship through the University of Michigan

Soil and groundwater have become contaminated with nitrotoluenes by the production and use of explosive materials. The impact of nitrotoluene pollution depends on the capacity of the soil system to chemically or biologically transform these pollutants into less harmful species or on the speed at which they can be removed through engineering technologies, such as "pump and treat" operations. On way to enhance pump and treat operations is to use surfactants that increase the aqueous solubility of the compound. To assess if surfactant-enhanced aquifer remediation (SEAR) is applicable for a compound, its equilibrium solubility in various surfactants should be determined. The objective of this work is to quantify the equilibrium solubility behavior of five nitrotoluenes (4-nitrotoluene, 2,3-dinitrotoluene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, and 2,4,6-trinitrotoluene) at room temperature in nine surfactants of varying structure to assess the influence of surfactant and solute structure on solubility behavior. The surfactants fall into three categories: polyoxyethylenated straight-chain alcohols (Brij-35 and Brij-58), polyoxyethylenated sorbitol esters (Tween 20 and Tween 80) and alkylphenol ethoxylates (Tergitol NP-8, NP-10, NP-13, NP-15, and NP-40). During this time period, the solubility of 2,4-dinitrotoluene in solutions of the nine surfactants (6 concentrations each) has been measured.

Degradation of Emergent and Explosive Contaminant Compounds in Natural Waters

Researchers: Assistant Professor Dianne J. Luning Prak and Associate Professor Daniel W. O'Sullivan
Sponsor: Strategic Environmental Research and Development Program (SERDP)

Nitrogenous energetic compounds can enter and pollute the aquatic environment through the fallout of unexploded ordnance at shooting ranges and the corrosion of underwater unexploded ordnance (UXO) casings. The impact of this pollution source on the aquatic systems depends on the capacity of the aquatic system to transform (chemically or biologically) these pollutants into less harmful species. Photolysis is one transformation process, and the presence of salts (marine systems) has been found to increase the photolysis rate for some organic compounds, but to decrease the rate for others. The objectives of this work are to quantify photodegradation rates of nitrogenous compounds such as TNT, cyclotrimethylenentrinitramine (RDX), and cyclotetramethylenentetranitramine (HMX) using samples of varying salinity and to identify and quantify degradation products. During this time period, the solubility of TNT and 2,4-dinitrotoluene was measured in seawater of varying ionic strengths at four temperatures (see publication) to help establish the upper concentration limit of these compounds. For the photolysis experiments, an optical cell holder was customed designed to maintain the sample temperature and allow various optical filters to be used (Dr. O'Sullivan). Photolysis experiments are being conducted in a Suntest CPS+ solar simulator. Preliminary experiments have shown an influence of wavelength and sodium chloride concentration on the photolysis of rate of TNT. Future work will quantify the influence of salinity (both seawater and sodium chloride solutions) and other components of seawater (*e.g.,* dissolved organic matter) on the photolysis rates of TNT and other nitrogenous energetic compounds.

Beacon Aptamers for the Detection of Small Molecules

Researcher: Assistant Professor Daniel P. Morse
Sponsor: National Institute of Neurological Disorders and Stroke (NINDS), National Institutes of Health (NIH)

RNA beacon aptamers are RNA molecules that fluoresce upon binding to a target ligand. In the absence of ligand, a beacon aptamer assumes a hairpin structure in which the 5' and 3' ends are base-paired. In this conformation fluorescence is low because a fluorophore and quencher attached to the ends of the RNA are near each other in space. Fluorescence greatly increases upon ligand binding because an induced conformational change separates the fluorophore from the quencher. In theory, beaon aptamers could provide a fast, simple, sensitive, and specific assay for any molecule of interest. The long-term objective of this proposal is to develop a reliable method for the rapid production of effective beacon aptamers. Previously, beacon aptamers have been produced in two steps. First, RNA molecules that bind to the target were selected from a randomized RNA pool. Second, a fluorophore and quencher were attached and the resulting molecules were tested for their ability to function as beacon aptamers. A new approach has been developed that selects, in a single-step, RNAs that bind to the target and undergo the appropriate conformational change. The selection strategy has been tested using the antibiotic tobramycin as the target. After 14 rounds of selection, two unique RNA molecules emerged. One of these RNAs has been synthesized and labeled with fluorophore and quencher. The labeled RNA is currently being tested for its ability to function as a tobramycin beacon aptamer.

Gas, Cloudwater, and Rain Hydrogen Peroxide and Methylhydroperoxide Measurements in RICO

Researchers: Associate Professor Daniel W. O'Sullivan and Dr. Brian G. Heikes (University of Rhode Island)
Sponsor: National Science Foundation (NSF), Division of Physical Meteorology

The Rain in Cumulus over the Ocean Experiment (RICO) investigates trade wind cumulus clouds and the surrounding clear air to further understanding of shallow cumulus cloud microphysics and dynamics, larger-scale meteorological interactions, and climate forcing induced by cumulus cloud impacts on radiation and moisture budgets. The RICO field project involved an international team of investigators employing *in situ* observations, remote sensing, and theoretical models. RICO traced the atmospheric physics and chemistry of particle evolution, from haze aerosol, to cumulus cloud droplet formation, alteration by clear-cloud air mixing and photochemistry, through to "warm-rain" precipitation development. In our collaborative sub-project of RICO, *in situ* chemical observations of gaseous hydrogen peroxide and methylhydroperoxide were made in clear and cloudy air in the marine boundary layer and lower free troposphere using the NCAR C-130 airborne platform. Observations of aqueous hydrogen peroxide and methylhydroperoxide condensed upon cloud size and larger droplets were attempted

using a counter-flow virtual impactor. The peroxides are integral to understanding and predicting the temporal evolution of aerosol sulfate, cloudwater sulfate, and cloud condensation nuclei activity. The peroxides are the leading oxidants of sulfur dioxide dissolved in atmospheric water and sulfur dioxide oxidation is the principle chemical process by which aerosol dry mass increases. The RICO (Lesser Antilles in winter 2004-05) photochemical environment was favorable to the formation of hydrogen peroxide and methylhydroperoxide. Sulfur dioxide was present from oceanic sulfur gas emissions, episodic volcanism, and long-range transport of anthropogenic emissions. USNA participated in the field measurement phase and continues to perform data analysis. In addition USNA provided the organic peroxide standards. Methylhydroperoxide is not commercially available and was synthesized and purified at the Naval Academy. Final data from the HPLC based peroxide measurements were submitted to the RICO data archive in December 2005. Data analysis and interpretation of the observations continues as final papers are prepared.

INTEX-A Analysis and INTEX-B Measurement of H_2O_2, CH_3OOH, and CH_2O on the Medium or Low Altitude Sub-orbital Platform

Researchers: Associate Professor Daniel W. O'Sullivan and Dr. Brian G. Heikes (University of Rhode Island)
Sponsor: National Aeronautical and Space Administration (NASA), Global Tropospheric Chemistry Program

The project involves a collaborative effort for the analysis of airborne observations of hydrogen peroxide, methylhydroperoxide, peracetic acid and formaldehyde from INTEX-NA and the measurement and analysis of hydrogen peroxide, methylhydroperoxide, and formaldehyde during INTEX-B. The named gases have been identified as priority measurements on the low- and medium-altitude platform aircraft for Airborne Validation/Science Experiments by NASA. The method for hydrogen peroxide and methylhydroperoxide involves gas-to-aqueous collection, HPLC separation and post-column fluorescence detection. A 30-sec sample can be collected and analyzed every 75 seconds. The formaldehyde method involves gas-to-aqueous collection followed by fluorescence detection. Improvements to the system made in INTEX-NA now permit continuous formaldehyde sampling on a 1-min basis. These instruments have been flown onboard the NASA DC-8 and P3-B sub-orbital platforms and on the NCAR C-130 aircraft in multiple experimental programs. We provided instruments and personnel to equip and staff measurements from the NASA DC-8. Specific science objectives include 1) intercontinental ozone and photochemical oxidant chemistry, 2) vertical transport of odd-hydrogen radical reservoir species through cloud from low altitude production regions to the mid and upper troposphere, 3) secondary sulfate production in cloud and wet aerosol, 4) tropospheric processing of hydrocarbons and "oxygenates", and 5) characterization of air masses impacting western North America. Formaldehyde is also a priority 2 measurement for direct validation of AURA level 2 column densities of formaldehyde and our measurements of formaldehyde contribute needed data for OMI validation. Further, new technologies are under development for faster and more sensitive measurements of the hydroperoxides using chemical ionization mass spectrometry and we participated in comparison studies with this new technology on the same platform and in comparisons between these instruments on different platforms with other groups supported to measure hydroperoxides. Similarly, we participated in inter and intra-platform comparisons of formaldehyde instruments with other groups funded to measure CH_2O.

Biotic and Abiotic Attenuation of Nitrogenous Energetic Compounds (NEC) in Coastal Waters and Sediments

Researchers: Associate Professor Daniel W. O'Sullivan and Dr. Michael Montgomery (NRL)
Sponsor: Strategic Environmental Research and Development Program (SERDP), Department of Defense-Navy

This project was through the SERDP program for the Navy to address clean-up and disposal procedures for underwater unexploded ordnance (UXO). UXO casings eventually breach and release NECs through mechanical stress, corrosion, and low-order remedial detonations. These compounds can remain intact in the sediment, dissolve into the overlying waters (dissolution), or bind to particles and resuspend into the overlying waters (phase transformation). Over time, various chemical, biological, and physical processes (for example sequestration, metabolism and photolysis) change the NEC to other chemical forms that have different transport and toxicity properties in various ecosystems. Although SERDP has sponsored much work on NEC transformation in terrestrial and groundwater systems, very little information is available on rates of attenuation or transport of energetics in coastal aquatic systems. In lieu of evidence that these materials are rapidly degraded to nontoxic substances or metabolized by microbial assemblages, the Department of Defense (DoD) is being pressured to recover all UXO from coastal waters. Recent experimental work by the PI's has demonstrated that biodegradation and

photodegradation rates of 2,4,6-trinitrotoluene (TNT) in marine waters are surprisingly rapid in comparison to their degradation rates in terrestrial environments. This information may help DoD remain in compliance with environmental regulations at critical operational ranges, and reduce UXO recovery and sediment clean up costs. The USNA component of the multi-institution SERDP project is directed at developing a quantitative understanding of the photochemical degradation rates of NECs (TNT, HMX and RDX) in marine systems. Laboratory experiments to determine the solubility of TNT and 2,4-DNT in seawater media were completed this year. Experiments to determine the rate of TNT photolysis in seawater media are underway with colleagues at NRL-DC.

High-Pressure Crystallography of Explosives

Researcher: Associate Professor Wayne H. Pearson
Sponsor: Research and Technology Department, Naval Surface Warfare Center (NSWC), Indian Head Division

The work performed during the summer and fall of 2005 was a continuation of a previous study that took place during the summer of 2004. The goal of the project was to determine the molecular structure of the explosive, RDX, at pressures of 1 GPa and higher, using single crystal data obtained from a synchrotron source. A structure at 1.0 GPa has been determined. New data were collected at the CHESS synchrotron source for pressures of 1.5 GPa and 5.5 GPa. The 1.5 GPa data have been indexed to a new monoclinic cell. Previously, it was believed that the structure may still be orthorhombic at this pressure. Peak integration and structure solution need to be accomplished for the structure at this pressure. The higher pressure data at 5.5 GPa have yet to be examined quantitatively.

Extent and Biological Impact of Chemical Variation within the Canopies of Riparian Trees

Researcher: Assistant Professor Brian J. Rehill
Sponsor: Naval Academy Research Council (NARC)

Three tree species were chosen: tulip poplar, sweetgum, and sycamore. Data were equivocal at best, with only some consistent with the hypothesis of developmentally based variation in phytochemistry. For sycamore, concentrations of foliar condensed tannins were significantly higher in the upper, mature portion of the canopy than those in the lower, juvenile part. Even lower concentration of condensed tannins in the foliage of saplings and seedlings would be predicted, but the opposite was found. Analogous results were found with sweetgum, and for tulip poplar. The equivocal data indicate that experimentation is required to elucidate the underlying patterns. Since planting of cuttings of known pedigree in a greenhouse will be necessary to pursue this research, and appropriate facilities are not available locally, it has been suspended.

Isolation and Characterization of Methionine Sulfoxide Reductase (MsrA) Proteins from the Psychrophile *Colwellia psychrerythraea*

Researchers: Assistant Professor Jamie L. Schlessman, Assistant Professor Tammy L. Domanski, Assistant Research Professor Richard G. Baumann and Assistant Professor Virginia F. Smith
Sponsor: Crowley Bioscience Fellowship

Enzymes from psychrophilic organisms, whose optimal growth temperature is 0-15 ^{o}C, hold promise as catalysts in bioremediation and low-temperature industrial applications. Limited studies suggest that psychrophilic organisms evolved cold-adapted proteins that overcome kinetic barriers associated with low temperatures by displaying increased structural flexibility to enhance their catalytic efficiency. The recent publication of the genome sequence of *Colwellia psychrerythraea* has made large-scale production of recombinant psychrophilic proteins a reality. The enzyme methionine sulfoxide reductase A (MsrA1), which restores function to some oxidatively-damaged proteins, was selected as a candidate enzyme for study from the psychrophilic bacterium *Colwellia psychrerythraea*, because: (1) MsrA is ubiquitous in nature and several putative genes were identified in the *C. psychrerythraea* genome; (2) MsrA is a small monomeric enzyme; and (3) an MsrA functional assay exists. The *msrA1* gene was amplified from *C. psychrerythraea* genomic DNA using oligodeoxyribonucleotides and polymerase chain reaction. The *msrA1* gene was ligated into a DNA plasmid and transformed into competent *Escherichia coli* cells. Nucleotide sequencing confirmed the identity of the *msrA1* gene. Induced protein expression at 15°C produced soluble MsrA1, and purification of the protein is underway using affinity chromatography. Alignment of the deduced amino acid sequence for *C. psychrerythraea* MsrA1 with MsrA from *E. coli* and *Mycobacterium tuberculosis* identified putative active site residues 26-30 (GCLWG). This motif includes one invariant cysteine, which was shown to be in the active site for the *E. coli* and *M. tuberculosis* enzymes. The remaining two cysteine

residues, expected to be involved in MsrA1 function, are not conserved in the *C. psychrerythraea* MsrA1 relative to the other sequences, suggesting a potentially novel mode of activity for the *Colwellia* enzyme. Ultimately, potential differences that may account for cold-adaptation will be identified using a sequence- and structure-based approach.

Purified soluble MsrA1 will be characterized kinetically to assess its catalytic function using a methionine enkephalin substrate. Fluorescence spectroscopy and differential scanning calorimetry will be used to measure protein thermostability and flexibility. Protein crystallization studies will be initiated for use in x-ray crystallographic structure determinations. In addition, analogous studies will be carried out on *C. psychrerythraea* MsrA2, which appears to be a type B methionine sulfoxide reductase, based on amino acid sequence alignments and identification of a CXXC putative Zn^{2+}-binding motif.

Accommodation of Electrostatic Charge within Proteins: X-ray Crystallographic Studies of Staphylococcal Nuclease Mutants

Researcher: Assistant Professor Jamie L. Schlessman

Sponsor: National Scientific Foundation (NSF), Biophysics Department, The Johns Hopkins University

The thermodynamics of protein stability involved a complex set of interactions between protein and solvent and within the protein itself. Traditional explanations for protein stability rely of entropic considerations in which hydrophobic amino acids are separated from the polar solvent (water) by burying them in the protein core. Introduction of an electrostatic charge within the protein interior destabilizes the protein and may lead to protein unfolding. However, charges form and are transferred within a protein's interior in numerous biochemical processes including catalysis, electron transport, and proton transfer, so a more nuanced explanation of charge accommodation is needed. X-ray crystallographic methods have been used to determine the structures for a number of mutants of Staphylococcal nuclease into which a destabilizing electrostatic charge (lysine (+) or glutamic acid (-)) had been introduced by mutation. These preliminary results showed an array of accommodation methods by the protein, including water penetration into the protein core, localized protein unfolding and, in a few cases, domain swapping between neighboring protein molecules. Recent work (Schlessman, J. L., Isom, D., and Garcia-Moreno E., B., unpublished) of the nuclease PHS/L38K mutant identified a novel internal salt bridge as a mechanism for charge accommodation. Additional protein structure determinations are underway to confirm these mechanisms and identify new mechanisms in other mutants, and to correlate structural findings with spectroscopic characterization of pKa shifts of the mutated residues. Among these are structure determinations of internal mutations to arginine (+), aspartate (-), and asparagine (neutral) residues. The observed effects of water penetration at room- and cryo-temperatures have been studied in three mutants (PHS: V66N, V66Q, and V66Y) by a midshipmen research project. Results from this project confirmed that more internal waters were observed at 100 K than at 296 K for several mutants, raising concerns about the legitimacy of waters observed in cryo temperature crystal structures for molecular dynamics simulations. In a separate project, the effects of distant mutations on internal histidine pKa values and conformations has been studied crystallographically. Two structures have been completed for nuclease VIAGAN/E75A and VIAGAN/E75Q (Baran, K., Fitch, C., Schlessman, J, Garcia-Moreno, E. B., manuscript in preparation), and preliminary crystals for three glycine mutations have been obtained.

Seven crystal structures related to this project have been completed in 2005-2006 and data for 2 additional structures has been collected. The manuscript for the Baran *et al*. work has been written; final figures are being prepared for a submission to a peer-reviewed journal in June 2006. The water penetration project is in final stages, and a manuscript is expected to be submitted to a peer-reviewed journal by late summer 2006.

Polymer Coatings for Armor Protection

Researcher: Associate Professor Maria J. Schroeder

Sponsor: Naval Research Laboratory (NRL), Chemistry Division

Protecting military personnel and equipment from mines, bombs, and small arms fire is an area of great interest to the military. Recent studies of polymer-coated armor have revealed enhanced protective properties over the bare metal. Humvees with a polymeric spray-on coating were demonstrated to protect the occupants inside against explosions and shrapnel. Elastomeric coatings on concrete blocks have been shown to be effective against the shattering effects of a bomb blast. Although observations and physical tests of these materials have been obtained, the mechanisms of this polymer protection generally remain unknown. One of the objectives of this

project is to understand how various polymer coatings affect the impact and fracture performance of metals. Through laboratory-scale experiments with well-defined polymer systems, correlations between structure and property may lead to an understanding of the origin of this behavior. For example, protective properties of rubbery versus glassy polymers will be investigated as well as the effects of extension, temperature, and processing on the observed behavior. Application of this knowledge to improvements in armor protection for the military remains the ultimate goal.

Relaxation Studies of 1, 4-Polybutadiene

Researcher: Associate Professor Maria J. Schroeder
Sponsor: Naval Research Laboratory (NRL), Chemistry Division

The significance of the glass transition in liquids and polymers can hardly be understated. The cooperative dynamics of materials approaching vitrification has relevance in many diverse areas including protein biochemistry, superconductors, and engineering polymers. The glass transition is recognized as a major unsolved problem in condensed matter and has been the focus of experimental and theoretical efforts for more than fifty years. While structural relaxation receives most of the attention, there are other processes at higher frequency that reflect intramolecular degrees of freedom involving specific chemical groups.

From high resolution dielectric spectroscopy measurements on 1,4-polybutadiene (1,4-PBD), in addition to the structural alpha-relaxation and its high frequency precursors, a nearly constant loss (NCL) was observed at shorter times / lower temperatures in the spectra. The properties of this NCL were compared to those of another chemically-similar polymer, 1,4-polyisoprene. The higher frequency secondary relaxations in 1,4-PBD included the well-known Johari-Goldstein (JG) beta-relaxation and two other secondary peaks. The higher temperature behavior, referred to as the gamma-relaxation, fell between the JG-relaxation and the NCL. Seen previously by others, this gamma-relaxation was unique to 1,4-PBD and unlike the JG-process bears no relation to the glass transition. At very low temperatures, the existence of a weak peak was confirmed, reflecting dynamics which were almost temperature invariant.

Biocomplexity: Oceanic N_2 Fixation and Global Climate

Researcher: Assistant Professor Ronald L. Siefert
Sponsor: National Science Foundation (NSF)

Oceanic N_2 fixation has recently been identified as a significant part of the oceanic nitrogen (N) cycle and may directly influence the sequestration of atmospheric CO_2 in the oceans by providing a new source of N to the upper water column. The prokaryotic microorganisms that convert N_2 gas to reactive N are an unique subcomponent of planktonic ecosystems and exhibit a variety of complex dynamics including the formation of microbial consortia and symbioses and, at times, massive blooms. Accumulating evidence indicates that iron (Fe) availability may be a key controlling factor for these planktonic marine diazotrophs. The primary pathway of Fe delivery to the upper oceans is through dust deposition.

Research cruises were done in previous years to collect atmospheric aerosol samples and analyze these samples for various forms of iron. These results were used along with measurements by other research groups of biological productivity to understand the role of iron atmospheric deposition on biotic communities and productivity. During this past year, manuscripts have been prepared and submitted for publication based on the data collected in previous years.

Enzymatic Repair of Proteins Damaged by Oxidation

Researcher: Assistant Professor Virginia F. Smith
Sponsor: Research Corporation

Although oxygen is essential for life, too much oxygen can be disastrous. Modification of proteins, DNA and lipid molecules by certain oxygen-containing molecules (*e.g.,* superoxide, hydrogen peroxide, the hydroxyl ion, and water) have been shown to contribute to human disease and the aging process. Although most of these changes are irreversible, certain modifications can be repaired by enzymes present in our body. One such repair enzyme is methionine sulfoxide reductase (MsrA). Although MsrA is an essential protein – it has been found in the genome of

every organism sequenced to date – we are just beginning to understand how it works. In this project, biochemical assays, fluorescence spectroscopy and mass spectrometry were used to answer fundamental questions about MsrA and biological oxidation by observing how this interesting enzyme folds to its three-dimensional form, how it recognizes damaged proteins and how it then repairs them. Work on this project is ongoing.

Structural Investigation of the Ligand-binding Properties of the Chaperone Protein SecB of *Escherichia coli*

Researcher: Assistant Professor Virginia F. Smith
Sponsor: Department of Biochemistry, University of Missouri-Columbia

Chaperone proteins are a general class of proteins that perform a vital function in the cell by preventing improper interactions between proteins that might lead to degradation and aggregation. Many of these chaperone proteins, such as SecA, work according to relatively well-understood mechanisms that require cleavage of the chemical energy molecule adenosine triphosphate (ATP). However, less is known about the chaperone protein SecB of *Escherichia coli*, which does not require ATP in order to perform its job. Knowledge of the three-dimensional structures of SecA and SecB, which are both required for efficient export of certain bacterial proteins, was exploited to investigate reversible chaperone-ligand interactions. Site-directed mutagenesis, electron paramagnetic spectroscopy and isothermal titration calorimetry were used to investigate the properties of complexes formed between the chaperones SecA and SecB. This project is ongoing.

Biopolymer Nanocomposites

Researchers: Associate Professor Paul C. Trulove
Dr. Hugh C. De Long (AFOSR), Dr. Jeffery W. Gilman (NIST), Dr. Robert A. Mantz, (ARO),
Assistant Research Professor Douglas M. Fox and Assistant Research Professor Wesley L. Henderson (USNA),
Dr. Paul Maupin, Department of Energy (DoE)
Sponsor: Air Force Office of Scientific Research (AFOSR)

Although a material of ancient origin, silk has properties that rival many of our most advanced synthetic polymers. Much effort has gone into exploiting the properties of silk in composite materials, but success has been limited due primarily to our inability to reliably dissolve and reconstitute silk proteins. Ionic liquids represent a unique class of solvents that offer unprecedented versatility and tunability. Recent work has shown the potential of ionic liquids as solvents for the processing of biopolymers. In addition, ionic liquids have recently been shown to significantly enhance the interaction of nano-scale clays and carbon nanotubes with polymeric materials. In the proposed research we will investigate the dissolution and reconstitution of silk and related biopolymers (e.g., collagen, elastin, chitin) in and from ionic liquids; we will use ionic liquids to prepare silk composite materials that incorporate nano-scale layered silicates and carbon nanotubes; and we will employ a variety of methods to evaluate the macroscopic and microscopic properties of these unique biopolymer nanocomposite materials.

Development and Characterization of Advanced Dual Intercalating Molten Electrolyte Battery Systems

Researchers: Associate Professor Paul C. Trulove
Dr. Hugh C. De Long, (AFOSR), Assistant Research Professor Wesley L. Henderson, (USNA)
Sponsor: Naval Research Laboratory (NRL)

Room-temperature ionic liquids composed of perfluoroanions and nitrogen based organic cations possess a number of unique properties that make them ideal electrolytes for compact power sources. In particular, they are nonflammable, nonvolatile, and chemically inert, and they display wide electrochemical windows, high inherent conductivities, and wide thermal operating ranges. Also, unlike room-temperature ionic liquids based on chloroaluminate anions, these perfluoroanion electrolytes are not moisture sensitive.

For manufacturing and design optimization, solid-state electrolytes with high ionic conductivities are preferred to liquid electrolytes. In this research program we are investigating the generation of solid-state electrolytes that incorporate perfluoroanion ionic liquids into a poly(vinylidene fluoride)-hexafluoropropylene copolymer. These free-standing rubbery electrolytes appear to retain much of the desirable properties of the perfluoroanion ionic liquids. In this project we will be investigating the physical and electrochemical properties of

these gel electrolytes using thermal mechanical analysis, differential scanning calorimetry, imbedded microelectrode techniques, AC-impedance, and luminescent probe molecules. In addition this project will evaluate graphite intercalation anodes and cathodes with the ionic liquid-polymer gel electrolytes in solid-state cells employing the dual intercalating molten electrolyte (DIME) concept.

Conductive Nanocomposites as Indium Tin Oxide Replacements

Researchers: Associate Professor Paul C. Trulove
Dr. Hugh C. De Long, (AFOSR), Dr. Jeffery W. Gilman, (NIST), Dr. Robert A. Mantz, (ARO),
Assistant Research Professor Douglas M. Fox, (USNA)
Sponsor: Air Force Research Laboratory (AFRL)

Conductive nanocomposite materials represent a potential replacement to indium tin oxide (ITO) in low observable applications. These composite materials would not only replace the ITO that is currently used but would integrate the conductive material directly into the composite so the conductive element would not be a thin coating on an exterior surface were it is prone to damage. Recent work by our group has identified a unique method to disperse and compatibilize carbon nanotubes with organic polymers. We are now investigating the potential of generating conductive nanocomposite materials using carbon nanotubes as the high aspect ratio conductive element. To date many groups have attempted to disperse and compatibilize nanotubes in various polymers with limited success. If carbon nanotubes were effectively dispersed in a nanocomposite they should reach their percolation threshold at low filler concentration due to the high aspect ratio of the nanotubes. Our group has already show that the use of ionic liquids as dispersant / compatibilizer can generate high-quality carbon nanotube nanocomposites with polystyrene. We are currently working to extend this work to important engineering polymers such as polycarbonate. We are working to thoroughly characterize the interplay of ionic liquid treatment and processing conditions in order to maximize electrical conductivity through effective dispersion and compatibilization while simultaneously minimizing carbon nanotube loading.

Conformational Analysis: The Role of Stereoelectronic Effects

Researcher: Associate Professor Joseph J. Urban
Sponsor: Department of Defense (DoD) High Performance Computing Modernization Program

This ongoing research is focused on using computational chemistry techniques to study the fundamental intermolecular and intramolecular interactions that determine a molecule's conformational preferences. Molecular conformational preferences can play a major role in a variety of chemical, physical, and biological properties. The conformational distribution exhibited by a molecule under a given set of conditions represents a balance between the intramolecular interactions between the constituents of the molecule itself and the intermolecular interactions with the surrounding environment (solvent for example). For all but the simplest molecular systems, the energy differences between conformations are difficult, if not impossible, to measure experimentally. Thus, computational studies are often the only source of quantitative data for many systems of interest. The lack of available experimental data to calibrate approximate computational methods (molecular mechanics force fields), and the fact that the energy differences between conformations are typically very small makes it necessary to employ very high levels of theory, which requires the use of high performance computing resources. One of the specific goals of this work is to examine the effect of fluorination on the conformational preferences of model compounds and to evaluate the performance of a variety of computational methods in describing these effects. For a series of alkylamines, subtle stereoelectronic effects were seen to play a major role in determining the conformational preferences in fluorinated and trifluorinated compounds. However, in the alanyl didpeptide, fluorination in the beta position does not result in drastic changes in the backbone conformational preferences. In addition, compounds containing the difluoramine substituent were investigated to probe the substituent effects associated with this unusual group.

Mimicking Nature at the Molecular Level: Molecular Modeling Studies of Fluorinated Peptide Mimetics and Unnatural Amino Acids

Researcher: Associate Professor Joseph J. Urban
Sponsor: Kinnear Research Fellowship

The design of peptide mimetic compounds is greatly facilitated by the identification of functionalities that can act as peptide replacements. The fluoroalkene moiety has recently been employed for that purpose. The purpose

of this work is to characterize prototypical fluoroakenes (fluoroethylene and 2-fluoro-2-butene) with respect to key properties of peptides (amides) including structure, charge distribution, hydration, and hydrogen bonding. The results are compared to those obtained for model peptides (formamide, N-methylacetamide). Calculations have been carried out at the MP2 and B3LYP levels of theory with the 6-311++G(2d,p) and 6-311++G(2d,2p) basis sets. The results suggest that the fluoroalkene is similar in steric requirements to a peptide bond but that there is less charge separation. In studies of complexes with water molecules, the fluoroalkene is found to engage in interactions that are analogous to backbone hydrogen bonding interactions that govern many properties of natural peptides and proteins, but with smaller interaction energies. In addition, key structural differences are noted when the fluoroalkene is playing the role of hydrogen bond acceptor which may have implications in binding, aggregation, and conformational preferences in fluoroalkene peptidomimetics. The fluorolakene is found to exhibit cooperative effects that mirror those of the peptide, but are smaller in magnitude. Thus, pairwise addivitity of interactions appears to more adequately describe the fluoroalkenes than the peptides they are intended to mimic. In the future, this work will be extended to other peptide replacement systems as well to fluorinated amino acids that are used in the design of biomimetics.

Independent Research

Synthesis and Spectral Interpretation of Both Epimers of Menthane-1-Carboxylic Acid

Researcher: Associate Professor Debra K. Dillner

Both epimers of menthane-1-carboxylic acid have been synthesized and complete interpretation of their Nuclear Magnetic Resonance (NMR) spectra is being undertaken. The synthesis of the equatorial isomer followed literature procedures but no similar procedures existed for the less stable axial carboxylic acid isomer. This isomer was prepared in four synthetic steps from commercially available menthol. The first step involved conversion of the alcohol to the corresponding mesylate in quantitative yield. The mesylate was treated with potassium cyanide in dimethylsulfoxide to effect S_N2 displacement of the leaving group. This produced a compound with the requisite axial substituent. Attempts to effect hydrolysis of the nitrile directly to the axial acid resulted instead in epimerization of this center to produce the equatorial amide. The amide was resistant to further hydrolysis under a variety of conditions. A successful alternative was to reduce the axial nitrile with diisobutylaluminum hydride. The resultant aldehyde was immediately oxidized to the carboxylic acid with Jones' reagent, without loss of stereochemical integrity. With both acids available, detailed NMR investigations have been undertaken. The spectral interpretation of the equatorial isomer has been completed. The more complex spectral interpretation of the axial isomer is currently ongoing, with more advanced spectral acquisition methods being investigated.

Investigations into the Effects of Tripodal Ligands on Transition Metal Environments

Researcher: Associate Professor JudithAnn R. Hartman

The design of pre-organized ligands has been a major area of coordination chemistry for the last 40 years. Crown and cryptand designs have been successfully used to influence both ligand selectivity and the electronic environment of the complexed metal ions. However, it is unclear how much of the ligand effects are due to the cyclic or cage structures and how much to the pattern of linked chelant rings.

We have been exploring the properties of TREN-based podands to design an easily synthesized "pre-organized" ligand. Our initial work has involved the study of aminopyridyl tripodal and linear ligands. In this study we are expanding our work to include the "softer" aminothiophene ligands.

This past year, we have focused on Ni(II), Cu(II), and Co(II) complexes of TREN-thio (tris(2-((2-thiophene)amino)ethyl)amine), CYDA-thio (N', N''-bis(2-thiophene)-1,2-*t*-diaminocyclohexane), and DIPNEN-thio (1,14-bis(2-thiophene)-2,6,9,13-tetraazatetradecane). Six complexes were submitted to Wayne Pearson for crystal structures and four of these structures should be publishable. Electrochemical studies are in progress for these complexes and a manuscript should be written this summer. We are continuing our work in synthesizing new aminothiophene ligands and characterizing their Ni(II), Cu(II), Cu(I), and Co(II) complexes.

Ignition Studies of Cerium Nitrate Treated Towels

Researcher: Associate Professor JudithAnn R. Hartman

Cerium Nitrate soaked towels are used by DOE in the process of decommissioning weapons production facilities. As a result of a recent fire, there is interest in the self-heating properties of cerium nitrate soaked rags that have not been properly decontaminated. We have been studying the self-heating properties of these rags in self-heating oven test along with a group of coworkers at Hughes Associates and at USNA using TGA and DSC techniques. This work has resulted in a publication that is summarized in the Faculty Publication Section and a submitted paper with a midshipman coauthor studying the ability of laboratory methods to predict the self heating results from the larger scale, more time-consuming heating tests.

New Ligands and Complexes for Photovoltaic Applications

Researcher: Associate Professor William B. Heuer

Dye-sensitized solar cells (DSSC's) are currently the subject of intensive research and development efforts. Potential advantages of such cells over traditional silicon-based solar cell technology include cost and ease of fabrication, as well as the ability to design flexible panels that can be shaped to conform to surface contours. However, the overall energy conversion efficiency of DSSC's is currently around 10%, a value that must be improved before such cells can be economically competitive with Si-based solar cells. This ongoing research project focuses on synthesis of new ligands and metal complexes for use as sensitizers for TiO_2 photoanodes. A series of new chelating □-diimine ligands bearing electron-donating or -accepting groups has been prepared, and coordination complexes of these ligands with Ru(II) are currently being studied. Several new complexes have been isolated, and charcterization of their stuctural, electrochemical and photophysical properties in solution is currently underway. As part of collaborative research at Johns Hopkins University this summer, corresponding studies of these complexes adsorbed onto metal oxide semiconductor films will be carried out to assess their potential as sensitizers for DSSC applications.

A New Bridging Ligand for Supramolecular Assembly

Researcher: Associate Professor William B. Heuer

Multi-metallic supramolecular coordination complexes have attracted interest as potential sensitizers for photovoltaic applications. Use of such complexes can improve the efficiency of dye-sensitized solar cells (DSSC's) both by providing panchromatic light absorption, which improves electron injection quantum yields, and by transporting photogenerated holes away from the semiconductor surface, which reduces recombination losses. This project focuses on development of new types of bridging ligands for use in preparation of supramolecular sensitizer complexes. The new ligand 9'-[4,5-*bis*(2-cyanoethylthio)-1,3-dithiol-2-ylidene]-4,5-diazafluorene has been prepared via a simple cross-coupling reaction. Removal of the cyanoethyl protecting groups with base affords a new type of ditopic *bis*-chelating ligand incorporating both diimine and dithiolene coordination sites linked by a rigid, electronically delocalized framework. To date, several mono-metallic complexes containing this ligand coordinated to either the N,N (M=Ru(II)) or S,S (M=Ni(II)) sites have been prepared and charcterized, including an x-ray crystal structure of the Ni(II) complex. Formation of ligand-bridged bimetallic complexes based on this ligand is currently being investigated. Ultimately, these complexes will be adsorbed onto metal oxide films, and detailed spectroscopic and electrochemical studies of the resulting sensitized semiconductor interfaces will be carried out in conjunction with our collaborators at Johns Hopkins University.

Organic Small Molecule Additives for the Crystallization of Proteins

Researchers: Assistant Professor Shirley Lin and Assistant Professor Jamie L. Schlessman

The study of protein structure has been an important component of biochemistry for the last fifty years. One method to obtain a protein's structure is to crystallize the protein and have a good quality crystal for X-ray diffraction. 2-methyl-2,4-pentanediol (MPD) is the most frequently used small organic molecule additive in the crystallization of proteins. Few other small molecules have been tested in the crystallization of proteins, with none having greater success than MPD. This project is designed to identify alternative additives to MPD using egg-white lysozyme as the target protein.

Five organic compounds have been screened in the crystallization of lysozyme: 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,6-hexanediol, 1,2,6-hexanetriol, and cyclodextrin. Some crystals were obtained using 1,6-hexanediol in Spring 2004. These results have been reproducible but an x-ray diffraction quality crystal has not yet resulted. During Spring 2006, efforts were made by Midshipman 1/C Colby Abe to obtain a high-quality lysozyme crystal using 1,6-hexanediol. Some additional small molecule additives, such as ionic liquids, have been obtained and will be screened during the summer of 2006.

Condensation of Arylboroxine Structures on Lewis Basic Copolymers as a Noncovalent Means of Polymer Functionalization

Researchers: Assistant Professor Shirley Lin and Dr. Peter M. Iovine (University of San Diego)

The condensation of arylboroxines in the presence of Lewis bases is an efficient reaction. A copolymer of poly(styrene-*co*-4-vinylpyridine) (PS/4-VP) has been functionalized with 4-fluorophenylboroxine with varying ratios of 4-vinylpyridine to boroxine. ^{1}H and ^{19}F NMR reveal that ligation of the boroxine to the 4-vinylpyridine within the copolymer is complete. Differential scanning calorimetry (DSC) measurements on the functionalized copolymers demonstrates an increase in glass transition temperature (T_g) with increasing amounts of boroxine. Thermal gravimetric analysis (TGA) of the copolymers show an earlier onset of decomposition in the boroxine-containing samples as compared to the parent polymer; this result can be explained by the release of oxygen during boroxine decomposition which can catalyze the decomposition of the polymer.

A communication reporting this work is currently being prepared for *Macromolecules*. Future studies will focus upon comparison of these results to poly(styrene-*block*-4-vinylpyridine) and copolymers containing 2-vinylpyridine instead of 4-vinylpyridine.

Use of a Flow Reactor to Determine the Rates of Alkane Solubilization in Surfactant Solutions

Researcher: Assistant Professor Dianne J. Luning Prak

A key component to predicting the success of utilizing surfactants to enhance the removal of organic liquids from soil systems is quantifying micellar solubilization rates. This study seeks to determine the influence of surfactant and solute properties on the rates of solubilization of octane, decane, and dodecane in micellar solutions of a homologous series of purified dodecyl alcohol ethoxylates. This project consists of two parts: laboratory experiments, which were completed prior to this year, and computer modeling, which is ongoing. For the laboratory experiments, a flow reactor was employed to investigate the rates of alkane dissolution from organic liquid pools. The results show that the normalized effluent concentrations in surfactant solutions are less than in pure water. The lower effluent values may result from changes in the diffusion coefficient or from other limitations in the mass transport process. Results also show similar behavior among the linear alkanes tested. To analyze these results, mass transport was modeled using a finite element method program (COMSOL Multiphysics). The program was used to determine a mass transfer coefficient and interfacial concentrations for each surfactant/organic experiment. This year, over 500 simulations have been run and are being analyzed. The mass transfer parameters determined by these experiments can be useful in predicting the success of using surfactants to enhance the removal of organic liquids from soil systems.

RNA Editing Targets in Mouse Brain

Researcher: Assistant Professor Daniel P. Morse

Inosine in messenger RNA (mRNA) is produced by RNA editing enzymes called adenosine deaminases that act on RNA (ADARs). ADARs act on double-stranded regions of RNA to convert adenosines (A) to inosines (I). A to I conversion changes both the sequence and the structure of an RNA molecule. ADARs contribute to protein diversity by producing codon changes within messenger RNAs. In addition, structural changes caused by editing may affect the function of non-coding regions of mRNAs. The full range of biological functions for ADARs is an area of active research. It is known that ADARs play important roles in the regulation of nervous system function. Consistent with this function, ADARs are most highly expressed in brain. The goal of this project is to further our understanding of ADAR function by identifying new ADAR substrates. Of particular interest are

messenger RNAs that are edited within coding regions because the functional consequences of this type of editing are relatively easy to determine. Previously, a method was developed for identifying inosine-containing RNAs. This method was used to find new ADAR substrates in human brain. A large fraction of the new substrates were edited within a highly repetitive element found only in primates. (This repetitive element is called an "Alu sequence".) All of the new substrates were edited in non-coding regions of messenger RNAs. This project will identify new ADAR substrates in mouse brain. Although the mouse genome does contain repetitive elements, it does not contain Alu sequences. Thus, it should be easier to find ADAR substrates that are edited within the coding region of messenger RNAs.

Crystal Structures of Copper, Nickel, and Cobalt Compounds with Multidentate Ligands

Researchers: Associate Professor Wayne H. Pearson and Associate Professor JudithAnn R. Hartman

The crystal structures of several new copper, nickel, and cobalt compounds with multidentate ligands have been determined. The structures of four of these compounds have been solved. A manuscript for the crystal structure of (1,10-bis(2-pyridylmethyl)-1,4,7,10-tetraazadecane)-nickel(II) perchlorate monohydrate is in preparation. The other compounds in the series suffer from disorder and require additional refinement in order to obtain publishable results.

Crystal Structure of Bicyclo-[3.3.0]-octane

Researchers: Associate Professor Wayne H. Pearson and Associate Professor Debra K. Dillner

The crystal structure of bicyclo-[3.3.0]-octane at room temperature has been determined. Single crystal data were collected with copper radiation in an attempt to determine the configuration of the molecule and to investigate a C-H bond position that exhibits an anomalous chemical shift in the NMR experiment. The conformation of the ring was determined. Copper data does not allow for as high resolution as that obtained with molybdenum. As a result, this structure will be re-determined with molybdenum radiation in order to more accurately locate the problematic hydrogen.

Crystal Structures of New Ligands with Ruthenium and Nickel

Researchers: Associate Professor Wayne H. Pearson and Associate Professor William B. Heuer

Crystal structures of three new compounds have been determined. These ruthenium compounds are being developed as sensitizers for fundamental studies of photoinduced processes at semiconductor surfaces. Compounds in this series include a dicyano-bis-bipyridine ligand, a ruthenium complex with diester substituents and a nickel complex with coordinating sulfur linkages substituted on the bipyridine ring. With the exception of some disorder that needs to be modeled in the ruthenium complex, the structures are complete.

Powder Diffraction Studies of Pure and Mixed Phases of Ionic Liquids

Researchers: Associate Professor Wayne H. Pearson, Associate Professor Paul C. Trulove
and Assistant Research Professor Wesley A. Henderson

Powder diffraction studies were performed in order to model phase behavior of ionic liquids. Protocol for performing powder diffraction experiments were developed first since the departmental machine is a single crystal diffractometer and not optimized for powder data collection. Four pure phases were then studied at varying temperature to examine the effects of temperature on these disordered systems. A manuscript has been submitted that includes the analysis of these data. The work that is now ongoing involves the investigation of mixed phases of ionic liquids at -100 degrees Celcius in order to examine whether certain compositions result in a pure phase or retain two phases.

Biophysical Characterization of a Bifunctional Iron-binding Protein

Researcher: Assistant Professor Virginia F. Smith

Human cytoplasmic aconitase/iron-responsive element binding protein (hIRP-1) is a 98 kDa bifunctional enzyme involved in iron regulation. The protein alternates between aconitase and mRNA binding activities depending on the intracellular levels of iron. Spectroscopic characterization, enzyme activity assays and equilibrium

thermal and chemical denaturation of a recombinant form of hIRP-1 have revealed interesting properties. Specifically, hIRP-1 undergoes a multi-state unfolding transition as a function of urea, but an apparent two-state unfolding in response to thermal denaturation. As urea concentration increases, the tryptophan fluorescence intensity increases and undergoes a red shift, suggesting a quenching interaction that is relieved as the protein unfolds. A pair of tryptophans believed to be at the interface between two domains has been identified as the possible source of the observed hyperfluorescence. Enzyme activity is lost abruptly at ~2 M urea, consistent with a disruption of the active site, which is located in an interdomain cleft. The addition of a chelating agent to remove the [4Fe-4S] cluster does not significantly alter the unfolding properties of hIRP-1, suggesting that the cluster does not play a major role in the stability of the protein tertiary structure. This project is ongoing.

Investigations of Imidazolium Based Ionic Liquids in Preparation of Polymer Nanocomposites from Layer Silicates and Graphite

Researchers: Associate Professor Paul C. Trulove, Dr. Hugh C. De Long, (AFOSR), Dr. Jeffery W. Gilman, (NIST), Dr. Paul Maupin, (DOE), Assistant Research Professor Douglas M. Fox (USNA)

The objectives of this research program are to evaluate, and exploit tri-alkyl-imidazolium-based ionic liquids as novel, thermally stable treatments for layered-silicates and graphite for the purpose of preparing high quality polymer nanocomposites. Initial work has demonstrated the superior thermal stability of trialkylimidazolium treated layered-silicates (montmorillonite (MMT) and fluorinated synthetic mica (FSM)). For example, the onset of thermal decomposition of the hexadecyl-functionalized dimethylimidazolium montmorillonite (DHHDIM-MMT) is over 100 ^{o}C higher that MMT treated with standard tetraalkylammonium salts. In addition, the DHHDIM-MMT has shown excellent compatibility with polyamide-6 (PA-6), and hence forms high quality PA-6/MMT nanocomposites. The DMHDIM-MMT also forms good quality mixed intercalated and exfoliated nanocomposites with polystyrene. We have also recently been the first to successfully prepare nanocomposites with polyethyleneterephthalate (PET, m.p. 290°C) using conventional extrusion and the hexadecyl-functionalized dimethylimidazolium. A variety of techniques are being used to characterize these novel layered-silicates and nanocomposits; these range from TEM, XRD, TGA/DSC, and NMR.

Trident Scholar Project

Design, Synthesis and Testing of Novel Antimalarial Compounds (Trident Report # 343)

Researcher: Midshipman 1/C Marshall M. Hoffman, USN
Adviser: Assistant Professor Clare E. Gutteridge
Sponsor: Office of Naval Research (ONR)

The purpose of this project was to enhance the effectiveness of the class of chemicals known as isoquinolines against malaria. Many drugs are available to combat the parasite responsible for these deaths, but resistance has been recorded to nearly all of them. There is therefore a need for new antimalarial drugs against which the parasite is not resistant. As a contribution to the development of a new drug, this project involved modification of a lead compound, with known antimalarial properties, to enhance its effectiveness against the disease. The lead compound was a potent folate antagonist, a widely used class of antimalarial with significant resistance problems. Recent research had suggested that the lead compound acted against the disease through a distinct, unknown mechanism, in addition to that of folate antagonism. Six target compounds were designed to increase the activity by this unknown antimalarial mechanism, while removing activity via the folate mechanism. The design included use of a 3D computer-generated pharmacophore model, which described the structural requirements for maximum antimalarial activity by the unidentified mechanism. Reduction of the folate antagonist activity relied upon published data describing the structural requirements for folate antagonism. The antimalarial activity of the newly designed compounds was thus expected to be mediated by the unknown mechanism. As such, the compounds should be effective even against parasite resistant to folate antagonists. Six novel compounds were prepared by a seven step synthesis then submitted to the Walter Reed Army Institute of Research for *in vitro* antimalarial testing. The antimalarial data showed that the compounds possessed significant antimalarial activity and that the folate antagonist mechanism had been partially, if not completely, removed.

Bowman Scholar Projects

Synthesis of Sulfonated Polymers in Mesoporous Silica as Potential Electrochemical Separator Materials

Researcher: Midshipman 1/C Jon D. Stockton, USN,
Advisers: Associate Joseph F. Lomax,
Associate Professor Charles A. Edmondson and Professor John J. Fontanella (Physics Department)
Sponsor: Bowman Scholar Program (BSP)

An organic-inorganic composite was formed by cross-linking polystyrene (PS) into a SBA-15-type mesoporous silica (SBA/PS). The SBA-15/PS reacted with sulfuric acid according to published methods to sulfonate the benzene rings of the styrene (SBA-15/PS/SO_3). These two latter solids were investigated by TGA/MS to determine stability and decomposition mechanisms. Complex impedance measurements at 10-10^5 Hz were taken on (SBA-15/PS/SO_3) and Nafion cast films loaded with SBA-15 at a level of 1-10%, and similar films with SBA-15/PS/SO_3 in hopes that the mesoporous solids might impart desirable properties on the Nafion.

Synthesis of Potential Electrochemical Separators for Use in Direct Methanol Fuel Cells by Separation of Pillaring and Acidic Functions

Researcher: Midshipman 1/C Jon D. Stockton, USN,
Advisers: Associate Joseph F. Lomax,
Associate Charles A. Edmondson and Professor John J. Fontanella (Physics Department)
Sponsor: Bowman Scholar Program (BSP)

The goal of this project is to find ion exchange membranes which are thermally table at temperatures above 150°C for use as a possible high-temperature fuel cell membrane. Two complementary lines of layered zirconium phosphonate /phosphate research converge in this project 1) the thermal stability and conductivity of zirconium phosphonates substituted with acidic functional groups, and 2) the ability to create pillared α-Zr(O3P-R-P O3) compounds, varying the pillar length by varying the R radical. The pillaring holds the Zr-phosphate-like layers together thus preventing the swelling and contracting which prevented previous acid-substituted phophonates from making an effective electrochemical separator. By separating the functions of ion conductivity and pillaring, the synthesis of the compound is simplified while maintaining thermal and mechanical stability (from the pillar) and high ion conductivity (from the substituted phosphonate). This approach has been successful in making other mixed phosphonate/diphosphonate zirconium layered compounds. The important part is to match the size of the diphosphonate and the substituted phosphate and to choose the proper functional group on the phosphonate. The two-part thrust of the research deals with first -- the synthesis of different phosphonate and diphosphonate compounds and second – taking the resulting phosphonate and diphosphonate and reacting them with a Zr^{4+} salt. We have succeeded in making two terminal diphosphonates, the 1, 10-diphonphonodecane and the 1, 12-diphosphonododecane. Ongoing research is continuing.

Midshipman Research Course Projects

X-ray Crystallographic Studies of Staphylococcal Nuclease Mutants

Researcher: Midshipman 1/C Colby M. Abe, USN
Advisers: Assistant Professor Jamie L. Schlessman and Dr.Bertrand Garcia-Moreno E.,
Biophysics Department, The Johns Hopkins University
Sponsor: Office of Naval Research (ONR)

When proteins fold, ionizable groups are normally found at the molecular surface; however, sometimes these groups are found buried within the protein. These residues are thought to be important because of their role in electron transfer, catalysis reactions and substrate recognition. Placing a charged residue within the interior of a protein may cause the nonpolar core to become unstable. In order to offset these effects, structural rearrangements may occur in the protein or water molecules may bury themselves near the site of mutation. A study was conducted

on the staphylococcus nuclease V66E, where a valine was substituted with a glutamic acid (Denisov *et al*., 2004). The study showed there were differences in how water penetrated the protein at room temperature vice cryogenic (cryo) temperature (100K). This buried water effect was found to be true in the cryogenic temperature and not the room temperature system. To determine if this is a general effect within proteins, the structures of staphylococcal nuclease V66N (valine substituted with an asparagine) and V66Q (valine substituted with a glutamine) were determined at both 296 K and 100K. Both structures were determined at sufficient resolution for the water studies (2.1-2.2 Å resolution). The V66E trend of more internal water molecules observed at cryo temperature was confirmed by the V66N and V66Q models; however, fewer internal waters were observed overall in the asparagine and glutamine mutations. Results from these studies have implications for molecular dynamics algorithms involving long-lived water molecules in the protein interior.

Isolation and Purification of Methionine Sulfoxide Reductase A1 (MsrA1) from the Psychrophile *Colwellia psychrerythraea*

Researcher: Midshipman 1/C Andrew S. Bernhardson, USN
Advisers: Assistant Professor Jamie L. Schlessman, Assistant Professor Tammy L.Domanski, Assistant Professor Virginia F. Smith and Assistant Research Professor Richard G. Baumann
Sponsor: Crowley Bioscience Fellowship

Enzymes from psychrophilic organisms, whose optimal growth temperature is 0-15 ^{o}C, hold promise as catalysts in bioremediation and low-temperature industrial applications. Limited studies suggest that psychrophilic organisms have evolved cold-adapted proteins that overcome the kinetic barriers associated with low temperatures by displaying increased structural flexibility to enhance their catalytic efficiency. The recent publication of the genome sequence of *Colwellia psychrerythraea* has made large-scale production of recombinant psychrophilic proteins a reality. The enzyme methionine sulfoxide reductase A (MsrA1), which restores function to some oxidatively-damaged proteins, was selected as a candidate enzyme for study from the psychrophilic bacterium *Colwellia psychrerythraea*, because: (1) MsrA appears to be ubiquitous in nature and several putative genes were identified in the *C. psychrerythraea* genome; (2) MsrA is a small monomeric enzyme; and (3) a functional assay is available for MsrA. The *msrA1* gene was amplified from *C. psychrerythraea* genomic deoxyribonucleic acid (DNA) using complementary oligodeoxyribonucleotides and polymerase chain reaction methods. The *msrA1* gene was ligated into a DNA plasmid, and transformed into competent *Escherichia coli* cells. Nucleotide sequencing confirmed the identity of the *msrA1* gene. MsrA protein was produced recombinantly in *E. coli* at 22°C and found to express in the insoluble protein fraction. The MsrA1 protein was solubilized in 6 M urea and purified using Ni^{2+}-affinity chromatography. Several attempts to refold the protein, including dialysis and cold snap dilution, failed to refold the protein based on fluorescence studies. Incorporation of 20 μM Zn^{2+}, Mg^{2+}, and Ca^{2+} ions in the growth media failed to produce soluble MsrA. However, protein expression at 15°C produced soluble MsrA1, and purification of the protein under soluble conditions is underway. The deduced amino acid sequence for *C. psychrerythraea* MsrA1 was aligned with MsrA from *E. coli* and *Mycobacterium tuberculosis*, for which crystal structures are available, to identify a putative active site at positions 26-30 (**GCLWG**). This motif includes one invariant cysteine, and was shown to be in the active site for the *E. coli* and *M. tuberculosis* enzymes. The remaining cysteine residues, which are expected to be involved in MsrA1 function, are not conserved in the *C. psychrerythraea* MsrA1 relative to the other sequences, suggesting a new mode of activity for the *Colwellia* enzyme. Ultimately, potential differences that may account for cold-adaptation will be identified using a sequence- and structure-based approach.

Electrochemical Studies of Ketones in Ionic Liquids

Researcher: Midshipman 1/C Dana S. Canby, USN
Adviser: Professor Graham T. Cheek
Sponsor: Office of Naval Research (ONR)

This project involved a two-semester study of Lewis acid / base reactions in the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$). The negligible vapor pressure of ionic liquids makes them promising candidates for environmentally friendly solvents, and their use for Lewis acid / base reactions was studied in this work. Benzophenone and 9-fluorenone were chosen as representative Lewis bases, and their interaction with the Lewis acid BF_3 (as BF_3 etherate) was investigated. The electrochemical behaviors of 9-fluorenone and benzophenone were first studied by cyclic voltammetry, revealing significant ion-pairing interactions between 1-

ethyl-3-methylimidazolium cation and the ketone reduction products. The addition of BF_3 to solutions of the ketones was found to cause a positive potential shift in ketone reduction potential due to the complexation of the ketones by BF_3. An estimate of the K value (~270) for the fluorenone / BF_3 complexation was obtained by a titration procedure involving the stepwise addition of BF_3 etherate to fluorenone. Benzophenone was also found to undergo complexation by BF_3, resulting in an even larger potential shift than that for fluorenone. The first reduction process of fluorenone was characterized as a one-electron transfer using controlled-potential electrolysis, and HPLC of the reduction products indicated the formation of the pinacol coupling product.

Studying the Survival of *Staphylococcus aureus* on Surfaces

Researcher: Midshipman 1/C Jonathan Fujiwara, USN
Adviser: Assistant Professor Tammy L. Domanski
Sponsor: Office of Naval Research (ONR)

As staphylococcal outbreaks have become more prevalent in the community, especially among athletes and those in close quarters, many possible sources of infection must be considered. The goal of this study was to measure the survival of *S. aureus* on different types of materials over extended periods of time and in the absence of significant moisture and nutrition. *S. aureus* strain RN450 (a typical laboratory strain), strain CL25 (obtained from the medical clinic), and strain EN14 (isolated from the gymnastics mats in McDonough Hall) were analyzed. Several colonies of freshly cultured bacteria were grown in liquid media for several hours. The bacterial concentration was determined spectrophotometrically and an aliquot was placed onto the surface of plastic balls, coated cardboard book pages, and wrestling mat from the yard. Multiple samples of each surface were inoculated with the same volume of culture. The surface samples were allowed to dry and stored at room temperature. At specific time intervals the remaining bacteria on the surface were collected by vortexing the surface sample in a small volume of media, diluting the sample to a predicted concentration based on previous study, and growing the bacteria on solid media. Colony counts were performed to determine the concentration and fraction of surviving bacteria. It is clear that *S. aureus* can survive at least 648 hours on some surfaces, and potentially longer. The study is now focusing on obtaining multiple data sets from an expanded range of surface types.

Acidic Ionic Liquids

Researcher: Midshipman 1 /C Paul A. Fylstra, USN
Advisers: Associate Professor Paul C. Trulove and Assistant Research Professor Wesley A. Henderson
Sponsor: Air Force Office of Scientific Research (AFOSR) and Office of Naval Research (ONR)

Ionic liquids with acidic protons have been examined for use as solvents for biomaterials and as potential electrolytes for fuel cells. Recent work indicates that proteins and biopolymers such as silk and cellulose require hydrogen bonding for solvation in ionic liquids. In the present study, ionic liquids with imidazolium, guanidinium or ammonium cations containing acidic protons have been examined. These salts have simple anions such as Cl^-, NO_3^- and HSO_4^-. The synthesis and purification of these new ionic liquids, their thermal properties and their ability to dissolve biomaterials were investigated. These initial ionic liquids proved to be ineffective at dissolving silk. A new strategy was then attempted using ionic liquids with amino acid anions based upon glycine, alanine and serine. These latter ionic liquids were found to readily dissolve significant amounts of silk.

Automated Chemiluminescent Determination System for Hydrogen Peroxide Concentration in Seawater

Researcher: Midshipman 1/C Philip Galindo, USN
Adviser: Associate Professor Daniel W. O'Sullivan

An automated, continuous-flow hydrogen peroxide detection system was developed for chemiluminescent detection of hydrogen peroxide in surface seawater. This chemiluminescence detection method is advantageous because it eliminates the need for metals, enzymes, or catalysts. Additionally, chemiluminescence detection does not demonstrate the background noise that fluorescence detection exhibits in natural waters. Chemiluminescence detection of hydrogen peroxide is achieved through a reaction between hydrogen peroxide and acridinium ester (AE). In the presence of hydrogen peroxide, the ester is cleaved from the AE and an unstable intermediate state is formed. This excited intermediate further decays to an electronically stable *N-methylactidone* and emits a photon of

light at 470 nm. The concentration of hydrogen peroxide is directly proportional to the light produced. The method exhibited a linear response to hydrogen peroxide from 5 to 2500 nM, with a detection limit of 4 nM.

Relationships among Latitude, Tannin Content and Herbivory for Four Forest Trees

Researcher: Midshipman 1/C Jonathan R. Gower, USN
Adviser: Assistant Professor Brian J. Rehill
Sponsor: Office of Naval Research (ONR)

This project involved collection of leaf samples, extraction and isolation of tannin from the leaves and developing multiple chemical assays for use on this project. The initial data indicate that no linear relationship exists between latitudinal location and foliar tannin concentrations of sweetgum, white oak, and beech. Some correlations were found to exist between various types of herbivory, tannin concentration, and latitude. For instance, leaf loss due to chewing, galling, and mining, as well as total herbivory, were negatively related to condensed tannin concentrations in beech leaves (all: $p < 0.05$). Foliar condensed tannins in sweetgum were also negatively related to total herbivory as well as fungal spot, and total herbivory in sweetgum was also greater at lower latitudes, as predicted. Thus tannins (or some correlate of tannins) appear to play defensive roles versus herbivores over a wide latitudinal range, but latitude is a not a consistent predictor of levels of herbivory. More chemical analyses will be done to complete the project as the collaboration continues. A grant proposal to further this work has been submitted to the National Science Foundation.

Using Well Known Methods in Unprecedented Ways: the Dissolution/Reconstitution of Silk, Chitin and Chitosan Using Room Temperature Ionic Liquids

Researcher: Midshipman 1 /C John Marshall Green, USN
Advisers: Associate Professor Paul C. Trulove and Assistant Research Professor Douglas M. Fox
Sponsor: Air Force Office of Scientific Research (AFOSR)

Biopolymers have been used for thousands of years in fields spanning from the manufacturing of clothing to medical applications. Ionic liquids represent a unique class of solvents with highly variable properties which allow for a high amount of specification with regards to the desired product. Recent studies have demonstrated that room temperature ionic liquids are excellent solvents for the dissolution and reconstitution of biopolymers such as silk and cellulose. In this investigation we have applied recent success in using ionic liquids in biopolymer processing to the dissolution and reconstitution of *Bombyx mori* Silk, Chitin, and Chitosan. Details pertaining to the dissolution and reconstitution process are provided. In addition, the biopolymer topography was studied utilizing electron microscopy and structure characterization utilizing XRD and Raman spectroscopy.

Cloning, Expression, and Analysis of *Staphylococcus aureus* ClpB and Associated Heat-Shock Proteins

Researcher: Midshipman 1/C Ernest T. Hanes, USN
Advisers: Assistant Professor Tammy L. Domanski and Assistant Research Professor Richard G. Baumann
Sponsor: Crowley Bioscience Fellowship and Office of Naval Research (ONR)

ClpB is a "heat-shock" protein which is theoretically involved in promoting the thermo-tolerance of bacteria such as *Staphylococcus aureus*. The genes encoding *S. aureus* ClpB, DnaK, DnaJ and GrpE have been cloned and these proteins are being purified for biochemical study. A polymerase chain reaction was used to amplify these genes from *S. aureus* strain RN450, and each gene fragment was individually cloned into the bacterial expression vector pET/101. A 6x-histidine tag was engineered at the carboxyl-terminus of each protein to be used for affinity protein purification. Transformed *E. coli* BL21(DE3) cells were induced with isopropyl β-D-1-thiogalactopyranoside, and overexpression of the proteins was confirmed in cell lysates using SDS-PAGE analysis and Western blotting with an Anti-5X-Histidine primary antibody. Initial analysis revealed His tagged proteins of 95, 67, 42 and 25 kD, as expected, for the ClpB, DnaK, DnaJ and GrpE proteins, respectively. Analogous to studies in other bacterial systems, staphylococcal ClpB protein expression resulted in the dual translation of two proteins, a predominant ~95 kD full length product, and an ~80 kD lower molecular weight protein lacking the N-terminal region, resulting from internal translation initiation within the gene product. Refinement of the purification conditions for ClpB has allowed each subunit to be successfully purified in soluble form. The *S. aureus* ClpB amino acid sequence is considerably different from other ClpB proteins in three functionally important regions. Future

experiments will investigate the functional significance of these forms including their contributions towards host viability and their interactions with other heat shock proteins.

NMR Spectral Interpretation of Bicyclo-[3.3.0]-Octanes

Researcher: Midshipman 1 /C Stacey M. Lanham, USN
Adviser: Associate Professor Debra K. Dillner
Sponsor: Office of Naval Research (ONR)

Because bicyclo-[3.3.0]-octane systems are common in terpenoid natural products, the Nuclear Magnetic Resonance (NMR) chemical shifts of the protons and carbons of these systems are important in structure determination. A simple dimethylbicyclo-[3.3.0]-octane system has previously been synthesized in these laboratories. The assignment of all carbon and hydrogen resonances in the NMR spectral data of this compound was determined through the acquisition and interpretation of ^{1}H, ^{13}C, COSY (H-H correlation), HMQC (H-C correlation) data. An unusual chemical shift was found for one of the bridgehead hydrogens. Complete spectral determination, molecular modeling, and X-ray crystallography will be used to determine if factors such as distance from functional groups and molecular geometry contributed to the unusual shift. As a result of the detailed study of both spectra and conformational properties of this compound, the unusual shift is most likely due to chemical shift anisotropy due to close proximity of this proton to the ketone carbonyl. To further examine this, two additional compounds are being examined. The known unsubstituted system also shows a similar chemical shift effect for the analogous bridgehead carbon. The analog without the ketone will be synthesized to see if removing this carbonyl group leads to more usual chemical shift properties of the bridgehead hydrogens.

Detonation Simulations for Rhombohedral Cubane

Researcher: Midshipman 1/C Joshua J. Larson, USN
Adviser: Professor Mark L. Elert

Previous molecular dynamics studies of cubane detonation have employed a simplified cubic crystal structure, casting some doubt on the validity of the results. In fact, cubane crystallizes in a rhombohedral structure. Therefore, a model of the cubane crystal was developed with the proper rhombohedral structure, in which the body diagonal of each cubane molecule lies along the body diagonal of the unit cell. Furthermore, the twist angle around the molecular body diagonal was optimized within the AIREBO potential energy function to give the lowest-energy configuration. Periodic boundary conditions in this non-orthogonal system were developed. Preliminary detonation simulations using this model of rhombohedral cubane were performed.

Analysis of Toxic Alkaloids in Apple Juice and Milk Samples Using Capillary Elelctrophoresis

Researcher: Midshipman 1/C Douglas M. Marks, USN
Adviser: Associate Professor Christine L. Copper
Sponsor: Office of Naval Research (ONR)

Alkaloids can be isolated from various natural products and can be used for purposes that are helpful or harmful to humans. Previously, high performance liquid chromatography (HPLC) with absorbance detection has been used to separate and detect alkaloids in assorted matrices. In this work, we present an alternative to HPLC for the separation of several highly toxic alkaloids including strychnine, nicotine, colchicine, and aconitine. Specifically, alkaloids are extracted from spiked milk and juice samples and are separated by micellar electrokinetic chromatography (MEKC). Absorbance detection is employed in the MEKC studies. Effects on resolution by buffer type and pH, micelle type and concentration, and organic modifier addition are studied. Optimal extraction and separation conditions for four alkaloids are reported.

Plebe Safety 101: Laboratory Safety Instruction Video

Researcher: Midshipman 1/C Michael L. Matson, USN
Adviser: Assistant Professor Shirley Lin

This project was an investigation into the safety practices used at USNA with an end goal of creating a better safety video to display to the Plebe (freshmen) Chemistry courses. All plebes are required to watch an instructional video for SC111/SC112, ensuring they have received the proper instruction to begin work in a laboratory. A 20-minute film production was created that incorporated all pertinent safety practices, referred specifically to midshipmen lifestyle, and captured its midshipmen audience to convey all information.

The Effect of HCH-Salicortin on Caterpillar Performance

Researcher: Midshipman 1/C Mikal J Nelson, USN
Adviser: Assistant Professor Brian J. Rehill
Sponsor: Office of Naval Research (ONR)

Does HCH-salicortin possess stronger anti-herbivore activity than salicortin because of its dual hydroxy-cyclohexen-on-oyl moieties? Phenolic glycosides such as salicortin and tremulacin (found in aspen leaves) have clear linear dose effects on herbivores such as the gypsy moth caterpillar, and each compound contains a single hydroxy-cyclohexen-on-oyl (HCH) moiety. Thus, this project aimed to elucidate if phenolic glycoside effects on herbivores were due to the number of moles of HCH ingested. An HPLC scheme was developed to quantify and aid in the determination of purity of the isolated HCH-salicortin and salicortin products. Separation and purification of these compounds via liquid-liquid extraction and flash column chromatography provided the requisite amount to be added to the diet of gypsy moth larvae. Although no conclusions could be drawn with respect to the aforementioned hypothesis, two feeding studies provided useful information for setting up future experiments. The first study indicated that despite the possibility of degradation, compounds should be added to the diet before solidification, and not by infusion after solidification. Consumption of the diet was very low on infusion treatments. The second study showed some deterrent effect of HCH-salicortin. 2nd-instar larvae fed on a diet containing ca. 60 μmol/g diet of salicin, salicortin, or HCH-salicortin as well as a control diet without added phenolic glycoside gained less weight on the HCH-salicortin treatment than all other treatments. Given the lack of apparent effect of salicortin, we hypothesize that a co-eluting compound may account for the reduced weight gain, or that the amount of salicortin was below a required threshold to have any effect. Further work will be directed toward more isolation of the compounds and performing more feeding studies to test the hypothesis to produce a publishable unit.

A New Synthesis of Cyclobutenedione

Researcher: Midshipman 1/C Jennifer E. Proudfoot, USN
Adviser: Assistant Professor Shirley Lin
Sponsor: Office of Naval Research (ONR)

The goal of this project was to develop a short, efficient synthesis of cyclobutenedione. Squaric acid was converted to 3,4-dichlorocyclobutenedione in refluxing thionyl chloride. The hydrodehalogenation of 3,4-dichlorocyclobutenedione to yield cyclobutenedione using a variety of catalysts and hydrogen was investigated. Starting material conversion was improved by use of a polar solvent such as ethyl acetate and the presence of a base such as K_2CO_3 or $CsCO_3$. Dehydrohalogenation conditions using Pd/C or Lindlar catalyst produced 3-chlorocyclobutenedione and cyclobutanedione in addition to the desired cyclobutenedione.

The next step in this project will be to optimize the yield of cyclobutenedione and devise a method of separating the compound from the product mixture. In addition, other catalysts and/or bases may be tried in the dehydrohalogenation reaction.

Studies of the Formation of Carbonyl Sulfide in Ion-Irradiated Ices

Researcher: Midshipman 1/C Morgan M. Spiliotis, USN
Adviser: Professor Robert F. Ferrante
Sponsor: National Aeronautics and Space Administration (NASA)

Infrared absorptions near 2040 cm^{-1} have been detected in observations of young stellar objects embedded in dense molecular clouds and have been attributed to solid carbonyl sulfide, OCS, in icy grain mantles along the line of sight. The low abundances of gas-phase OCS in such regions imply that the material must be formed by active grain chemistry. OCS is also the presumed source of sulfur-containing compounds observed in cometary comae. This project involved the investigation of solid-state pathways to OCS through experimental studies of proton-irradiated ices containing simple sulfur, oxygen and carbon precursors. Gaseous mixtures of H_2S, SO_2 or CS_2 in CO_2 or CO were deposited onto a low-temperature (10K) surface to form ice films of known dimensions. Samples were irradiated to various doses with a 1-MeV proton beam from a van de Graaff accelerator. The experimental arrangement models ice film deposition and cosmic ray bombardment experienced by interstellar dust particles. Destruction of the parent compounds and formation of new species were monitored by FT-IR spectroscopy. Dose-related rates of formation of OCS, and the half-life for destruction by irradiation were determined. Thermal effects and the effect of the various matrices on line positions were also examined. This was the first systematic study of radiolysis routes to and stability of OCS in relevant cosmic ices. Additional work is continuing.

ELISA-based Detection of Polychlorinated Biphenyls in Freshwater Game Fish

Researchers: Midshipman 1/C Robert A. Spodarek, USN and Midshipman 1/C Joseph R. Piganelli, USN
Advisers: Associate Professor JudithAnn R. Hartman and Assistant Professor Virginia F. Smith

Polychlorinated biphenyls (PCBs) are an important class of nonbiodegradable compounds that have been widely introduced into streams, rivers, and lakes. Ingestion of PCBs has been linked to developmental delays, lowered birth rate, and decreased IQ in infants and children, and to cognitive damage in adults. Significant concentrations of PCBs have been found in the filet meat of game fish and there are state advisories limiting the suggested consumption of game fish in known problem areas. However, there has been no systematic effort to map the average concentration of PCBs in fish caught in the Susquehanna River watershed, in part due to the difficulty of measuring PCBs by the traditional gas chromatographic methods. This past year, we attempted to validate a recently published PCB specific enzyme linked immunosorbent assay (ELISA) to determine the concentration of PCBs in the filet meat of a variety of fish species caught in the Susquehanna River watershed. The filet meat from approximately 30 fish provided by Blaine Snyder (Tetratech, Inc.) was tested. In addition, liver samples were tested from approximately 6 fish. PCB levels above the detectable limit were observed in the livers but not in the filet meat. However, we were unable to rule out the presence of PCB's in the meat due to serious flaws that were discovered in the literature method. Studies to optimize the PCB assay and apply it to both Susquehanna River fish and Chesapeake Bay Oysters are being planned.

Computational Study on the Potential Energy Surface of the Cu + SO_2 Reaction Paths

Researcher: Midshipman 1/C Andrew J. Townsend, USN
Adviser: Associate Professor Roy E. McClean

The objective of this work was to explore the potential energy surface of the $Cu(^2S) + SO_2(^1A)$ reaction in doublet electronic states. These reactions are of interest, in part, because of the role sulfur dioxide plays in acid rain and in the corrosion of metals. The initial focus of the project was on using density functional theory (DFT) to determine the structures and energies of the possible $CuSO_2$ isomer products. These are the only products thermodynamically possible in thee 300 - 600 K range; abstraction channels are endothermic in this temperature range. Only the $\eta^2_{O,O}$ isomer (C_{2v} symmetry, where the Cu is bonded to the O-atoms) and an η^1_O isomer (C_s symmetry) were found to be stable relative to the ground state Cu + SO_2 asymptote. The $\eta^2_{O,O}$ isomer was the most stable, with a binding energy of 20 kcal mol^{-1}. A natural bond order analysis was performed on the isomers, with results indicating a partial charge transfer from Cu (out of the 4s orbital) to SO_2. Several potential energy surface scans were performed. Results indicate the interplay of multiple potential energy curves, with possible avoided crossings.

Investigation of the Substrate Recognition Mechanism of Peptide Methionine Sulfoxide Reductase of *Escherichia coli* by Isolation of Methionines in the Sequence of Staphylococcal Nuclease

Researcher: Midshipman 1 /C JessicaAnn Z. Tuia, USN
Adviser: Assistant Professor Virginia F. Smith
Sponsor: Research Corporation

Methionine oxidation, in the form of sulfoxide groups, has been implicated in numerous and diverse biological phenomena including pathology of human diseases as well as metabolic regulation and the aging process. Fortunately, methionine oxidation, unlike most other oxidative covalent modifications, can be reversed by enzymes known as methionine sulfoxide reductases. The mechanism by which methionine sulfoxide reductase A (MsrA), selectively reduces S-enantiomeric sulfoxides, recognizes its substrates was investigated. Since MsrA can repair oxidized methionine side chains in a variety of contexts it was proposed that the enzyme recognizes its substrate using generic features shared by many denatured proteins. This hypothesis was tested using unstructured peptides and the enzyme staphylococcal nuclease as substrates for recognition and repair. Specifically, an *in vitro* system was developed to measure MsrA repair activity of oxidized methionines directly by MALDI-TOF mass spectrometry and have used fluorescence spectroscopy to study the kinetics of association of MsrA with peptide and protein substrates. Work on this project continues.

Studies of the Formation of C_2H_4O Isomers in Ion-Irradiated Ices

Researcher: Midshipman 1/C Edward A. Valdez, USN
Adviser: Professor Robert F. Ferrante
Sponsor: National Aeronautics and Space Administration (NASA)

Ethylene oxide (ETO), acetaldehyde (AA) and vinyl alcohol (VA) are three isomers of C_2H_4O which have been observed in the interstellar medium. Gas phase chemistry cannot account for the observed abundances, suggesting the participation of icy grain surfaces as either storage locations or sites of active chemistry. This project explored solid-state pathways to and conversions among these isomers through experimental studies of irradiated ices containing simple precursors. Gaseous mixtures of C_2H_4, O_2, and H_2O were deposited onto a low-temperature (10K) surface to form ice films which were irradiated to various doses with a 1-MeV proton beam from a van de Graaff accelerator or with UV photons from a H_2 discharge lamp. The experimental arrangement models ice film deposition and the radiation environment of interstellar dust particles. Destruction of the parent compounds and formation of new species were monitored by FT-IR spectroscopy. To allow quantitative comparisons, integrated absorbance values ("A-values") for the three isomers were experimentally determined. Half-lives for destruction of ETO and AA by both proton- and photon-irradiation were also measured. Dose-related rates of formation of ETO and AA were determined in both the presence and absence of H_2O. The production of AA was dramatically increased when water was present. VA could <u>only</u> be formed in the presence of water. There was some evidence for the interconversion of VA to AA with extended proton irradiation. Additional work is continuing.

Synthesis of Novel α-Diimine Ligands for Surface Functionalization

Researcher: Midshipman 1/C Michael G. Zakaroff, USN
Adviser: Associate Professor William B. Heuer

Dye-sensitized solar cells (DSSC's) based on TiO_2 photoanodes are currently being investigated as an alternative to traditional Si-based solar cell technologies. The overall efficiency of such cells is dependent upon the nature of the surface-binding group used to attach the sensitizer dye to the surface of the semiconductor film. Previous work has shown that carboxylate and phosphonate groups are both effective surface-anchoring groups for functionalization of metal oxide surfaces. The objective of this project is to prepare new types of α-diimine ligands bearing such surface-binding groups, and to study the electrochemical and photophysical properties of Ru(II) complexes of these ligands. To date, three novel 4,5-diazafluoren-9-ylidene ligands bearing carboxylate-ester and/or nitrile substituents have been synthesized, and several Ru(II) complexes of these ligands have been prepared and partially characterized, including the x-ray crystal structure of one bis(carboxlate ester)-substituted complex. Currently, efforts are underway to complete the purification and characterization of two additional complexes, and to prepare an analogous series of ligands/complexes bearing phosphonate anchoring groups.

Publications

Journal (Refereed) Manuscripts

CHEEK, G. T., Professor (co-author), "Impedance Studies of the Passive Film on Aluminum," *Corrosion Science*, Vol. 47, pp. 3187–3201, 2005.

> Impedance spectroscopy has been used to study the characteristics of aluminum in 0.10 M NaCl solution at potentials below the pitting potential (-1.50 VSCE to -0.70 VSCE). Two semicircular impedance features have been identified over this range of potentials, the first of which broadens considerably as potential increases. The resistance derived from the high-frequency feature is observed to increase monotonically as the potential is increased up to the point where metastable pitting begins to occur. Previous work using XPS and x-ray absorption near edge structure (XANES) data allowed a calculation of the concentration of chloride in the passive film, and a correlation has been established between the impedance of the first semicircular feature and the concentration of chloride in the passive film. The relationship suggests that incorporation of chloride into the passive film results in a more resistive film. At the onset of metastable pitting, both the impedance and chloride concentration decrease from the measured maxima. In contrast to XPS studies, the impedance results do not reveal oxide thinning prior to the onset of metastable pitting. Modeling from impedance data indicates that the thickness of the oxide layer sampled by impedance is much thinner than the oxide measured with surface analytical techniques, suggesting that the impedance method senses only the space charge layer in the oxide and not the total film thickness.

COPPER, C.L., Associate Professor (co-author), "Micellar Electrokinetic Chromatography and Capillary Electrochromatography of Nitroaromatic Explosives in Seawater", *Electrophoresis*, Vol. 27, pp. 778-786, 2006.

> The ability to separate nitroaromatic and nitramine explosives in seawater sample matrices is demonstrated using both MEKC and CEC. While several capillary-based separations exist for explosives, none address direct sampling from seawater, a sample matrix of particular interest in the detection of undersea mines. Direct comparisons are made between MEKC and CEC in terms of sensitivity and separation efficiency for the analysis of 14 explosives and explosive degradation products in seawater and diluted seawater. The use of high-salt stacking with MEKC results, on average, in a three-fold increase in the number of theoretical plates, and nearly double resolution for samples prepared in 25% seawater. By taking advantage of long injection times in conjunction with stacking, detection limits down to sub mg/L levels are attainable; however, resolution is sacrificed. CEC of explosive mixtures using sol-gels prepared from methyltrimethoxysilane does not perform as well as MEKC in terms of resolving power, but does permit extended injection times for concentrating analyte onto the head of the separation column with little or no subsequent loss in resolution. Electrokinetic injections of 8 min at high voltage allow for detection limits of explosives below 100 mg/L.

FITZGERALD, Jeffrey P., Professor; (co-author), "Chloro and Hydroxo Forms of Boron(III) Subtriazaporphyrin Macrocycle," *Inorg. Chem.,* Vol. 45, pp. 6148-6151, 2006.

> *cis*-3,4-Dicyano-3-hexene undergoes cyclotrimerizaton with BCl_3 to form the new subtriazaporphyrin chloro[hexaethylsubtriazaporphyrinato]boron(III). The hydroxo derivative of this macrocycle has also been made and the X-ray crystal structure of the hydroxyl form was determined. Electronic absorption and magnetic circular dichroism spectra of the hydroxo monomer species were interpreted using time-dependent density functional theory calculations.

FOX, Douglas M., Assistant Research Professor and TRULOVE, Paul C., Associate Professor (co-authors), "Regenerated Silk Fiber Wet Spinning from an Ionic Liquid Solution," *J. Mat. Chem.*, Vol. 15, pp. 4206–4208, 2005.

> Regenerated silk fibroin from Bombyx mori silkworms was extruded into fibers from a 1-ethyl-3-methylimidazolium chloride ionic liquid solvent system. The preliminary work presented demonstrates the feasibility of spinning fibers from Bombyx mori fibroin solubilized in ionic liquids. The effect of the

coagulation bath solvent indicated that methanol worked best for solidifying the fibers. The methanol bath induced β-sheet crystallite formation; however, post-spin drawing was required to induce crystallite alignment. Acetonitrile and water coagulation baths also worked to a limited degree, but the resulting fiber properties were not desirable. These initial data do not eliminate the possibility of using acetonitrile and water as coagulation bath solvents, as shear in the spinneret could induce β-sheet crystallite formation, leading to fibers with more desirable properties.

FOX, Douglas M., Assistant Research Professor and TRULOVE, Paul C., Associate Professor (co-authors), "TGA Decomposition Kinetics of 1-Butyl-2,3-dimethylimidazolium Tetrafluoroborate and the Thermal Effects of Contaminants," *J. Chem. Thermodynamics*, Vol. 37, pp. 900-905, 2005.

Thermal gravimetric analysis (TGA) has been used to determine the kinetics of decomposition for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BMMIM][BF_4]) and to identify the effects of contaminants on the decomposition temperatures. Data was collected from both isothermal and constant ramp rate programs for the decomposition of [BMMIM][BF_4] under N_2. The isothermal data was fit to a global kinetic model and the apparent Arrhenius parameters were determined. The constant heating rate data was used to determine the apparent activation energy using the isoconversional method developed by Friedman. The effects of up to 10 wt% water, NH_4BF_4, NH_4Cl, and [BMMIM][Cl] impurities on [BMMIM][BF_4] decomposition temperatures were investigated. The only contaminant to significantly affect the decomposition was NH_4Cl, resulting in some decomposition at the temperatures associated with [BMMIM][Cl] decomposition.

GAO, G., Visiting Research Professor, VAN WORKUM, K., Visiting Research Professor, SCHALL, J. D., Visiting Research Professor, and HARRISON, J. A., Professor, "Elastic Constants of Diamond from Molecular Dynamics Simulations", *J. Phys Condens. Matter*, Vol. 18, pp. 1, 2006.

The elastic constants of diamond between 100 K and 1100 K have been calculated for the first time using molecular dynamics and the second-generation, reactive empirical bond-order potential (REBO). This version of the REBO potential was used because it was re-designed to be able to model the elastic properties of diamond and graphite at 0 K while maintaining its original capabilities. The independent elastic constants of diamond, C_{11}, C_{12}, and C_{44} and the bulk modulus were all calculated as a function of temperature and results from three methods are in excellent agreement. By extrapolating the elastic constant data to 0 K, it is clear that the values obtained here agree with the previously calculated 0 K elastic constants. Because the second-generation REBO potential was "re-fit" to obtain better solid-state force constants for diamond and graphite, the agreement with the 0 K elastic constants is not surprising. In addition, the functional form of the second-generation REBO potential is able to qualitatively model the functional dependence of the elastic constants and bulk modulus of diamond at non-zero temperatures. In contrast, reactive potentials based on other functional forms do not reproduce the correct temperature dependence of the elastic constants. The second-generation REBO potential also correctly predicts that diamond has a negative Cauchy pressure in the temperature range examined.

HARTMAN, JudithAnn R., Associate Professor (co-author), "Ignition Studies of Cerium Nitrate Treated Towels," *Fire and Materials*, Vol. 30, pp. 223-240, 2006.

This study evaluated the ignitability of cotton towel material saturated with an oxidizer solution of 0.5 N cerium(IV) nitrate in 2 N nitric acid. Four types of ignition testing were performed in this work; self-heating oven tests, hot object ignition tests, radiative smoldering ignition tests, and piloted flaming ignition/burning rate tests. Results indicate that cerium nitrate significantly enhances the ignitability of the towels. Self-heating properties of cerium nitrate treated towels were measured using the standard constant temperature oven method described by Bowes. Based upon these self-heating properties, self-heating is not a hazard for storage scenarios other than bulk storage (depths of several meters) of cerium nitrate treated towels at room temperature. Surface ignition for hot objects was observed for object temperatures as low as 250ºC placed upon room temperature cerium nitrate treated towels. Ignition for hot objects buried within a pile of towels occurred for object temperatures as low as 230ºC. Radiant heating tests of cerium nitrate treated towels showed initiation of smolder at heat fluxes as low as 3 kW/m^2 at surface temperatures as low as 175ºC. This compares with ordinary cellulosic materials that require 7-8 kW/m^2 heat fluxes and

temperatures of 250ºC. All four scenarios demonstrate enhanced ignitability and burning rates of cerium nitrate treated towel.

HENDERSON, Wesley A., Assistant Research Professor, Young, V., FYLSTRA, Paul A., Midshipman 1/C (USN), De Long, H., and TRULOVE, Paul C., Associate Professor, "Crystal Packing, Steric Effects and Heteroatoms: Comparison of *N*,*N*-Dimethylpyrrolidinium, Piperidinium and Morpholinium Iodide Salts," *Cryst. Growth & Design,* Vol. 6, pp. 1645-1648, 2006.

N,*N*-dimethylpiperidinium iodide ($PIP_{11}I$) has $P2_1/n$ symmetry at -150 °C. The crystal packing of the ions of $PIP_{11}I$ is compared with that reported for *N*,*N*-dimethylpyrrolidinium iodide ($PYR_{11}I$) and *N*,*N*-dimethylmorpholinium iodide ($MORP_{11}I$). Despite the differences in cation structure, $PYR_{11}I$ and $PIP_{11}I$ have essentially identical ion crystal packing. This is not the case, however, for $PIP_{11}I$ and $MORP_{11}I$. The phase behavior and thermal stability of the three salts have also been compared to examine the influence of crystal packing on thermal properties.

HENDERSON, Wesley A., Assistant Research Professor, Herstedt, M., Young, V., Passerini, S., De Long, H., and TRULOVE, Paul C., Associate Professor, "A New Disordering Mode for $TFSI^-$ Anions: The Nonequilibrium, Plastic Crystalline Structure of Et_4NTFSI," *Inorg. Chem.*, Vol. 45, pp. 1412-1414, 2006.

A new bis(trifluoromethanesulfonyl)imide ($TFSI^-$) anion disordering mode has been discovered in a supercooled plastic crystalline phase of tetraethylammonium TFSI which may, in part, account for the low melting points of $TFSI^-$ salts with organic cations thereby forming ionic liquids and the intriguing properties of LiTFSI for lithium battery applications.

HENDERSON, Wesley A., Assistant Research Professor, Young, V., Passerini, S., TRULOVE, Paul C., Associate Professor; and De Long, H., "Plastic Phase Transitions in *N*-Ethyl-*N*-methylpyrrolidinium bis(trifluoromethane-sulfonyl)imide," *Chem. Mater.*, Vol. 18, pp. 934-938, 2006.

Plastic Phase Transitions in *N*-Ethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($PYR_{12}TFSI$). Crystal structures have been determined for the $PYR_{12}TFSI$ salt in both the low temperature phase (phase IV) in which all of the ions are ordered and in a higher temperature phase (phase III) in which all of the ions are disordered. The two structures are compared to determine the mechanism for the solid phase transition and manner in which the ions become disordered.

LUNING PRAK, Dianne J., Assistant Professor and O'SULLIVAN, Daniel W., Associate Professor, "Solubility of 2,4-Dinitrotoluene and 2,4,6-Trinitrotoluene in Seawater," *Journal of Chemical Engineering Data,* Vol. 51, pp. 448-450, 2006.

Nitrogenous energetic compounds can enter and pollute the aquatic environment through the fallout of unexploded ordnance at shooting ranges and the corrosion of underwater unexploded ordnance (UXO) casings. The transformation and transport of this pollution source depends on its solubility in water. The purpose of this project was to measure the solubility of 2,4-dinitrotoluene (2,4-DNT) and 2,4,6-trinitrotoluene (2,4,6-TNT) in seawater with varying ionic strengths and temperatures. In the publication, solubility measurements were reported for ionic strengths equal to 0.3352, 0.5071, and 0.6820 $mol \cdot L^{-1}$ and for pure water at 4 °C, 20 °C, 30 °C, and 40 °C. The pure water solubility values compared well with values reported previously. The solubility in seawater was lower than that in pure water due to the presence of the salts. The average salting-out coefficients for 2,4-DNT and 2,4,6-TNT were 0.11 and 0.12 $L \cdot mol^{-1}$, respectively, which are consistent with measurements for other nitroaromatic compounds. The salting-out coefficients did not show any significant variation with temperature over the range examined.

MCCLEAN, Roy E., Associate Professor (co-author), "A Kinetic Study of the Reactions of Vanadium, Iron, and Cobalt with Sulfur Dioxide," *Physical Chemistry Chemical Physics,* Vol. 7, pp. 2489-2497, 2005.

A kinetic study of the reactions of ground state V, Fe, and Co with SO_2 is reported. V, Fe, and Co were produced by the 248 nm photodissociation of VCl_4, ferrocene, and $Co(C_5H_5)(CO)_2$, respectively, and were

detected by laser-induced fluorescence. V + SO_2 proceeds by an abstraction reaction with rate constants given by k = (2.33 ± 0.57) x 10^{-10} exp[-(1.14 ± 0.19) kcal mol^{-1} / RT] cm^3 $molecule^{-1}$ s^{-1} over the temperature range 296 - 571 K. Fe + SO_2 was studied in the N_2 buffer range of 10 – 185 Torr between 294 and 498 K. The limiting, low-pressure third order rate constants are given by k_0 = (3.45 ± 1.19) x 10^{-30} exp[-(2.81 ± 0.24) kcal mol^{-1} / RT] cm^6 $molecule^{-2}$ s^{-1}. Co + SO_2 was studied in the CO_2 buffer range of 5 – 40 Torr between 294 and 498 K. This reaction is independent of temperature over the indicated range and has a third order rate constant of k_0 = (5.23 ± 0.28) x 10^{-31} cm^6 $molecule^{-2}$ s^{-1}. Results of this work are compared to previous work on the Sc, Ti, Cr, Mn, and Ni + SO_2 systems. The reaction efficiencies for the abstraction reactions depend on the ionization energies of the transition metal atoms and on the reaction exothermicities, and the reaction efficiencies of the association reactions are strongly dependent on the energies needed to promote an electron from a $4s^2$ configuration to a $4s^1$ configuration.

MIKULSKI, P. T., Assistant Professor (Physics Department), HERMAN, L. A, Midshipman, USN, and HARRISON, J. A., Professor, "Odd and Even Self-Assembled Monolayers: Links between Friction and Structure," *Langmuir*, Vol. 21**,** pp. 12197-12206, 2005.

The friction between an amorphous carbon tip and *n*-alkane monolayers has been examined using classical molecular dynamics simulations. The friction of two monolayers with the same packing density but that differ in the length of the alkane chains by one $–CH_2–$ unit is compared. The simulations show that the monolayers composed of C_{13} chains have higher friction than those composed of C_{14} chains when sliding in the direction of chain cant; the difference in friction becomes more pronounced as the load is increased. Examination of the contact forces between the chains and the tip, along with conformational differences between the two chain types, lends insight into the friction differences.

O'SULLIVAN, D.W., Associate Professor (co-author), "Photochemical Production of Hydrogen Peroxide and Methylhydroperoxide in Coastal Waters," *Marine Chemistry*, Vol. 97, pp. 14-33, 2005.

Hydrogen peroxide (H_2O_2) has been observed in significant concentrations in many natural waters. Because hydrogen peroxide can act as an oxidant and reductant, it participates in an extensive suite of reactions in surface waters. Hydrogen peroxide is produced as a secondary photochemical product of chromophoric dissolved organic matter (CDOM) photolysis. Apparent quantum yields for the photochemical production of hydrogen peroxide were determined in laboratory irradiations of filtered surface waters from several locations in the Chesapeake Bay and in Arctic coastal waters with varying levels of CDOM. The apparent quantum yield for H_2O_2 decreases by about an order of magnitude from 280 nm to 500 nm, and the majority of H_2O_2 production occurs at wavelengths less than 340 nm. The apparent quantum yield for H_2O_2 production at 290 nm ranged from 4.2 x 10^{-4} to 2.1 x 10^{-6} mol H_2O_2 (mol photons)$^{-1}$ from fresh to marine waters. A linear relationship was found between the production of H_2O_2 and change in CDOM absorbance characterized as photobleaching (loss of absorbance). No significant relationship was observed between DOC concentration and peroxide production. Methylhydroperoxide (CH_3O_2H) was the only short chain peroxide produced during the irradiations, and its production is at least an order magnitude less than that of hydrogen peroxide. Peroxide production was greatest in waters containing significant amounts of terrigenous C in the form of humic substances. Surface waters whose synchronous fluorescence spectra indicated the presence of polyaromatic and or extensive conjugated compounds exhibited the greatest peroxide production. CDOM photobleaching is not significantly linked to apparent quantum yields for peroxide production.

PATTERSON, Stephanie, Midshipman 1/C, USN, STANLEY, John T. Midshipman 1/C, USN, DILLNER, Debra K.., Associate Professor; LIN, Shirley, Assistant Professor; and Traficante, Daniel, "^{13}C NMR Chemical Shifts of Carbonyl Groups in Substituted Benzaldehydes and Acetophenones: Substituent Chemical Shift Increments," *Magnetic Resonance in Chemistry*, Vol. 44, pp. 797-806, 2006.

^{13}C NMR Substituent chemical shift (SCS) increments have been determined for the carbonyl carbon of a variety of substituted benzaldehydes and acetophenones. The ^{13}C NMR chemical shift of the carbonyl carbon can be predicted for many di- and trisubstituted benzaldehydes and acetophenones through simple additivity of the SCS increments. The magnitude and sign of the SCS increments have been explored using Hartree-Fock 6-31G* calculations to determine the natural atomic charges of the carbonyl carbon. When a

substituent capable of intermolecular hydrogen bonding is present, deviations from additivity on the order of two ppm are observed in dilution experiments; deviations of up to 6 ppm can result from intramolecular hydrogen bonding.

REHILL, B. J., Assistant Professor (co-author), "Host Plant Genetics Affect Hidden Ecological Players: Links among Populus, Condensed Tannins, and Fungal Endophyte Infection," *Canadian Journal of Botany*, Vol. 83, pp. 356-361, 2005.

Recent studies have shown effects of host plant genetics on community and ecosystem processes, which make understanding the impacts of genetically based traits on hidden or non-apparent organisms more important. Here we examined links among genetic variation in hybrid cottonwoods, plant phytochemistry, and twig fungal endophytes (i.e., a common hidden organism). We found three major patterns: (1) twig fungal endophyte infection was positively related to the introgression of Fremont cottonwood (Populus fremontii S. Wats.) RFLP genetic markers, (2) condensed tannin concentration in twig bark tissue was negatively correlated to the introgression of Fremont genetic markers, and (3) fungal endophyte infection was negatively related to condensed tannin concentration in twig bark. These data demonstrate that plant genotype can impact hidden ecological players (i.e., fungal endophytes) resulting in community and ecosystem consequences.

REHILL, B.J., Assistant Professor (co-author), "A Genetic Similarity Rule Determines Arthropod Community Structure." *Molecular Ecology*, Vol. 15, pp. 1379-1391, 2006.

We define a genetic similarity rule that predicts how genetic variation in a dominant plant affects the structure of an arthropod community. This rule applies to hybridizing cottonwood species where plant genetic variation determines plant-animal interactions and structures a dependent community of leaf-modifying arthropods. Because the associated arthropod community is expected to respond to important plant traits, we also tested whether plant chemical composition is one potential intermediate link between plant genes and arthropod community composition. Two lines of evidence support our genetic similarity rule. First, in a common garden experiment we found that trees with similar genetic compositions had similar chemical compositions and similar arthropod compositions. Second, in a wild population, we found a similar relationship between genetic similarity in cottonwoods and the dependent arthropod community. Field data demonstrate that the relationship between genes and arthropods was also significant when the hybrids were analyzed alone, i.e. the pattern is not dependent upon the inclusion of both parental species. Because plant-animal interactions and natural hybridization are common to diverse plant taxa, we suggest that a genetic similarity rule is potentially applicable, and may be extended, to other systems and ecological processes. For example, plants with similar genetic compositions may exhibit similar litter decomposition rates. A corollary to this genetic similarity rule predicts that in systems with low plant genetic variability, the environment will be a stronger factor structuring the dependent community. Our findings argue that the genetic composition of a dominant plant can structure higher order ecological processes, thus placing community and ecosystem ecology within a genetic and evolutionary framework. A genetic similarity rule also has important conservation implications because the loss of genetic diversity in one species, especially dominant or keystone species that define many communities, may cascade to negatively affect the rest of the dependent community.

SIEFERT, R.L., Assistant Professor (co-author), "Estimation of Iron Solubility from Observations and a Global Aerosol Model," *Journal of Geophysical Research*, Vol. 110, D23307, 2005.

Mineral aerosol deposition is the dominant source of iron to the open ocean. Soil iron is typically insoluble and understanding the atmospheric processes that convert insoluble iron to the more soluble forms observed over the oceans is crucial. In this paper, we model several proposed processes for the conversion of Fe(III) to Fe(II), and compare with cruise observations. The comparisons show that the model results in similar averaged magnitudes of iron solubility as measured during 8 cruises in 2001 - 2003. Comparisons show that results of cases including cloud, SO2 and hematite processing are better than the other approaches used using the reaction rates we assume in this paper; unfortunately the reaction rates are not well known, and this hampers our ability to conclusive show one process is more likely than another. The total soluble iron deposited to the global ocean is estimated by the model to range from 0.36 to 1.6 Tg y(-

1), with 0.88 Tg y(-1) being the mean estimate; however there are large uncertainties in these estimates. Comparison shows that the regions with largest differences between the model simulations and observations of iron solubility are in the Southern Atlantic near South America coast and North Atlantic near Spain coast. More observations in these areas or in the South Pacific will help us identify the most important processes. Additionally, laboratory experiments that constrain the reaction rates of different compounds that will result in a net solubilization of iron in aerosols are required to better constrain iron processing in the atmosphere. Additionally, knowing what forms of iron are most bioavailable will assist atmospheric scientists in providing better budgets of iron deposited to the ocean surfaces.

SMITH, Virginia F., Assistant Professor (co-author), "Characterization of Three Areas of Interactions Stabilizing Complexes between SecA and SecB, Two Proteins Involved in Protein Export," *Protein Science*, Vol 15 (6), pp. 1379-1386, 2006.

The general secretory, Sec, system translocates precursor polypeptides from the cytosol across the cytoplasmic membrane in Escherichia coli. SecB, a small cytosolic chaperone, captures the precursor polypeptides before they fold and delivers them to the membrane translocon through interactions with SecA. Both SecB and SecA display two-fold symmetry and yet the complex between the two is stabilized by contacts that are distributed asymmetrically. Two distinct regions of interaction have bee defined previously and here we identify a third. Calorimetric studies of complexes stabilized by different subsets of these interactions were carried out to determine the binding affinities and the thermodynamic parameters that underlie them. We show here that there is no change in affinity when either one of two contact areas out of the three is lacking. This fact and the asymmetry of the binding contacts may be important to the function of the complex in protein export. This project is complete.

SMITH, Virginia F., Assistant Professor, (co-author), "The Relationship between Chain Connectivity and Domain Stability in the Equilibrium and Kinetic Folding Mechanisms of Dihydrofolate Reductase from *E. coli,*" *Protein Engineering, Design and Selection,* Vol. 19*,* pp. 175-185, 2006.

The role of domains in defining the equilibrium and kinetic folding properties of dihydrofolate reductase (DHFR) from *E. coli* was probed by examining the thermodynamic and kinetic properties of a set of variants in which the chain connectivity in the discontinuous loop domain (DLD) and the adenosine-binding domain (ABD) was altered by permutation. To test the concept that chain cleavage can selectively destabilize the domain in which the N- and C-termini are resident, permutations were introduced at one position within the ABD, one within the DLD, and one at a boundary between the domains. The results demonstrated that a continuous ABD is required for a stable thermal intermediate and a continuous DLD is required for a stable urea intermediate. The permutation at the domain interface had both a thermal and urea intermediate. Strikingly, the kinetic folding responses of all three permuted proteins were very similar to the wild-type protein. These results demonstrate a crucial role for stable domains in defining the energy surface for the equilibrium folding reaction of DHFR. If domain connectivity affects the kinetic mechanism, the effects must occur in the sub-millisecond time range. This project is complete.

SMITH, Virginia F., Assistant Professor, (co-author), "Mapping of the Docking of SecA onto the Chaperone SecB by Site-directed Spin Labeling: Insight into the Mechanism of Ligand Transfer during Protein Export," *Journal of Molecular Biology,* Vol. 353, pp. 295-307, 2005.

Export of protein into the periplasm of *Escherichia coli* via the general secretory system is achieved by action of a ternary complex comprising the polypeptide ligand, the chaperone SecB and SecA, a peripheral component of the membrane translocon, which is itself an ATPase. The unfolded ligand is captured initially by SecB and must be transferred to SecA and subsequently through the membrane translocon into the periplasm. We have taken the first steps in the elucidation of the mechanism of this dynamic transfer by determining the interface of interaction between SecB and SecA. Site-directed spin labeling and electron paramagnetic resonance spectroscopy were combined to identify which of the residues on SecB showed changes in spectral line shape upon addition of SecA. In all, 43% of the surface of SecB was covered by the 41 positions examined. A model of docking between SecB and SecA is proposed based on the pattern of amino acid residues on SecB shown to make contacts when in complex with SecA. This model in

combination with previously published biochemical data provides insight into the transfer of the unfolded polypeptide from the chaperone SecB to SecA. Project is ongoing.

URBAN, Joseph J., Associate Professor, "A Computational Study of Stereoelectronic Effects in Fluorinated Alkylamines," *Journal of Physical Organic Chemistry,* Vol. 18 (11), pp. 1061-1071, 2005.

A systematic evaluation has been carried of the stereoelectronic effects in a series of fluorinated amine compounds. A variety of computational methods have been employed including molecular mechanics, semiempirical, density functional, and ab initio methods. An analysis of the natural bond orbital populations has been carried out and the effect of solvent was also considered via a continuum solvation model (PCM). The results indicate a preference for conformations which result in an anti-periplanar arrangement between the nitrogen lone pair and the C-X bond (X=F or CF_3). There are variations in geometry and natural bond orbital population with conformation that are consistent with a stereoelectronic effect whereby electron density from the nitrogen lone pair is delocalized into the C-X σ^* orbital. Similar results are obtained for trifluoromethyl methyl amines although the magnitude of the stereoelectronic effect is somewhat attenuated resulting in greater expected conformational diversity for these compounds. The PCM results suggest that these preferences should persist in solution. A comparison among the computational methods used reveals that there is good agreement among the ab initio and density functional methods (at the HF/6-31+G(d), MP2/6-31+G(d), MP2/6-311+G(2d,p) and B3LYP/6-31+G(d) levels) and these methods agree well with the available experimental data for ethylmethyl amine.

Conference Proceedings

ELERT, Mark L., Professor, (co-author), "Reactive Molecular Dynamics Simulations of Shock-Induced Chemistry in Hydrocarbons," *Lecture Series on Computer and Computational Sciences,* Vol. 4, T. Simos and G. Maroulis, eds., Bell Academic Publishers, The Netherlands, pp. 1134-1137, 2005.

Chemical reactions induced by shock impact are of importance in several contexts, including energetic materials, material response to shock waves, and astrophysical and geophysical phenomena. Molecular dynamics (MD) simulations can provide insight into the molecular-level mechanisms of shock-induced chemical processes. MD simulations of shock-induced chemistry in several molecular hydrocarbons have been carried out, using an empirical potential energy function which accurately reproduces geometries and energetics of reacting hydrocarbon systems.

ELERT, Mark L., Professor, (co-author), "Extreme Chemistry at the Nanoscale in Detonation Simulations," *Lecture Series on Computer and Computational Sciences,* Vol. 4, T. Simos and G. Maroulis, eds., Bell Academic Publishers, The Netherlands, pp. 1130-1133, 2005.

Processes at condensed phase detonation fronts can occur on such short time and length scales that they are ideal for molecular dynamics simulations that follow individual atomic trajectories. Over more than a decade we have developed a series of potentials and computational methods for atomistic simulations of shock-induced chemistry and detonations in solids. An overview will be given of some of our progress in using molecular dynamics simulations to link directly atomic-scale processes to the continuum behavior of condensed phase detonations. These results indicate that the classic continuum view of a detonation can be meaningfully extended to the nanoscale.

Book Chapter

HARRISON, J.A., Professor (co-author), "Computational Modeling of Nanometer-Scale Tribology," in *Introduction to Nanotribology and Nanomechanics*, Ed. by B. Bhushan, (Springer-Verlag, Heidelberg, Germany, 2005), Chapter 13, pp. 623-691.

Patent

CHEEK, Graham T., Professor, and O'Grady, William E., "Low Temperature Refining and Formation of Refractory Metals", Patent # 6,958,115, awarded 25 October 2005.

> Titanium is currently produced by reduction of TiO_2 by either magnesium (Kroll process) or sodium (Hunter process). These processes involve very high temperatures and require further processing to produce titanium metal. The present patent application proposes that the reduction be carried out in room-temperature molten salts as well as traditional nonaqueous solvents. Preliminary experiments have been carried out in the basic aluminum chloride: 1-ethyl-3-methylimidazolium chloride molten salt system. Titanium foil strips were oxidized in a furnace at 550°C to form a TiO_2 layer on the titanium substrate. Cyclic voltammetric scans at this electrode showed two small reduction processes. Holding the potential past these processes gave a narrow oxidation peak on the reverse scan, indicating formation of the metal during the reduction processes. Similar experiments were carried out using TiO_2 anatase powder contained in a Ti gauze basket. Electrochemical reduction of the powder caused the granules to change color from white to dark gray. X-ray photoelectron spectroscopy (XPS) on the granules showed that approximately 12% of the titanium on the sample surface is metallic titanium. Another experiment using a platinum basket gave 20% yield for the titanium.

Presentations

BERNHARDSON, Andrew S., Midshipman 1/C, USN, BAUMANN, Richard G., Assistant Research Professor, SMITH, Virginia F., Associate Professor, DOMANSKI, Tammy L., Assistant Professor, and SCHLESSMAN, Jamie S., Assistant Professor, "Isolation and Purification of MsrA1 Protein from the Psychrophile *Colwellia psychrerythraea*," American Society for Biochemistry and Molecular Biology Annual Meeting, San Francisco, CA, 1-5 April 2006.

CANBY, Dana S., Midshipman 1/C, USN, SANDERS, Eli, Ensign, USN, and CHEEK, Graham T., Professor, "Electrochemical Study of Aromatic Ketones in 1-Ethyl-3-methylimidazolium Tetrafluoroborate," 209th Electrochemical Society Meeting, Denver, CO, 7 May 2006.

CHEEK, Graham T., Professor and O'Grady, William E., "Voltammetric Study of Titanium Chlorides in the Ionic Liquid 1-Ethyl-3-methylimidazolium Tetrafluoroborate," 208th Electrochemical Society Meeting, Los Angeles CA, 16-21 October 2005.

CHEEK, Graham T., Professor; O'Grady, William E., and Lawrence, Steven H., "Determination of Water in 1-Ethyl-3-methylimidazolium Tetrafluoroborate," 209th Electrochemical Society Meeting, Denver, CO, 10 May 2006.

COPPER, C. L., Associate Professor, MARKS, Douglas M., Midshipman 1/C, USN, and Collins, G. E., "Capillary Electrophoresis for Detection of Several Alkaloids in Food Samples," 231st National American Chemical Society Meeting, Atlanta, GA, 26-30 March 2006.

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ELERT, Mark L., Professor, Mowrey, R. C., and White, C. T., "Quantum Dynamics of Energy Transfer under Shock Conditions," American Physical Society National Meeting, Baltimore, MD, 13-17 March 2006.

ELERT, Mark L., Professor, and White, C. T., "Atomic Simulation of Energetic Materials," Second Eglin Symposium on Nano Energetics, Shalimar, FL, 22-23 March 2006.

ELERT, Mark L., Professor, Zybin, S. V., REVELL, S. M., Midshipman 1/C, USN, and White, C. T., "Shock-Induced Chemical Reactions of Polycyclic Aromatic Hydrocarbons," American Physical Society National Meeting, Baltimore, MD, 13-17 March 2006.

FERRANTE, Robert F., Professor, Mastrapa, Rachel M., Moore, Marla H., Hudson, Reggie L., and Brown, Robert H., "Proton Irradiation of Crystalline Water Ice: Timescales for Amorphization in the Kuiper Belt", 37th Annual Meeting of the Division of Planetary Sciences, American Astronomical Society, Cambridge, UK, 4-9 September 2005.

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FERRANTE, Robert F., Professor, VALDEZ, Edward A., Midshipman, USN, Hudson, Reggie L., and Moore, Marla H., "Studies of the Formation of Ethylene Oxide Isomers in Ion-Irradiated Ices", 231st American Chemical Society National Meeting, Atlanta, GA, 26-30 March 2006.

FITZGERALD, Jeffrey P., "USNA Core Chemistry Curriculum," USNA Academic External Review Group, Washington, DC, 4 October 2005.

FYLSTRA, Paul A., Midshipman 1/C, USN, HENDERSON, Wesley A., Assistant Research Professor, De Long, H., and TRULOVE, Paul C., Associate Professor, "Acidic Ionic Liquids," Ionic Liquids: Not Just Solvents Anymore, 231st American Chemical Society National Meeting, Atlanta, GA, 26-30 March 2006.

GREEN, John M., Midshipman 1/C, USN, FOX, Douglas M., Assistant Research Professor, De Long, H., and TRULOVE, Paul C., Associate Professor, "Using Well Known Methods in Unprecedented Ways: The Dissolution/Reconstitution of Chitin and Chitosan Using Room-Temperature Ionic Liquids," Ionic Liquids: Not Just Solvents Anymore, 231st American Chemical Society National Meeting, Atlanta, GA, 26-30 March 2006.

GUTTERIDGE, Clare E., Assistant Professor, "Chalcone-like Molecules: Antimalarial Activity of 2,4-Dimethoxy-4'-Butoxychalcone and its Metabolites, American Society of Hygiene and Tropical Medicine Annual Meeting, 11-15 December 2005.

GUTTERIDGE, Clare E., Assistant Professor, "Chalcone Synthesis, Quarterly Review," Walter Reed Army Institute of Research, 28 September 2005, 14 December 2005 and 21 March 2006.

HANES, Ernest T., Midshipman 1/C, USN, DOMANSKI, Tammy L., Assistant Professor, and BAUMANN, Richard G., Assistant Research Professor, "Cloning, Expression, and Analysis of *Staphylococcus aureus* ClpB and Associated Heat-Shock Proteins," American Society for Biochemistry and Molecular Biology Annual Meeting, San Francisco, CA, 1-5 April 2006.

HARRISON, Judith A., Professor, "Molecular Dynamics Simulations of Nanocrystalline Diamond", ICNDST & ADC Joint Conference, Raleigh, NC, 15-18 May 2006.

HARRISON, Judith A., Professor, *Burt L. Newkirk Lecture*, "Links between Friction and Structure Elucidated using Molecular Dynamics", Rensselaer Polytechnic Institute, Troy, NY, 28 April 2006.

HARRISON, Judith A., Professor, Examination of the Tribology of DLC and SAMS using Molecular Dynamics, Frontiers in Boundary Lubrication Films, Lyon, France, 9-14 April 2006.

HARRISON, Judith A., Professor, "Links between Interface Structure (Disorder) and Friction in Model SAMS," 231st American Chemical Society National Meeting, Atlanta, GA, 26-30 March 2006.

HARRISON, Judith A., Professor, "The Molecular-Scale Tribology of Solid Lubricants for MEMS Applications: Molecular Dynamics Studies," AFOSR-MURI Tribology Review, Raleigh, NC, 11-14 October 2005.

HARRISON, Judith A., Professor, "Multi-functional Extreme Environment Surfaces: Thrust area II: Cryogenic and Space Applications," AFOSR-MURI Tribology Review, Raleigh, NC, 11-14 October 2005.

HARRISON, Judith A., Professor, "The Tribology of Carbon, Hydrogen and Silicon-containing Solid Lubricants," World Tribology Congress III, Washington, DC, 12-16 September 2005.

HARRISON, Judith A., Professor, GAO, G. T., Assistant Research Professor, VAN WORKUM, K., Assistant Research Professor, SCHALL, J. D., Assistant Research Professor, Chateauneuf, G. M.; and MIKULSKI, P. T., Assistant Professor (Physics Department), "Elucidation of the Atomic-Scale Mechanisms of Friction in Model SAMs and DLC Films," American Physical Society Meeting, Baltimore, MD, 13-17 March 2006.

HARRISON, Judith A., Professor, Chateauneuf, G. M., SCHALL, J. D., Assistant Research Professor, GAO, G., Assistant Research Professor, and VAN WORKUM, K., Assistant Research Professor, "Effect of Counterface Roughness on Sliding Friction of Alkane Monolayers," American Physical Society Meeting, Baltimore, MD, 13-17 March 2006.

HARRISON, Judith A., Professor, GAO, G. T., Assistant Research Professor, VAN WORKUM, K., Assistant Research Professor, and SCHALL, J. D., Assistant Research Professor, "Mechanical and Tribological Properties Of Amorphous Carbon Films," American Physical Society Meeting, Baltimore, MD, 13-17 March 2006.

HARRISON, Judith A., Professor, SCHALL, J. D., Assistant Research Professor, VAN WORKUM, K., Assistant Research Professor, and GAO, G. T., Assistant Research Professor, "Multi-Functional Extreme Environment Surfaces: Thrust Area II: Cryogenic and Space Applications", AFOSR-MURI Tribology Review, Irvine, CA, 20 February 2006.

HARRISON, Judith A., Professor, SCHALL, J. D., Assistant Research Professor, VAN WORKUM, K., Assistant Research Professor, and GAO, G. T., Assistant Research Professor, "Molecular Dynamics Simulations of Nanocomposite Diamond-Like Carbon," World Tribology Congress III, Washington, DC, 12-16 September 2005.

HARRISON, Judith A., Professor, GAO, G. T., Assistant Research Professor, VAN WORKUM, K., Assistant Research Professor, and SCHALL, J. D., Assistant Research Professor, "Friction And Wear Studies of Hydrogenated Amorphous Carbon Films Containing Silicon", World Tribology Congress III, Washington, DC, 12-16 September 2005.

HARRISON, J. A., Professor, Robbins, M. O., Luan, B., Hyun, S., and Bernstein, N., "Effect Of Atomic-Scale Surface Roughness On Friction," World Tribology Congress III, Washington, DC, 12-16 September 2005.

HERMAN, L. A., Midshipman 1/C, USN, MIKULSKI, P. T., Assistant Professor (Physics Department), and HARRISON, Judith A., Professor, "A Molecular-Dynamics Study Of The Odd-Even Effect In Self-Assembled Monolayers," American Physical Society Meeting, Baltimore, MD, 13-17 March 2006.

HARTMAN, JudithAnn R., Associate Professor (co-author), "Ignition Studies of Cerium Nitrate Treated Towels," Department of Energy Fire Safety Workshop, Atlanta, GA, 25 April 2006.

HEUER, William B., Associate Professor, PEARSON, Wayne H., Associate Professor, and ZAKAROFF, Michael G., Midshipman 1/C, USN, "Novel Ru(II) Complexes with 4,5-Diazafluoren-9-ylidene Ligands," 231st ACS National Meeting, Atlanta, GA, 26-30 March 2006.

LANHAM, Stacey M., Midshipman 1/C, USN, and DILLNER, Debra K., Associate Professor, "NMR Spectral Interpretation of Bicycle-[3.3.0]-Octanes," 231st American Chemical Society National Meeting, Atlanta, GA, 17 March 2006.

LIN, Shirley, Assistant Professor, (co-author), "Synthesis and Characterization of Arylboroxine Assemblies: Versatile Organizing Elements in Nanoscale Molecular Assemblies and Polymers," 231st ACS National Meeting, Atlanta, GA, 26-30 March 2006.

O'SULLIVAN, Daniel W., Associate Professor, (co-author), "Hydrogen Peroxide and Methylhydro- peroxide Observations during RICO, RICO Science Team Meeting, Boulder, CO, 26-29 June 2005.

O'SULLIVAN, Daniel W., Associate Professor, (co-author), "DC-8 Peroxide Observations during ICARTT via Two Chemically Independent Techniques," ICARTT 2005 Data Workshop, Durham, NH, 9-12 August 2005.

O'SULLIVAN, Daniel W., Associate Professor, (co-author), "INTEX-NA Observations in Relation to Photochemical Theory," ICARTT 2005 Data Workshop, Durham, NH, 9-12 August 2005.

O'SULLIVAN, Daniel W., Associate Professor, (co-author), "Intercontinental Transport of Formaldehyde and its Precursors — INTEX-NA," ICARTT 2005 Data Workshop, Durham, NH, 9-12 August 2005.

O'SULLIVAN, Daniel W., Associate Professor, (co-author), "Intercomparison of Chemically Independent Peroxide Observations During INTEX-NA," American Geophysical Union Fall National Meeting, San Francisco, CA, 5-8 December 2005.

O'SULLIVAN, Daniel W., Associate Professor, (co-author), "Peroxyacetic Acid Ubiguitous during ICARTT," American Geophysical Union Fall National Meeting, San Francisco, CA, 5-8 December 2005.

O'SULLIVAN, Daniel W., Associate Professor, (co-author), "An Examination of Photochemical Theory Based on INTEX Observations, American Geophysical Union Fall National Meeting, San Francisco, CA, 5-8 December 2005.

O'SULLIVAN, Daniel W., Associate Professor, (co-author), "Peroxide and Formaldehyde Measurement Techniques and Inter-comparisons during MILAGRO, MILAGRO Science Team Meeting, Houston, TX, 11 March 2006.

PEARSON, Wayne, Associate Professor, Peiris, Suhiti, and Butcher, Ray, "X-ray Diffraction Studies of Single Crystals at High Pressure using Synchrotron Radiation," Joint 20th AIRAPT – 43th EHPRG, Karlsruhe, Germany, 27 June – 1 July 2005.

PIGANELLI, Joseph R., Midshipman 1/C, USN, SPODAREK, Robert A., Midshipman 1/C, USN, SMITH, Virginia F., Assistant Professor, Snyder, Blaine, and HARTMAN, JudithAnn R., Associate Professor, "ELISA-Based Detection of Polychlorinated Biphenyls in Freshwater Game Fish," 231st American Chemical Society National Meeting, Atlanta, GA, 3 April 2006.

PROUDFOOT, Jennifer E., Midshipman 1/C, USN, and LIN, Shirley, Assistant Professor, "A New Synthetic Route to Cyclobutenedione," 231st American Chemical Society National Meeting, Atlanta, GA 26-30 March 2006.

STOCKTON**,** Jon D., Midshipman 1/C, USN, LOMAX**,** Joseph F, Associate Professor, EDMONDSON, Charles A., Associate Professor (Physics Department), FONTANELLA, John J., Professor, (Physics Department), and WINTERSGILL, Mary C., Professor (Physics Department), "Studies in Mesoporous Silicates: Impedance Measurements on SBA-15 loaded with Sulfonated-Polystyrene and Nafion with SBA-15 Filler," Combined 11th International Ceramics Congress and 4th Forum on New Materials, Acireale, Italy, 6 June 2006.

SCHLESSMAN, Jamie L., Assistant Professor, ABE, Colby, Midshipman l/C, USN, Gittis, Apo, Karp, Dan, Dolan, Michael; and Garcia-Moreno E., Bertrand, "Water Penetration as a Factor for Stabilizing Internal Ionizable Groups in Proteins," Biophysical Society Meeting, Salt Lake City, UT, 18-22 February 2006.

SCHLESSMAN, Jamie, Assistant Professor (co-author), "Domain Swapping, Local Unfolding and Other Structural Consequences of the Ionization of Internal Groups In Proteins," Biophysical Society Meeting, Salt Lake City, UT, 18-22 February 2006.

SCHROEDER, Maria J., Associate Professor (co-author), "Fast Dynamics of PI and PBD: Precursors to Structural Relaxation," Gordon Research Conference on Elastomers, Networks, and Gels, New London, NH, 17-22 July 2005.

SIEFERT, R. L., Assistant Professor (co-author), "Measurement of Vehicular Ammonia Emissions in the Fort McHenry Tunnel, Baltimore, Maryland," 230th American Chemical Society National Meeting, Washington, DC, 28 August – 1 September 2005.

SIEFERT, R. L., Assistant Professor (co-author), "Determination of the Physical Constants of Ferric and Ferrous Complexes of Phytic Acid by Proton Nuclear Magnetic Resonance and Resistance of Complexes to Enzymatic Dephosphorylation by Aspergillus Ficcum," 231st American Chemical Society National Meeting, Atlanta, GA, 26-30 March 2006.

SIEFERT, R. L., Assistant Professor (co-author), "A Comparison of Ammonia Emission Rates Between a Tunnel and Sidewall Ventilated Broiler House," Workshop on Agricultural Air Quality: State of the Science, Bolger Conference Center, Potomac, MD, 5-8 June 2006.

SMITH, Virginia F., Assistant Professor; TUIA, JessicaAnn, Midshipman 1/C, USN, "Investigation of the Substrate Recognition Mechanism of Methionine Sulfoxide Reductase of *E.coli*," 50th Annual Meeting of the Biophysical Society, Salt Lake City, UT, 12-16 February 2006.

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TRULOVE, Paul C., Associate Professor, Phillips, D., Drummy, L., Naik, R., De Long, H., and Mantz, R., "Silk Regeneration with Ionic Liquids," Ionic Liquids: Not Just Solvents Anymore, 231st American Chemical Society National Meeting, Atlanta, GA, 26-30 March 2006.

TRULOVE, Paul C., Associate Professor, Gilman, J., FOX, Douglas M., Assistant Research Professor, De Long, H., and Stenger-Smith, J., "Flammability Properties of Ionic Liquids," Ionic Liquids: Not Just Solvents Anymore, 231st American Chemical Society National Meeting, Atlanta, GA, 26-30 March 2006.

TRULOVE, Paul C., Associate Professor, HENDERSON, Wesley A., Assistant Research Professor, Passerini, S., Young, V., and De Long, H., "Crystal Packing and the Hows and Whys of Ionic Liquids," Ionic Liquids: Not Just Solvents Anymore, 231st American Chemical Society National Meeting, Atlanta, GA, 26-30 March 2006.

TRULOVE, Paul C., Associate Professor, Young, V., HENDERSON, Wesley A., Assistant Research Professor, and Passerini, S., "Low-Melting Organic Salts: Phase Transitions, Twinning, and Disorder," American Crystallographic Association Annual Meeting, Honolulu, HI, 21-26 July 2005.

TRULOVE, Paul C., Associate Professor, Stux, A., Swider-Lyons, K., HENDERSON, Wesley A., Assistant Research Professor, "Incorporating Ionic Liquids into Li-ion Microbatteries," Second International Conference on Polymer Batteries and Fuel Cells Meeting, Las Vegas, NV, 12-17 June 2005.

TRULOVE, Paul C., Associate Professor, HENDERSON, Wesley A., Assistant Research Professor, Passerini, S., and De Long, H., "A Clear and Perplexing Packing Puzzle," 1st International Congress on Ionic Liquids, Salzburg, Austria, 19-22 June 2005.

URBAN, Joseph J., Associate Professor, "Hydrogen Bonding in Fluorinated Peptide Mimetics: A Computational Investigation," 231st American Chemical Society National Meeting, Atlanta, GA, 25-30 March 2006.