Division of Mathematics and Science

CAPT K. Scott Pugh, USN
Director

Chemistry Department

Professor Jeffrey P. Fitzgerald
Chairman

The 2002-2003 Academic Year was a productive year for research within the Naval Academy's Chemistry Department. Twenty-one faculty members conducted funded research on twenty-nine different projects. Funding came from thirteen different outside sources including the prestigious Camille and Henry Dreyfus Foundation, the Air Force Office of Scientific Research, the National Aeronautic and Space Administration, the Office of Naval Research, the Naval Research Laboratory, the Research Corporation and the Petroleum Research Fund. In addition to the above, four faculty members carried out unfunded research in their laboratories at the Naval Academy and five senior midshipmen participated in one or more semesters of research. The above effort resulted in twenty-three publications in refereed journals, three conference proceeding and thirty-five presentations, including three by students at national conferences.

Faculty members whose accomplishments are particularly noteworthy include the following. Professor Mark Campbell, in the final year of his appointment as a Dreyfus Foundation Teacher/Scholar, published three papers on the kinetics of metal atoms reacting with small molecules as studied by laser-induced fluorescence. Professor Mark Elert supported a post-doctoral associate with whom he published two book chapters and two journal articles on shock-wave chemistry. Professor Judith Harrison continues to receive international recognition for her molecular dynamics studies of friction and wear. She supported two post-doctoral associates and her publications this year include one in the Journal of the American Chemical Society, the premier chemistry journal. LCDR Gregory Cotten, USNR, also supported a postdoctoral associate at the Naval Research Laboratory. Associate Professor Daniel O'Sullivan did field work in the Chesapeake Bay as part of his ONR-funded research on the aqueous chemistry of photochemically-produced peroxides and dissolved organic matter. Assistant Professor Clare Gutteridge received a U.S. Patent (U.S. 20030125357) for "Therapeutic Compounds for Treating Dyslipidemic Conditions." Associate Professor William Heuer was awarded the Kinnear Fellowship through the Naval Academy Alumni Association in support of his work on supramolecular complexes of dyes. Finally, Associate Professor Craig Whitaker and Assistant Professor Tammy Domanski agreed to serve as advisors for Midshipmen 1/C Katharine Folz and Daniel Bowers, respectively, who were selected as 2003-2004 Naval Academy Trident Scholars.

Sponsored Research

Kinetics of Gas Phase Oxidation Reactions of Transition Metal Atoms with Oxygen-containing Oxidants

Researcher: Professor Mark L. Campbell
Sponsor: The Camille and Henry Dreyfus Foundation

The objective of this research is to determine the rate constants for reactions of ground state and low-lying excited state transition metal atoms in the gas phase with oxygen-containing oxidants as a function of temperature and pressure. In particular, three projects are in varying stages of completion: (1) reactions of transition metals with N_2O, (2) reactions of ground state and low-lying excited states of niobium and tantalum with several oxidants, and (3) reactions of zirconium and hafnium with water. By obtaining Arrhenius parameters for these reactions, geometric factors and energy barrier effects have been determined. The experimentally measured rate constants and barriers were analyzed to determine if a relationship exists between these values and the physical properties of the transition metals and reactants. Results for the reactions with N_2O were compared to the calculated values from a theoretical model developed by Fontijn and co-workers. The reactions of niobium and tantalum indicate the importance electronic effects have on the reaction rate. The reactions of zirconium and hafnium with water yield a better understanding of chemical reactions which may occur during accidents in nuclear reactors. Completion of this research will greatly enhance our understanding of transition metal chemical reactions.

Impedance Studies of Aluminum Electrodes in Chloride Media

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

During Fiscal Year 2002, work was continued on the impedance behavior of aluminum in 0.10 M NaCl solutions. Experiments were conducted on aluminum rods, as opposed to planar electrodes, giving better current distribution and more reliable impedance data. Careful analysis of the impedance values in these systems, combined with X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge spectroscopy (XANES) data, has resulted in a clearer picture of the role of chloride in the aluminum corrosion process.

In studies of aluminum in 0.10 M NaCl at potentials in the passive oxide region (-1.50 V_{SCE} to -0.70 V_{SCE}), two semicircular impedance features in Nyquist plots are observed. From modeling of this data, the film resistance was found to increase over the potential range given above. It was found earlier from XPS and XANES methods that the chloride ion concentration in the film actually increases over this potential range, a finding seemingly at odds with the XPS results. The capacitance values, on the other hand, undergo a decrease over the same potential range. This implies that the oxide layer on aluminum does not undergo thinning before metastable pitting, in contrast to the results obtained from XPS and XANES studies.

Studies of Redox Systems at Boron-Doped Diamond Electrodes

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

Initial studies were begun on electrochemical reactions at boron-doped diamond electrodes. Cyclic voltammograms of potassium ferrocyanide solutions in 0.10 M NaCl showed reversible behavior at these diamond electrodes. Oxidation of phenol at diamond electrodes involved relatively large currents on the first scan; however, successive scans produced much lower currents. It was found that the electrodes could be partially cleaned by potential excursions to very negative potentials (-2.0 V vs Ag/AgCl, 0.10M NaCl, no phenol), after which the current response for phenol oxidation increased significantly. In work at fluorine-capped diamond electrodes, the electrochemical response to potassium ferricyanide was found to be distorted compared to the reversible behavior found at uncapped diamond electrodes. Further studies are planned to explore the reasons for this behavior.

Isolation and Characterization of Metabolic Intermediates from Polycyclic Aromatic Hydrocarbon Biodegradation

Researcher: Associate Professor Christine L. Copper
Sponsor: Dr. Tom Boyd, Research Chemist, Chemical Dynamics and Diagnostics Branch, Naval Research Laboratory (NRL)

This project has been on-going for several years now. One major impact from petroleum related industries and petroleum users (such as Navy ships and planes) is the release of hydrocarbon waste products into the environment. The aim of this work, which is a continuation of work performed last summer in the NRL-USNA Cooperative Program, is to study techniques (especially capillary electrophoresis, liquid chromatography, and mass spectrometry) that could be used to isolate and characterize a variety of metabolic intermediates in the field (including Navy shipyards and waterways around them) as a tool for assessing biodegradation status.

Separation and Detection of Explosives by Microchip Capillary Electrophoresis

Researcher: Associate Professor Christine L. Copper
Sponsor: Dr. Greg Collins, Research Chemist, Chemical Dynamics and Diagnostics Branch, Naval Research Laboratory (NRL)

Capillary Electrophoresis (CE) is a separation method that has advantages of high efficiency, fast analysis time, small sample requirement, and minimal waste production when compared to other separation methods. When CE is performed on a microchip, additional advantages such as portability and reduced cost per sample are obtained. The work

for which funding has been secured for the summer of 2003 (and that was started in January 2003) focuses on developing traditional, packed-capillary, and microchip CE methods for the separation, identification, and quantitation of explosives in seawater. There is also work in progress to detect cyanide levels in atmospheric, soil, and water samples using the methodologies mentioned above. The results of this work will be presented at the Eastern Analytical Symposium in New Jersey in November 2003.

Platinum-Free and Low-Platinum Nanocomposite Catalysts for Oxygen Reduction at Fuel Cell Cathodes

Researcher: LCDR Gregory B. Cotten, USNR
Sponsor: Naval Research Laboratory (NRL)

A new nanocomposite catalyst has been developed for oxygen-reduction on the cathode of PEM fuel cells. This electro-catalyst comprises Pt incorporated within the amorphous structure of hydrous iron phosphate. The Pt – iron phosphate catalyst material is chemically stable in the acidic environment of a PEM fuel cell. The micro-porous support material provides channels for fast proton, oxygen and water transport to the Pt site and enhances the catalytic Oxygen Reduction Reaction (ORR). Our Pt - iron phosphate catalyst shows increased ORR performance compared to the standard 20 wt.% Pt-VC electrodes for a Pt-loading of 0.1 mg(Pt).cm^{-2}. Half-cell measurements show the ORR activity is increased by 30% at 0.95V vs RHE.

The observed improvement is attributed the material characteristics of the Pt – iron phosphate catalyst. First, the Pt is atomically distributed across the micro porous iron phosphate and exists in the oxidized $Pt^{2+/4+}$ states. The ionic charge prevents coagulation of the Pt over time, leading to decrease of active surface area. Secondly, the iron phosphate support is shown to preferentially adsorb oxygen from its surroundings. The oxygen species are stored as iron-hydro-peroxide complexes and stabilized by the presence of Lewis acid sites (P) and the $Fe^{2+/3+}$ redox couple. The oxygen complexes supply the ORR on the Pt reaction site and even increase the ORR rate under reduced atmospheric oxygen concentrations, such as in air.

The Pt – iron phosphate catalyst shows activity towards hydrogen- and CO oxidation as well, but does not exhibit their characteristic adsorption. This suggests that Pt is less sensitive to poisoning when incorporated within iron phosphate structure. It is assumed that the 'stored oxygen' enables rapid oxidation and adsorption of these species, thus keeping the Pt interface in constant equilibrium with its surroundings. Pt – iron phosphate has been applied on both the anode and the cathode of a symmetric fuel cell and operated successfully under hydrogen and air. Generally, the improved fuel tolerance of the catalyst would decrease the dependence on high purity gasses and greatly benefit the feasibility of the fuel cell.

This work has recently been filed in a patent and it is in the process of publication; the first manuscript is in its final stages. We have presented these results on several occasions (oral: ECS 2002 Salt Lake City, DOE review in Washington 2002, Penn University 2003; poster: Gordon Conference Ventura Beach 2003, Electrochemistry Review ONR in Annapolis 2003). The interest in this catalyst material has led to number of collaborations. We have visited the Los Alamos Laboratories and General Motors to learn about their Fuel Cell experiences. We have signed Non Disclosure Agreements (NDA) with General Motors, E-tek and RPI.

Human Cytochrome P450 2B6: The Effect of Single Site Mutations on the Oxidation of the Anti-Depressant Bupropion

Researcher: Assistant Professor Tammy L. Domanski
Sponsor: Naval Academy Research Council (NARC)

The long-term goal of this research is to elucidate the mechanism of action of cytochromes P450 (CYP) and determine their role in xenobiotic metabolism with a particular focus on understanding human members of this superfamily at the molecular level. Although once thought to have only a minor role in metabolism in the human liver, additional CYP2B6 substrates have been identified, including the anti-cancer agent cyclophosphamide and the anti-depressant bupropion, providing evidence that CYP2B6 is of clinical relevance. Thorough analyses have been conducted with rat 2B1, rabbit 2B4 and 2B5, and canine 2B11, but human 2B6 displays a very different substrate specificity and pattern of expression. Consequently, it has been difficult to make accurate predictions concerning the function of CYP2B6 from what is known of other species.

Previously, a series of CYP2B6 mutants were generated in the first study of CYP2B6 substrate specificity. In that study three substrates, androstenedione, 7-ethoxy-4-trifluoromethylcoumarin (7-EFC), and 3-cyclopentyloxy-N-(3,5-dichloro-4-pyridyl)-4-methoxybenzamide (RP 73410), were utilized to characterize the function of the panel of thirteen CYP2B6 mutants. The results of the study suggested that two CYP2B6 amino acid residues, phenylalanine at position 107 and leucine at position 363, play a role in substrate selectivity.

Bupropion is an anti-depressant that is also prescribed for smoking cessation. CYP2B6 has been reported to be the major bupropion oxidizing enzyme in humans. However, other than modeling predictions, there is no data concerning the CYP2B6 bupropion binding site. In this study, bupropion hydroxylation assays were performed. The activity associated with each mutant was compared to the 7-EFC O-deethylase activity. Nineteen separate CYP2B6 mutant protein samples were analyzed in this study. In general, the rate of bupoprion hydroxylation observed in this study was lower than previously published. However, when comparing the relative rate of hydroxylation by each mutant to the level demonstrated by the wildtype 2B6, one mutant containing a single amino acid substitution from leucine to valine at position 363, was of particular interest. This mutant displayed a near three-fold increase in activity. In a previous study utilizing a different substrate, the same mutant displayed decreased activity toward the substrate. The new findings suggest a very specific and subtle role for leucine 363 in determining the proteins ability to effectively metabolize a substrate. In light of the widespread use of bupropion, the possibility that polymorphisms, natural mutants found in the population, affect the metabolism of this drug *in vivo* can not be ignored.

Molecular Dynamics Simulations of Shock Processes in Hydrocarbons

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

Computer simulations can be used to study molecular-level events resulting from the passage of shock waves through condensed materials. Due to the high speed and destructive nature of shock wave and detonation processes, details of shock wave structure and reaction kinetics are not readily accessible to experimental measurement. Over the past decade, methods have been developed to accurately but rapidly simulate the forces between carbon and hydrogen atoms in reactive systems, making it possible to conduct large-scale molecular dynamics simulations of shock-induced chemistry in hydrocarbons.

Simulations were conducted to analyze shock-induced chemical reactions in the condensed phases of representative small hydrocarbon molecular systems, including solid acetylene, ethylene, and methane. These molecules were chosen in part because of their astrophysical significance. Polymerization and other reactions of hydrocarbons induced by the impact of meteors and comets may have an important role in the formation of complex organic materials in the solar system.

A reactive empirical bond order (REBO) potential for hydrocarbons, originally developed at the Naval Research Laboratory and extended during the past decade to include torsional effects and intermolecular forces, was employed to simulate shock-induced chemical reactions in solid acetylene, ethylene, and methane. Acetylene was found to undergo significant polymerization reactions for flyer plate impact speeds above 10 km/s. These conditions are similar to those which would be experienced upon planetary impact of comets, which are known to contain condensed-phase acetylene. Ethylene exhibits similar reactivity above 15 km/s. Methane undergoes hydrogen abstraction reactions at flyer plate impact speeds of 16 to 20 km/s and produces hydrocarbon chains at higher impact speeds. The latter results are significant for elucidating the fate of atmospheric methane upon cometary or meteor impact, and for predicting the initial reaction steps in the reactivity of methane ices in the high-pressure, high-temperature interiors of Neptune and Uranus.

Spectroscopic Studies of Ion-Irradiated N_2-Rich Ices

Researchers: Dr. Marla H Moore (NASA/Goddard), Dr. Reggie L. Hudson (Eckerd College), and Professor Robert F. Ferrante, (USNA; co-PI)
Sponsors: NASA/Goddard Space Flight Center; NASA Laboratory for Planetary Atmospheres Program; NASA Space Astrophysics Research and Analysis Program

Icy surfaces rich in nitrogen and containing some hydrocarbons are found on icy bodies near the outer edge of the solar system, such as Triton (a moon of Neptune) and Pluto, and are also possible in some interstellar environments.

These surfaces are subject to radiation processing by ambient sources, such as the solar wind, resulting in formation of numerous small nitrogen-containing molecules or ions, such as HCN, HNC, HNCO, NH_3, NH_4^+, CN^-, OCN^-, and resulting ionic salts. It is well understood that many of these molecules can serve as precursors to biomolecules, such as amino acids and peptides, even at low temperatures. Documentation of the presence and concentrations of such species by near infrared (NIR) astronomical observations and, in the future, by space probes, is an ongoing endeavor. We have a unique experimental setup which permits the formation and preservation of ice samples of known composition at pertinent temperatures (10K–100 K), with provision for MeV proton-beam irradiation, VUV photolysis, and NIR and IR analysis of the products, including high-temperature residues. We are continuing to study the production of such species as a function of ice concentration, temperature and irradiation dose, with the aim of modeling the conditions and reaction mechanisms responsible for their formation in the astrophysical system, and predicting the conditions most favorable for formation of biologically significant compounds.

Antimalarial Chalcones

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

A project was initiated in collaboration with the Walter Reed Army Institute of Research (WRAIR) to identify antimalarial azachalcones with sufficient in vitro potency to warrant in vivo antimalarial testing.

Chalcones are known to exhibit antimalarial activity. One potentially interesting class of structures are the azachalcones, containing a heterocyclic B-ring. However, with only one isolated example it is impossible to understand the influence of the various groups of the molecule on its antimalarial activity. Aldol condensations of various acetophenone and aldehydes were therefore used to synthesize the related analogs.

The analogs targeted were successfully synthesized at the Naval Academy, then assayed at WRAIR for their ability in inhibit the growth of Plasmodium falciparum, the causative agent of malaria. The minimum concentration of each analog required to inhibit Plasmodium growth by 50% is shown in the figure under the corresponding structure (IC50 values). Trends emerging are the relative unimportance of the position of the nitrogen, and the importance of methoxy substitution at the 2-, 3- and 4-positions.

In conclusion, a more potent analog has already been discovered, along with trends in activity which will be used to design even better compounds. This research work is on-going.

Molecular Dynamics Investigations of the Tribology of Diamond Surfaces and Films

Researchers: Dr. Ginger M. Chateauneuf (ONR Post-doctoral Fellow) and Associate 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 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 spiroalkanedithiols and a single structurally related normal alkanethiol chains bound to Au surfaces. Various surface science techniques were used to ascertain the order of the monolayers. These studies clearly show that the more ordered monolayer (more tightly packed)

has lower friction measured with the AFM. We have used our re-fit potential energy function to examine the friction of n-alkane chains on diamond with different packing densities. (This potential energy function has been published in the *Journal of Chemical Physics*.) Simulations show that the tightly packed monolayers (or more ordered) have lower friction than the loosely packed (less ordered) monolayers in agreement with the experimental trend. The origin of this difference in friction appears to be related to differences in carbon-carbon bond-length distributions. This work was published in the *Journal of the American Chemical Society*. An analysis of other system properties that are related to friction appeared in *Tribology Letters*.

Molecular Dynamics (MD) Investigations of the Friction and Tribology of Solid Lubricants

Researchers: Dr. Guangtu Tu Gao (AFOSR Post-doctoral Fellow) and Associate 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 conducted to investigate the atomic scale friction and wear when hydrogen-terminated diamond (111) counterfaces are in sliding contact with diamond (111) surfaces coated with amorphous, hydrogen-free carbon films. Two films, with approximately the same ratio of sp^3-to-sp^2 carbon, but different thicknesses, have been examined. Both systems give a similar average friction in the load range examined. Above a critical load, a series of tribochemical reactions occur resulting in a significant restructuring of the film. This restructuring is analogous to the ``run-in'' observed in macroscopic friction experiments and reduces the friction. The contribution of adhesion between the probe (counterface) and the sample to friction was examined by varying the saturation of the counterface. Decreasing the degree of counterface saturation, by reducing the hydrogen termination, increases the friction. Finally, the contribution of long-range interactions to friction was examined by using two potential energy functions that differ only in their long-range forces to examine friction in the same system.

NIRT: Multi-Scale Modeling and Simulation of Adhesion, Nanotribology, and Nanofluidics

Researchers: Dr. Mark O. Robbins, Dr. Jean-Francois Molinari,
and Dr. Shiyi Chen (The Johns Hopkins University),
Dr. N. Bernstein (Naval Research Laboratory),
and Associate Professor Judith A. Harrison
Sponsor: National Science Foundation (NSF)

This Nanoscale Interdisciplinary Research Team's (NIRT) goal is to develop modeling techniques that can be used over a wide range of length scales to model adhesion, nanotribology, and nanofluidics. The team brings together experts in finite element (FE) analysis (Molinari and Chen), molecular dynamics (MD) (Robbins and Harrison), and in coupling these techniques (Bernstein). Coupling course-grained (FE) and atomistic-scale (MD) techniques should allow one to study problems such as adhesion over very long, (*e.g.,* nanometer length) scales. Results from these nanometer length-scale simulations should be directly comparable to experimental devices, such as, microelectromechanical systems. For the past academic year, Prof. Harrison has been working on this project at The Johns Hopkins University.

Investigations into the Effects of Tripodal Ligands on Transition Metal Environments

Researcher: Associate Professor JudithAnn R. Hartman
Sponsor: American Chemical Society Petroleum Research Fund B

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. To deconvolute the podand effects from the linked-chelate effects, we have synthesized a series of linear (pyridyl) amino ligands and podands that contain different permutations of ethyl and propyl linkages to give both 5- and 6-membered chelant rings. We have synthesized a series of the Ni(II) and Cu(II) complexes of theses ligands and have been exploring their electronic and structural properties in the gas, liquid, and solid phases. We have completed our work with the complexes that contain only 5-membered chelant rings and have extended our work to include complexes that contain 5- and 6-membered, and only 6-membered chelant rings. In addition, since our gas phase method involves a comparison of the reactivity of the complexes with a series of monodentate ligands such as pyridine, we plan to isolate and determine the crystal structures of the metal complex·pyridene reaction products in order to better understand our gas-phase results.

Influence of Supramolecular Confinement upon Photoinduced Intramolecular Charge-Transfer in Transition Metal Donor-Acceptor Complexes

Researcher: Associate Professor William B. Heuer
Sponsor: Naval Academy Research Council (NARC)

Highly polarizable transition metal complexes possessing intense metal-to-ligand charge transfer (MLCT) absorptions are of interest owing to their potential applications as nonlinear optical (NLO) materials, molecular sensors and sensitizers for photovoltaic cells and photocatalytic solar energy conversion. The efficiency of photovoltaic cells is determined by the lifetime of the charge-separated state arising from photoexcitation, which is in turn determined by the rate of back electron transfer from the reduced acceptor back to the oxidized donor. This project explores the use of supramolecular complexation by amylose as a means of stabilizing the photoinduced charge-separated state in donor-acceptor (D-A) hybrid molecules having a photosensitive *tris*-(2,2'-bipyridine)ruthenium(II) donor complex, $[Ru(bpy)_3]^{2+}$, covalently linked through a saturated hydrocarbon bridge to a N,N'-dialkyl-4,4'-bipyridinium (viologen) acceptor group. A series of 2,2'-bipyridine (bpy) ligands bearing viologen groups linked through a five-carbon (C_5) tether to an alkyl-substituted viologen group have been synthesized. Alkyl groups of different lengths (C_8, C_{12} and C_{16}) are appended to the viologen unit, giving the ligands amphiphilic properties. Reaction of these ligands (L^{2+}) with dichloro-*bis*-(bpy)ruthenium(II) followed by counterion metathesis with KPF_6 in acetone yields $[Ru(bpy)_2L]^{4+}$ D-A complexes as the PF_6^- salts. The composition of these complexes has been verified using MALDI-TOF mass spectrometry. Supramolecular complexes formed between

these D-A molecules and amylose (a purified form of starch) in dimethylsulfoxide (DMSO)-water mixures have been studied by UV-VIS absorption spectroscopy, luminescence spectroscopy and cyclic voltammetry. Results of these studies suggest that interaction with amylose induces a more extended conformation of the D-A conjugate, increasing the D-A distance and consequently decreasing the efficiency of the intramolecular electron transfer (ET) quenching of the excited Ru(II) luminophore by the tethered viologen. Future studies of dynamic intramolecular ET rates by laser flash photolysis, which may provide a direct measure of the enhancement of the lifetime of the photoinduced charge-separated state upon amylose complexation, are planned.

Synthesis of Radiotracers for the Study of the Nicotinic Acetylcholine Receptor

Researcher: Associate Professor Christopher M. Kinter
Sponsor: Division of Nuclear Medicine and Radiation Health Sciences, The Johns Hopkins University

The endogenous cholinergic neurotransmitter, acetylcholine, exerts its biological effect via two types of cholinergic receptors: the muscarinic acetylcholine receptor (mAChRs) and the nicotinic acetylcholine receptors (nAChRs). Considerable effort has been directed at identification and characterization of ligands for nicotinic acetylcholine receptors. The interest in these compounds stems in part from evidence that agents acting at this receptor may have therapeutic utility in the treatment of a variety of central nervous system disorders including Alzheimer's and Parkinson's diseases, attention deficit or hyperactivity disorders, Tourette's syndrome and depression. Additionally, this receptor has been implicated in a variety of central processes such as learning, memory, and the relief of pain. Several potential compounds have been identified for use in the study of the nicotinic acetylcholine receptor and efforts have been directed towards their synthesis and radiolabeling with positron emitting isotopes.

New Synthetic Approaches to Geminal Difluoramino Compounds

Researcher: Associate Professor Christopher M. Kinter
Sponsor: Naval Surface Warfare Center (NSWC), Indian Head Division

The overall goal of the research effort is to provide efficient synthetic routes to high energy oxidizers that contain nitramine-gem difluoramine functionality. These compounds have been chosen as reasonable synthetic targets due to results in theoretical and experimental studies.

The classical method for the introduction of gem-difluoramino substituents into organic compounds relies on the reaction of difluoramine (HNF_2) with a ketone under strongly acidic reaction conditions. This method can suffer from the relatively harsh reaction conditions that are required, long reaction times, and the incompatibility of heterocyclic precursors with the acidic conditions. As such, alternate approaches for the production of organic compounds containing gem-difluoramino groups are currently being investigated.

One alternate method for the production of gem-difluoramino compounds that we are currently exploring relies on the reaction of carbamates or amides with elemental fluorine. These reaction conditions have previously been shown by Grakauskas and Baum to produce alkyl difluoramino products. This method is advantageous as it avoids the use of explosive difluoramine and does not require the highly acidic oxidizing conditions of the classical method. However, as the required gem-dicarbamates are difficult to prepare, we are exploring the use of vicinal substituted diaziridines as structural equivalent to gem-dicarbamates.

A DFT/RRKM Study on $RuSO_2$

Researcher: Associate Professor Roy E. McClean
Sponsor: Naval Academy Research Council (NARC)

A density functional theory/RRKM Study on $RuSO_2$ is reported. The objective of this work was to calculate the third order association rate constant, k_{assoc}, for the reaction $Ru + SO_2 + Ar \rightarrow RuSO_2 + Ar$ $k_{assoc} = k_{dissoc}/K_{eq}$ at 298K, where k_{dissoc} is the dissociation rate constant of $RuSO_2$ and K_{eq} is the equilibrium constant. This work is important in determining the mechanism of SO_2/transition metal interaction and is of interest because of the role SO_2 plays as a air pollutant.

The Gaussian 98 suite of programs was used for the DFT calculations. They were run on Poseidon, a unix-based computer in the Division of Engineering & Weapons at USNA. The well documented B3LYP model (a hybrid of Hartree Fork theory and DFT) was used. The LANL2DZ basis set was employed because the complex contains a second-row transition metal. With this model, electrons near the nucleus are treated via effective core potentials which include some relativistic effects.

The optimized geometry for quintet $RuSO_2$ has c_{2v} symmetry and lies 70 kcal/mol below the $Ru(a^5F_5) + SO_2(X^1A_1)$ asymtote (at this level of theory). Other stable structures were not found on the quintet surface. k_{dissoc} was calculated from unimolecular rate theory (RRKM), and K_{eq} from statistical mechanics. Vibrational frequencies, rotational constants, and other molecular parameters of $RuSO_2$ that were needed were obtained from the DFT results. Combining K_{eq} and k_{dissoc}, the value $k_{assoc} = 6.4 \times 10^{-28}$ cm^6 molecule^{-2} s^{-1} at 298 K is obtained. This value is based on a dissociation energy (with necessary zero-point energy corrections) of 70 kcal/mol and is in line with other transition metal/SO_2 systems. k_{assoc} is only an order of magnitude estimate; it depends on the binding energy which could be off by ±20 kcal/mol. The value of k_{assoc} is expectedly large and indicates that Ru has the potential of effectively removing SO_2. (Transition metal atoms with valence s^1 orbital occupancies are expected to be very reactive.)

Future plans include experimentally measuring k_{assoc} by a laser photolysis/laser-induced fluorescence technique. This work is on hold until the laser lab is up and running.

Development of a Fluorescence Assay for Inosine in Messenger RNA

Researcher: Assistant Professor Daniel P. Morse
Sponsor: Naval Academy Research Council (NARC)

Inosine in messenger RNA is produced by RNA editing enzymes called adenosine deaminases that act on RNA (ADARs). The long-range goal of this project is to develop a simple and rapid method to measure the total amount of inosine in cellular mRNA. To achieve this goal, I will develop a new approach for selecting RNA molecules (called "beacon aptamers") that act as sensitive sensors for small molecules such as inosine.

A beacon aptamer is an RNA molecule that fluoresces upon binding its ligand. Fluorescence results from a ligand-induced conformational change that separates covalently attached fluorophore and quencher that were in close proximity in the unliganded RNA. Previously, beacon aptamers have been produced in two steps. First, molecules that bind to a target are selected from a randomized pool of RNA (such RNAs are called, "aptamers"). Second, a fluorophore and quencher are covalently attached to regions of the RNA that are in close proximity. The resulting molecules are tested for an increase in fluorescence in the presence of ligand.

To facilitate the production of effective beacon aptamers, a one-step method that will simultaneously select RNA molecules that bind to a target and undergo the appropriate conformational change was tested. A "proof-of-principle" experiment was conducted by using the antibiotic tobramycin as the target. Preliminary data suggested that the selection protocol successfully enriched for tobramycin aptamers. If fully successful, the selection method can be used to produce beacon aptamers to any small molecule of interest (including inosine). Beacon aptamers will be useful to researchers in a variety of fields including biochemistry, medicine, environmental science, and forensics.

Gas Phase Measurements of Hydrogen Peroxide, Methylhydroperoxide, and Formaldehyde during TRACE-P

Researchers: Associate Professor Daniel W. O'Sullivan (co-PI)
and Dr. Brian G. Heikes (PI; University of Rhode Island)
Sponsor: National Aeronautics Space Administration (NASA)

Measurements of gas-phase hydrogen peroxide, methylhydroperoxide, and formaldehyde on board the NASA DC-8 aircraft were taken as part of the NASA/GTE TRACE-P mission during the Spring of 2001. These chemical compounds are involved in the chemical reactions leading to tropospheric oxidants and ozone formation in the lower troposphere. These species act as sources of odd-hydrogen and odd-oxygen radicals, as reservoirs of these radicals, and as conductors in their loss. The target species are coupled to the gas-phase and, more significantly, to the heterogeneous chemistry of sulfur dioxide and its

oxidation to sulfuric acid. The species to be measured provide mechanistic insight and chemical constraints to chemical model simulations and provide an additional measure of confidence in their results. Multi-dimensional space-time models suggest that atmospheric motions, the vertical transport and mechanical redistribution of the hydroperoxides, may have a profound effect on odd-O and odd-H chemistry in the upper troposphere. The hydrogen peroxide, methylhydroperoxide, and formaldehyde measurements added needed information on transport, chemical redistribution, and scavenging by cloud and precipitation systems. The data collected during the field phase of this project were finalized and submitted to the NASA GTE data archive in December 2001. The data became available to the public through the NASA GTE archive in January 2002. Measurement distributions and correlations with other species have been examined with respect to air mass characterization and cloud processing. Analysis and interpretation of our measurements with respect to tropospheric oxidants, net oxidant production, and sulfur gas oxidation is underway and will be performed collaboratively with other members of the science team using our own and more sophisticated meteorological transport and photochemical models. Long term changes in the distribution of peroxide species in the Pacific troposphere using data from five GTE mission over the last ten years were also examined.

Examination of the Relationship between Photochemical Peroxide Production and Chromophoric Dissolved Organic Matter (CDOM) Alteration in Chesapeake Bay Waters

Researcher: Associate Professor Daniel W. O'Sullivan

Sponsors: Office of Naval Research (ONR) and Naval Research Laboratory (NRL) via cooperative agreement

The goal of this work is to develop a quantitative understanding of the relationships between measures of photochemical transformations in CDOM, for example loss of absorbance or fluorescence, and peroxide production in surface waters from the Chesapeake Bay.

An analytical technique for the determination of gas phase hydoperoxide concentrations was modified for work in surface waters of the Chesapeake Bay. Surface seawater samples were collected in acid cleaned glass vials or PFA Teflon vials and analyzed immediately. If the samples could not be analyzed immediately they were frozen to preserve the peroxides for later analysis. The peroxide content of the samples was determined after thawing to room temperature using the modified high performance liquid chromatographic (HPLC) fluorometric method. Surface seawater samples for peroxide analysis and seawater for laboratory photolysis experiments were collected on two research cruises on the R/V Cape Henlopen from 3 – 6 June and 3 – 6 September 2002. Surface seawater samples were collected periodically from the flowing seawater line on the R/V Cape Henlopen, filtered through a 0.20 μm filter and analyzed immediately, during the June cruise. Samples were also collected from CTD casts during this cruise. During the September cruise samples were collected from CTD casts and deck board photolysis experiments. These samples were frozen after filtration through a 0.20 μm filter, for later analysis in the laboratory. Filtered surface water samples from several locations in the Chesapeake Bay with varying levels of CDOM were irradiated in a solar simulator to determine the wavelength dependence of peroxide production, and the relationship between peroxide production and CDOM optical property changes. Preliminary result suggest that more humic waters produced substantial amounts of HP and MHP, the latter being, to our knowledge, the first data showing photochemical production of MHP in natural waters

Structural Studies of Single-Point Mutants of the DNA-Binding Domain of the Yeast Heat Shock Transcription Factor (HSF)

Researchers: Assistant Professor Jamie L. Schlessman
and Dr. Hillary C. M. Nelson, University of Pennsylvania School of Medicine,
Department of Biochemistry and Biophysics (Philadelphia, PA)

Sponsor: Naval Academy Research Council (NARC)

The heat shock transcription factor (HSF) regulates expression of numerous heat shock proteins in response to a variety of cellular stresses, including heat. These heat shock proteins work as molecular chaperones to prevent protein misfolding, maintain correct protein folding, or repair misfolded proteins. HSF exists in an inactive or low-activity state in the absence of stress, but quickly switches to a highly active transcriptional activator when stress is sensed. HSF consists of several distinct functional domains, including a central DNA-binding domain (DBD, designated HSF(260-583), corresponding to amino acid residues 260-583 of the 833-residue full-length HSF). Details of how HSF functions are poorly understood, but are believed to relate, in part, to its ability to bind to its specific DNA promoter sequence. Previous protein crystallographic studies of the HSF DNA-binding domain from yeast revealed its atomic structure (Harrison, Bohm and

Nelson (1994) *Science* 263: 224-227). Subsequent genetic and biochemical studies have identified a population of single amino acid mutations within the DNA-binding domain that significantly affect transcription levels without disrupting HSF protein expression levels (Bulman, Hubl and Nelson (2001) *Journal of Biological Chemistry* 276: 40254-40262). These amino acids are distributed throughout the surface of the DNA-binding domain, suggesting a complex mechanism of HSF regulation. In order to understand better the molecular basis of this regulation, I propose to determine the crystal structures of several of the DNA-binding domain mutants. These atomic structures will be compared with that of the wild-type protein and correlated with existing genetic and biochemical data for the proteins to provide a structural database.

Crystallization experiments of several single-point mutants of DBD have been initiated at USNA. These mutants have been selected from a group of six that displays reduced growth phenotype: Lysine-178 (K178A), Aspartate-185 (D185A), Arginine-206 (R206A), Asparagine-222 (N222A), Histidine-236 (H236A), and Lysine-237 (K237A). These mutant DBDs have been characterized by mass spectroscopy and circular dichroism (CD) (Bulman, Hubl and Nelson (2001) *Journal of Biological Chemistry* 276: 40254-40262). CD spectra of several mutants suggest a change in secondary structure that would necessitate high resolution structural studies. As a starting point for the USNA studies, single crystals of the wild-type protein were obtained. During summer 2003, diffraction-quality crystals for mutants N222A and H236A were obtained. Successful candidate crystals will be taken to the University of Pennsylvania School of Medicine for x-ray diffraction analysis.

Synthesis and Characterization of Polydimethylsiloxane Star Polymers

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

Silicone polymers are utilized in products ranging from elastomers to lubricating oils to adhesives. Characterizing the behavior of these materials can lead to improvements in their synthesis and application. This project focuses on the synthesis and characterization of simple star geometries of polydimethylsiloxane (PDMS), the most common silicone polymer. Linear PDMS chains of known molecular weight containing a single vinyl-terminated end group were utilized. Their chain sizes included those above and below the entanglement molecular weight for PDMS. In the presence of a platinum catalyst, the vinyl-terminated end of the PDMS chains reacted with the active sites of the crosslinking agent. By using trifunctional and tetrafunctional crosslinking agents, model 3-arm and 4-arm star polymers were synthesized at room temperature in the absence of solvent. A dramatic increase in the viscosity of the sample was observed upon reaction. Gel permeation chromatography (GPC) studies indicated a mixture of molecular sizes in the samples. Separation procedures to isolate the star polymer are currently being conducted in hopes of ultimately studying the effects of branching on the conformational dynamics of PDMS systems.

Characterization of New High-Performance Polycarbonates

Researchers: Associate Professor Maria J. Schroeder, and
Associate Professor John T. Bendler (USNA Physics Department)
Sponsor: Department of Defense (DoD), U.S. Army Research Office (ARO)

The United States Army is currently investigating the development of new synthetic polymers for use in transparent armor and coatings applications. Novel synthesis procedures have been developed for 1,1-dichloro-2,2-bis[4'-(4-hydroxyphenyl)phenyl]ethene and bis[4'-(4-hydroxyphenyl)phenyl]propane monomers which have been incorporated into new polycarbonate polymers. With the aid of molecular modeling, these materials have been designed to provide greater impact resistance, processability, heat resistance, and chemical stability over the current polycarbonate materials. Characterization studies of these new polymers have included thermal analysis by differential scanning calorimetry (DSC) and molecular weight determinations by gel permeation chromatography (GPC). This project included synthesis and characterization of new polycarbonate materials, in the hope of determining the origin of their enhanced properties and advancing the development of high-performance materials for military applications.

Structural Investigation of the Ligand-Binding Properties of the Chaperone Protein Secb of *Escherichia Coli*

Researcher: Assistant Professor Virginia F. Smith
Sponsor: Dr. Linda L. Randall, 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 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. We exploited our knowledge of the three-dimensional structure of SecB to obtain information about the mechanism by which SecB recognizes the proteins it binds to and determine how it prevents them from aggregating or becoming degraded. Using chemical crosslinking and high-resolution separation techniques, we investigated the ligand-binding mechanism of SecB in order to obtain a detailed picture of the protein-protein interactions that confer protection.

Enzymatic Repair of Proteins Damaged by Oxidation

Researcher: Assistant Professor Virginia F. Smith
Sponsor: Cottrell College Science Awards, Research Corporation, Tucson, AZ

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) has 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, protein folding methods are 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.

Effects of Fluorine Substitution on the Conformational Preferences and Intermolecular Interactions of Organic Compounds

Researcher: Associate Professor Joseph J. Urban
Sponsor: 2002 Kinnear Fellowship

This research involves a computational investigation of several model fluorinated organic compounds that have been chosen to allow for an assessment of the effects of fluorine substitution on the electronic distribution, conformational equilibria, and intermolecular interactions of the parent compounds. The motivation for this work stems from the fact that fluorination of organic compounds is an attractive strategy for manipulating the electronic properties of organic compounds without a large steric penalty for subsequent use in the polymer and medicinal chemistry fields. It is typically assumed that substituting a fluoro group for a hydrogen or hydroxyl causes a very small perturbation in the size of an organic compound. However, there are data in the literature to suggest that the electronic effects mediated by flouro substitution can have unavoidable conformational consequences. Thus, while the small size of fluorine is attractive, there may be factors which cause the shape (conformation) of the parent compound to be significantly altered. This can have implications in medicinal chemistry where the size and shape of a compound are crucial in determining its activity and in the polymer industry where size and shape can impact reactivity, chain-chain interactions, and macroscopic properties of a polymer.

Natural Product Antifouling Coatings Based on the Controlled Delivery of Biofouling Repellents

Researchers: LT Eric R. Welsh, USNR and Mr. Ronald R. Price (Naval Research Laboratory)
Sponsor: Naval Research Laboratory (NRL)

The scope of this research is to design and develop antifouling coatings that use an active agent derived from seaweed in a controlled-release system composed of an entrapping agent and a bio-derived polymer with adjustable degradation properties.

Significant progress has been made in the scale-up and synthesis of the active agents, known as furanones, polymer (chitosan), and a cross-linker. Initial controlled release studies of the active agent from the entrapping system have been conducted and further investigations are under way. Test panels of initial prototypes were tested for antifouling ability in Australia and failed after 4 months exposure. A second round of testing is scheduled to start on new panels with new formulations in Key West, Hawaii, and the Chesapeake. Studies on the cross-linking system have yielded 1 publication in *Biomacromolecules*, 1 publication accepted for publication in *Carbohydrate Polymers,* which derived from a collaborative effort with researchers at NIST on chitosan hydrogels, and 2 additional manuscripts have been submitted to *Biomacromolecules* and *The Journal of the American Chemical Society.* Recently, significant progress has been made on coating systems and on grafting the active agent onto chitosan.

New Approaches to Organic Materials for Photovoltaic Applications

Researcher: Associate Professor Craig M. Whitaker
Sponsor: Office of Naval Research (ONR) in collaboration with the Naval Research Laboratory (NRL)

The last two years have seen an extraordinary growth of interest in photovoltaic (PV) cells made from organic conducting polymers. Organic materials are attractive for photovoltaics devices primarily due to the prospect of manufacturing ultra thin, flexible devices. Polymeric photovoltaic cells also present a tantalizing possibility for producing coatings that function as sunlight-harvesting paints on roofs or even as an integral part of fabrics to produce electricity from sunlight. This project focused on the design, synthesis, and characterization of a novel electron-transporting monomer. The first example of an electron-transporting monomer and a light-harvesting unit covalently attached together was completed, and this material is the precursor for a new conducting polymer system.

Independent Research

Synthesis and NMR Spectral Characterization of Menthol Derivatives

Researcher: Associate Professor Debra K. Dillner

Menthol derivatives have been gaining use as chiral auxiliaries, which are groups used as ligands or easily removable subunits. These derivatives are used to introduce chirality into other, less easily accessible molecules. Several such auxiliaries have been previously synthesized and their purported nuclear magnetic resonance (NMR) assignments have been published by other groups. Details of these spectral assignments are elucidated in this project. Specifically, menthyl carboxylic acid and it's epimer, neomenthyl carboxylic acid, are being synthesized by new routes. Once these two compounds were synthesized, extensive NMR spectral data was collected. Complete assignment of all peaks and coupling constants of these compounds and their synthetic precursors are underway, in collaboration of Dr. Daniel M. Traficante, currently Chemistry Chairman at Naval Academy Preparatory School (NAPS) in Rhode Island.

Analysis of a Heat Shock Protein from Sulfolobus Solfataricus

Researchers: Assistant Professor Tammy L. Domanski,
and Dr. Harold Schreier and Dr. Frank Robb, Center of Marine Biotechnology, Baltimore, MD

Genetic manipulation of the archael thermophile *Sulfolobus solfataricus* was conducted to clone and express a small heat shock protein. The bacteria was successfully cultured and maintained at temperatures exceeding 70 degrees Celsius. In addition, two separate vectors were analyzed to determine which would be more suitable for use, due to the inconsistent results obtained when attempting to maintain vectors in *S. solfataricus*. One vector was successfully maintained within the bacterium and cloning studies were initiated. Further analysis will be necessary to study the persistence of the vector and to determine if the DNA of interest was, in fact, cloned into the vector.

Antibacterial Chalcones

Researcher: Assistant Professor Clare E. Gutteridge

An independent project was initiated to identify chalcones able to selectively inhibit the growth of *Staphylococcus aureus* and to simultaneously develop a research-based laboratory program, suitable to complement an upper-level medicinal chemistry lecture course.

Synthesis of some known antibacterial chalcones was proposed to determine the suitability of the synthesis for an undergraduate teaching laboratory. The desired compound was synthesized in two steps – an aldol condensation (1 hour reaction, aqueous work-up, followed by silica column chromatography) and in a second step via an N-alkylation (overnight reflux, solvent evaporation, silica column chromatography). The procedure was deemed suitable for undergraduate hands. A second molecule is being considered for study, and the antibacterial assay will be developed by an undergraduate research student during the fall semester 2003. The successful synthesis and assay procedure will be used to showcase drug discovery in a medicinal chemistry special topics course to be offered in the spring semester 2004 (SC486H).

Molecular Dynamics Simulations of the Bending of Filled Carbon Nanotubes

Researchers: Dr. Susan Sinnott, (University of Florida), Dr. Boris Ni, (University of Florida), Assistant Professor Paul Mikulski (USNA Physics Department), and Associate Professor Judith A. Harrison

The overall goal of this project is to examine the mechanical properties of carbon nanotubes. Nanotubes are filled with CH_4, C_{60}, and Ne. Mechanical properties as a function of filling gas, tube length, and temperature have been examined. This collaboration just resulted in a publication in *Physical Review Letters*.

Synthesis of Polythiophene-Containing Block Copolymers from Ring-opening Metathesis of Cyclobutenediones

Researcher: Assistant Professor Shirley Lin

One of the challenges of polymer chemistry is the synthesis of new, multifunctional materials with desirable properties. The properties of many homopolymers, polymers composed of a single type of monomer unit, are known. One way to create multifunctional polymers is through the selective combination of different monomers. Recently, the development of block copolymers, polymers in which one segment, composed of only one monomer, is attached to another segment composed of another monomer, has led to a wealth of materials with multiple desirable properties.

This project involves a new synthetic route to block copolymers containing poly(thiophene), an electrically conductive polymer useful in the fabrication of molecular electronic and optical devices. Unlike conventional syntheses of block copolymers containing poly(thiophene), which involve more than one polymerization method, we propose to create the thiophene units through post-polymerization modification of another polymer. Specifically, we propose to investigate the ring-opening metathesis polymerization (ROMP) of a highly-strained monomer, cyclobutenedione, that would result in a polymer containing 1,4-carbonyl functionality capable of cyclization into thiophene units. Given the versatility of recently developed ROMP catalysts, this route to block copolymers containing poly(thiophene) should lead to the development of entirely novel materials.

Laboratory space and equipment suitable for accomplishing this project was established. Some trial syntheses of 3-phenyl-3-cyclobutene-1,2-dione were conducted.

Web-Based Data Analysis and Feedback for General Chemistry Laboratory: Improving Analysis with Timely, Distance Feedback: Advances

Researchers: Associate Professor Joseph F. Lomax and Associate Professor Debra H. Dillner

The Midshipman Online Laboratory System (MOLS) is a web-based system that allows students to input their numerical data and analysis. To give the students direct and immediate feedback, an error flag visually indicates a calcula-

tion error. Instructors can use the input values to evaluate student work thus providing a valuable tool to speed grading. The system has over 15 general chemistry labs and as an assessment performed by Capt Melonie Teichert, USAF has shown, it has been well received by the hundreds of students and two dozen faculty who have used it over the last three years. Additional laboratory experiments have been added to MOLS. Improvements have been made in the structure of the programs.

Solid State Synthesis: Host Synthesis and Intercalation Chemistry: An Undergraduate Inorganic Chemistry Laboratory

Researchers: Associate Professor Joseph F. Lomax
and Mr. Matthew Schroeder, Chemist (USNA Chemistry Department)

Solid state chemistry is important in electrochemical systems (batteries and fuel cells), catalysis and solid state semi-conductors. However, few solid state systems are investigated in the undergraduate laboratory. This is because 1) the most common analytical technique used is Powder X-Ray Diffraction (Powder XRD), 2) the original syntheses for these reactions often involve high temperature (over 700° C) reactions, and 3) most involve non-stoichiometric compounds. A solid state reaction class of high importance is intercalation. An intercalation is a reaction where the basic structure of a solid is maintained during a chemical reaction. Though some hosts are commercially available, synthesis of the host can be very instructive. The high temperature reactions are often difficult and unreliable, but the synthesis of a metal disulfides of Groups IV and V are reasonably straight-forward to run with the proper equipment. One low temperature (refluxing water) host synthesis is the formation of $VOPO_4 \cdot 2H_2O$. Recent developments in the field show that mild reducing agents such as sodium borohydride and potassium iodide are often sufficiently strong to effect intercalation at slightly elevated temperatures (<100°C). In this project, we refined and extended this work. New difficulties with the PXRD presented themselves and further refinement should lead to publication.

Effects of Pre-Class Preparation and Reading Quizzes On Student Study And Learning

Researchers: Captain Melonie A. Teichert, USAF, Assistant Professor Dianne J. Luning-Prak,
Assistant Professor Jamie L. Schlessman, Assistant Professor Jane E. Smedley,
Assistant Professor Tammy L. Domanski, Associate Professor Wayne H. Pearson,
Assistant Professor William F. Stephen and Lieutenant Tracey T. Hoffman, USNR

One of the most important ways that instructors can impact student achievement is their use of class time. Instructors often use valuable class time to discuss basic material covered in the textbook because students do not read the text or prepare in any way before attending class. This study required students to read the text book to prepare for class so that class time could be spent on more cognitively advanced activities. Instructors encouraged advanced preparation by giving open-note quizzes on the text readings before the material was covered in class. We have investigated the use and effects of reading quizzes over three separate semesters (summer 2001, summer 2002, and fall 2002) and with eight different instructors. Data on instructor feedback, student pre- and post-surveys of study habits and attitudes, and course materials are currently being analyzed to assess the influence of student preparation on success in chemistry and our methods of encouraging student preparation.

A DFT Study on $FeSO_2$

Researcher: Associate Professor Roy E. McClean

A computational study on isomers of $FeSO_2$ using density functional theory (DFT) is reported. The objective of this work was to determine which isomer is the likely product (initially) of the $Fe(a^5D_4) + SO_2(X^1A_1)$ association reaction (gas phase) on the quintet surface.

The Gaussian 98 suite of programs was used for the computations. They were run on a Pentium III personal computer and on unix-based computers at USNA. The B3LYP model was used. Basis sets employed were 6-311G(2d) for S; 6-311G(d) for O, and 6-311+G(d) for Fe. This computational method was optimal in terms of cost and accuracy.

The $\eta^2_{O,O}$ isomer is the global minimum at 24.4 kcal/mol below the Fe + SO_2 asymtote. We were unable to find a stationary point with an $\eta^2_{S,O}$-type coordination; the geometry always transformed into an η^1_O-type isomer with an unstable wavefunction. Stationary points were found for the other isomers, with results indicating that the $\eta^3_{O,S,O}$ and η^1_S isomers are

transition states on the potential energy surface and therefore, cannot be the product of the Fe + SO_2 reaction. A population analysis indicates that the occupancy of the 4s orbital of Fe changes from $4s^2$ in the isolated atom to $4s^1$ in the association complexes. There is also some charge transfer from Fe to SO_2. As the association complex becomes more stable, the degree of charge transfer increases.

RRKM calculations were performed on the Fe + $SO_2 \rightarrow FeSO_2$ reaction to determine which isomer is the primary product. The molecular parameters needed for $FeSO_2$ were obtained from the DFT work, and molecular parameters needed for Fe and SO_2 were obtained from standard literature sources. Using the experimentally determined activation energy (determined previously in the laser lab at USNA) in the calculations indicate that the $\eta^2_{O,O}$ isomer is the primary product of the reaction. Thus, we conclude that Fe reacts with SO_2 via a termolecular reaction to produce a coordination complex where the Fe is bonded to the two O-atoms in a c_{2v}-type structure.

Accommodation of Electrostatic Charge within Proteins: Crystallographic Studies of Staphylococcus Nuclease Mutants

Researchers: Assistant Professor Jamie L. Schlessman and Dr. Bertrand Garcia-Moreno,
The Johns Hopkins University, Department of Biophysics (Baltimore, Maryland)

The thermodynamics of protein stability involve a complex set of interactions between protein and solvent and within the protein itself. Traditional explanations for protein stability rely on entropic considerations in which hydrophobic amino acids are separated from the polar solvent (water) by burying them in the protein core, and hydrophilic amino acids are located on the protein surface where they may interact with polar solvent molecules. Any charged amino acids found in the protein interior generally form salt bridges, interact with internal water molecules, or form part of the active site. Introduction of an electrostatic charge within the protein core might be expected to destabilize the protein and lead to protein unfolding, yet charges form and are transferred within a protein's interior in countless biochemical processes including signal transduction and electron transport. Understanding this apparent contradiction could have general application to nearly all biochemical systems.

To understand how proteins accommodate internal electrostatic charge, systematic mutations of neutral amino acids throughout the core to either lysine (+) or aspartate (-) were made within hyperstable variants of the protein *Staphylococcal* nuclease. These hyperstable variants are used to provide a background (or "wild-type") protein with enhanced stability such that subsequent mutations result in proteins that are more likely to remain in a globally folded state. Intriguingly, the vast majority of resultant proteins were expressed in *E. col*i successfully. Of 25 amino acids mutated to lysine or glutamate (50 individual mutations), only 3 failed to fold globally. Each folded nuclease mutant has been studied *in vitro* using fluorescence and circular dichroism spectroscopies to determine its stability against heat-, acid-, or chemical- denaturation (using DDG), and clear differences from the "wild-type" hyperstable proteins were observed. Several sets of mutants, including those in which residue 66 or 92 was converted to either lysine or aspartate, have been studied crystallographically. Accommodation of the electrostatic charge appears to have taken two forms: (1) introduction of discrete water molecules near the mutated residue allows formation of ion-dipole interactions that stabilize the protein (these waters were not visible in the wild-type crystal structure); or (2) structural rearrangement of the protein (relative to the wild-type structure) to maximize favorable interactions with the introduced charge. Structural information is needed for numerous other nuclease mutants to serve as a baseline for explaining the spectroscopic data.

The crystal structure of a hyperstable variant of *Staphylococcal* nuclease with the valine at amino acid position 66 mutated to glutamate (denoted PHS/V66E) collected at -160 ^{o}C had been determined previously and found to contain a network of ordered water molecules in the protein's interior. To address questions about the nature of ordered solvent molecules in the protein's interior under physiologically relevant conditions, we determined the structure at room temperature. Diffraction data from a single PHS/V66E crystal were collected at room temperature, then processed and scaled. Data were 97.7% complete to 2.1 Å resolution, with an R-merge of 0.070. Molecular replacement techniques using atomic coordinates from the cryo-temperature crystal structure were used to generate an initial protein model for the room-temperature data. Following initial coordinate refinement, excellent quality electron density maps were generated. Iterative rounds of model building and refinement yielded a final model with R-factor of 0.194 and R-free of 0.216 to 2.1 Å resolution.

The room-temperature PHS/V66E model contained amino acids 7 – 141, with one loop unmodeled due to conformational disorder (amino acids 45 – 53), and 31 water molecules. The average B-factor for the atoms in the model

was 34.8 Å^2. RMS deviation between the Ca atoms of the cryo and room-temperature coordinates was 0.45 Å, indicating strong agreement between the models. The room temperature model contained only 31 water molecules, while the cryo model contained 64 waters, consistent with expectations for a room-temperature experiment. Significantly, the cryo model contained a network of 4 water molecules near the mutated glutamate residue at position 66, while the room temperature model contained only 2 of those waters. The most interior and least interior waters were not seen in electron density maps for the room temperature model. The absence of the most interior water molecule is consistent with results from molecular dynamic modeling and NMR spectroscopies performed at room temperature, and resolves long-standing controversy between these techniques and the cryo-temperature model.

We have obtained diffraction-quality crystals of several other mutants of Staphylococcus nuclease, including L36K, T62K, and L125K, each expressed within a hyperstable "PHS" background. Diffraction data for PHS/T62K and PHS/L125K have been collected at -160°C, and structural determinations are underway. Crystallizations for 12 additional PHS mutants of nuclease have been initiated.

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.

Molecular Modeling Studies of Fluoroolefin Peptide Mimetics

Researcher: Associate Professor Joseph J. Urban

This research involves a computational investigation of several model peptide mimetics. A peptide mimetic is a compound that is designed to mimic the structural and electronic properties of a peptide, but has had its peptide bonds replaced by some other moiety that is not susceptible to cleavage by peptidase enzymes. The compounds focused upon in this work are peptide mimetics that incorporate a fluorolefin group as a replacement for the peptide bond. A series of model compounds has been chosen to be representative of both cis and trans peptides. The properties of greatest interest are the dipole moments, geometries, conformational preferences, electrostatic potentials, and hydrogen bonding of the mimetics and the parent peptides they are designed to mimic. Because fluorinated organic compounds can exhibit several subtle electronic effects, a careful approach is required where high level ab initio calculations on the smallest model compounds are carried out first to determine the basic properties of the fluoroolefin linkage and to provide the accurate data that is needed to parameterize molecular mechanics force fields for these types of systems. The preliminary results indicate that there are significant differences in dipole moment between the model mimetics and model peptides. The trend observed thus far is for the mimetics to have much smaller separation of charge and thus much smaller dipole moments than the corresponding peptides. The work is currently being extended to include studies at higher levels of theory and larger model systems.

Midshipman Research Course Projects

Lewis Acid / Base Interactions in Glyme-Based Solvents

Researcher: Midshipman 1/C Brett G. Bujac, USN
Adviser: Professor Graham T. Cheek

Lewis acid/base interactions have been investigated in glyme-based solvents using aluminum chloride and boron trifluoride as Lewis acids. Interactions of these Lewis acids with benzophenone and fluorenone were studied by cyclic voltammetry, using sodium tetrafluoroborate as supporting electrolyte. The complexation of the ketones with the acids was evident by the potential shift for ketone reduction; for example, fluorenone reduction in tetraglyme / 1 M $NaBF_4$ shifted from –1.77 V vs. ferrocene to –1.26 V after the addition of aluminum chloride. Benzophenone also exhibited a potential shift upon addition of boron trifluoride.

Antimalarial Activity of Methoxylated Naphthyl-Containing Chalcones

Researcher: Midshipman 1/C Joseph V. Vo, USN
Adviser: Assistant Professor Clare E. Gutteridge

Midshipman 1/C Joseph V. Vo was mentored in a collaborative project with the Walter Reed Army Institute of Research (WRAIR) to assess the antimalarial activity of methoxylated naphthyl-containing chalcones.

A potentially interesting class of antimalarial chalcones are those bearing a naphthyl B-ring. Previous studies have demonstrated that such structures possess promising *in vivo* antimalarial activity. However, the analogs described in the literature have not been optimized on the A-ring. Using aldol condensation of various acetophenone and naphthaldehydes, the synthesis of six analogs was planned to explore the relationship between molecular structure and antimalarial activity in this class of compound.

The analogs targeted were successfully synthesized at the Naval Academy, then assayed at WRAIR for their ability in inhibit the growth of *Plasmodium falciparum*, the causative agent of malaria. The minimum concentration of each analog required to inhibit cell growth by 50% is shown in Figure 3 under its corresponding structure (IC_{50} values). Two trends emerged: that 1-naphtyl substitution is preferable to 2-naphtyl substitution and that 2,4-dimethoxy substitution is better than 2,3,4-timethoxy substitution with 4-methoxy substitution being least beneficial.

In conclusion, three single-digit micromolar inhibitors were produced, and trends in activity were established which will be useful in designing more potent compounds. The results of this study were presented in a seminar by Midn 1/C Joseph Vo at the Eastern Colleges Science Conference (ECSC) held in Ithaca, New York on 12 April 2003.

Gas, Solution, and Solid State Coordination Environments for the Copper(II) Complexes of a Series of Aminothiophene Ligands of Varying Coordination Number

Researcher: Midshipman 1/C Erin R. McKenzie, USN
Faculty Adviser: Associate Professor JudithAnn R. Hartman
Sponsor: American Chemical Society Petroleum Research Fund B

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 expanded the investigation to include the “softer” aminothiophene ligands.

The following series of aminothiophene ligands were synthesized and characterized: TREN-thio (tris(2-((2-thiophene)amino)ethyl)amine), EN-thio (1,7-bis(2-thiophene)-2,6-diazaheptane), DIEN-thio (1,9-bis(2-thiophene)-2,5,8-

triazanonane), TRIEN-thio (1,12-bis(2-thiophene)-2,5,8,11-tetraazadodecane), and DIPNEN-thio (1,14-bis(2-thiophene)-2,6,9,13-tetraazatetradecane). Copper(II) and nickel(II) complexes were prepared from these ligands. Most of the complexes were isolated as oils or glasses, but the Cu(II)TREN-thio complex was isolated as a solid perchlorate salt. Magnetic susceptibility measurements, electronic spectra, UV-vis spectra, and electrochemistry were used to analyze the copper (II) TREN-thio complexes.

Supramolecular Complexation of a Merocyanine Dye by Amylose

Researcher: Midshipman 1/C Benjamin F. Visger, USN
Adviser: Associate Professor William B. Heuer

We continue to be engaged in the synthesis and study of functionalized organic donor-acceptor dyes bearing long alkyl-chain substituents. These chromophores have been specifically designed to function as guests for supramolecular complexation by amylose, a linear polysaccharide which adopts a rigid, helical structure in solution. Supramolecular complexes of hemicyanine and merocyanine chromophores are of fundamental interest for their possible application in fabrication of non-linear optical (NLO) devices. Besides preventing undesirable aggregation effects and protecting the chromophore against oxidative degradation, supramolecular complexation may even enhance the nonlinear susceptibility of the chromophore itself. In the present study, we have prepared a series of alkyl-substituted merocyanine chromophores and studied their interaction with amylose in buffered DMSO-water solutions. In particular, we have investigated the effect of supramolecular inclusion upon the acid-base properties of the merocyanine chromophore. The UV-VIS absorption spectra and emission spectra of the merocyanine dyes in buffered 50% DMSO-water mixtures were studied as a function of pH both in the presence and absence of amylose. Our results indicate that the pK_a of the C16-substituted merocyanine indicator dye increases by nearly a full unit upon inclusion by amylose, due to preferential stabilization of the charge-neutral base form of the dye by the hydrophobic interior of the amylose helix. In addition, the emission properties of the amylose-dye complex suggest involvement of an excited-state proton-transfer equilibrium; specifically, the excited form of the dye appears to be a considerably stronger acid than the ground state, such that excitation of the ground state acid form results in emission from the excited state base form. This interpretation implies a strong enhancement of the excited-state lifetime of the merocyanine chromophore upon supramolecular inclusion by amylose, and efforts are currently underway to obtain direct experimental confirmation of this. The possibility of pH-dependent switching of the NLO properties in this system will also be investigated.

Crosslinking in the Presence of Solvent: Mechanical Effects on End-linked Polydimethylsiloxane and Copolymer Networks

Researcher: Midshipman 1/C Colin M. Browning, USN
Adviser: Associate Professor Maria J. Schroeder

In order to evaluate theories of polymer network behavior, materials of well-known structure must be utilized. However the uncertainty inherent in many synthesis methods, which rely on the random joining of different segments of two polymer molecules, prevents clear structure-property relationships from being established. Procedures for creating networks of well-defined structure have recently been described but even these materials suffered from network inhomogeneities. Therefore, a novel synthesis procedure was developed which utilized crosslinking in the presence of solvent to create uniform networks. Presumably, the presence of solvent during the crosslinking process increased chain mobility and allowed the network to form without defects such as microbubbles. End-linked polydimethylsiloxane (PDMS) networks and diphenylsiloxane-dimethylsiloxane (PVD) copolymer networks were prepared by crosslinking vinyl-terminated PDMS and PVD copolymer chains with tetrafunctional silanes in the presence of varying concentrations of solvent. The resultant networks were evaluated by tensile measurements, swelling tests, and fracture behavior. Polymer networks crosslinked under appropriate solvent conditions exhibited enhanced physical and mechanical properties over those synthesized in the absence of solvent.

Polydimethylsiloxane: A Versatile Polymer for Teaching in the Laboratory

Researcher: Midshipman 1/C Colin M. Browning, USN
Adviser: Associate Professor Maria J. Schroeder

Polydimethylsiloxane (PDMS) polymers are a unique and versatile class of materials which can serve as the basis for teaching a polymer chemistry laboratory course. A variety of chain geometries exists or can be easily synthesized by students for further study in the laboratory. Linear PDMS chains of varying molecular weight and functionality are commercially available. By using simple experimental procedures, interesting linear, branched and network systems of well-defined structure can be synthesized quickly and safely unlike other polymerization methods involving hazardous materials, complicated equipment, or the need for inert environments. By varying the PDMS starting materials or altering the synthesis conditions, students can investigate the effects of the synthesis procedure on the end product. Characterization of the product by chromatography, spectroscopy, viscosity, thermal methods, and/or mechanical testing illustrates the structure/property relationships necessary for tailoring materials for specific applications. This project resulted in the creation of a laboratory experiment that was used in the Integrated Laboratory curriculum (SC364, Spring 2003 semester).

Journal (Refereed) Manuscripts

CAMPBELL, Mark L., Professor, "Kinetics of the Termolecular Reaction of Ground State Pd(a^1S_0) with Methane," *Chemical Physics Letters*, 365 (2002), pp. 361-365.

The gas-phase removal rate constants for the reaction of ground state palladium (a^1S_0) with methane in argon buffer are reported as a function of total pressure and temperature. The pressure dependence indicates a termolecular mechanism. The limiting low-pressure third-order rate constant, k_o, in argon buffer at room temperature is $(2.0\pm0.7)\times10^{-30}$ molecule^{-2}cm^{6}s^{-1}. Second-order rate constants were measured at 20.0 Torr from 348 to 523 K. Derived third-order rate constants can be expressed as $\log k_o(T) = -201.5 + 141(\log T) - 29(\log T)^2$ over the temperature range 294 - 523 K.

CAMPBELL, Mark L., Professor, "Kinetic Study of Reactions of Gas Phase Pd(1S0), Ag(5s 2S1/2), Au(6s 2S1/2), Cd(5s2 1S0) and Hg(6s2 1S0) Atoms with Nitrous Oxide," *Journal of Physical Chemistry* A, 107 (2003), pp. 3048-3053.

The reactivity of gas phase Pd(a^1S_0), Ag(5s $^2S_{1/2}$), Au(6s $^2S_{1/2}$), Cd(5s^2 $^1S_0$) and Hg(6s^2 $^1S_0$) with N_2O as a function of temperature and pressure is reported. The transition metal atoms were produced by the photodissociation of an appropriate precursor molecule and detected by laser-induced fluorescence. The reaction of palladium with N_2O is pressure dependent indicating adduct formation. The room temperature limiting low-pressure third-order rate constant is $(2.5\pm0.8)\times10^{-30}$ molecule^{-2}cm^{6}s^{-1} in argon buffer. The limiting low-pressure third-order rate constant can be expressed as $\log k_o(T) = -219.06 + 152(\log T) - 30.5(\log T)^2$ molecule^{-2}cm^{6}s^{-1} over the temperature range 294 - 523 K. The reactions of ground state silver, gold, cadmium and mercury with N_2O are very slow and only upper limits for the rate constants can be reported for these reactions.

CAMPBELL, Mark L., Professor (co-author), "Kinetic Study of the Recombination Reaction of Gas Phase Pd($^1S_0$) with O_2 from 294 – 523 K," *Journal of Physical Chemistry A*, 107 (2003), pp. 3747-3751.

The gas-phase removal rate constants for the reaction of ground state palladium (a^1S_0) with oxygen in argon buffer are reported as a function of temperature and pressure. Palladium atoms were produced by the photodissociation of palladium(II) trifluoroacetate and detected by laser-induced fluorescence. The reaction is pressure dependent, indicating recombination to form PdO_2. Fall-off behavior is observed at pressures above about 20 Torr. Quantum calculations indicate that the reaction proceeds on a triplet surface to form bent PdO_2(^{3}A"), which has a low frequency bending mode of only 129 cm^{-1} and a bond energy D_0 = 95 kJ mol^{-1}. RRKM theory, fitted to the experimental data, shows that D_0 should lie below 155 kJ mol^{-1} and predicts the following expression for the rate coefficient from 200 to 600 K: $k_{rec,0} = 1.09 \times 10^{-30} (T / 300\ \text{K})^{-2.76}$ cm^6 molecule^{-2} s^{-1}, $k_{rec,\infty} = 2.52 \times 10^{-10} \exp(-69.3/T)$ cm^3 molecule^{-1} s^{-1}, and $F_c = 0.61$.

COPPER, Christine L. Associate Professor, and Callahan, John H., "Capillary Electrophoresis as a Method for Ozone Determination in Atmospheres," *Talanta*, 58 (2002), pp. 823-830.

Capillary electrophoresis (CE) is used to quantify nitrate and nitrite extracted from nitrite-impregnated glass fiber filters (IGFF) that are used to monitor ozone in atmospheres. The amount of nitrate produced from conversion of nitrite in the filters is directly related to the amount of ozone passed over the filter. The limit of detection for ozone using the CE method is 1.17 ppm·L and the method is linear over two orders of magnitude. The effect of the excess nitrite in the IGFF on the limits of detection is discussed. Results from CE analyses of both active and passive filters are presented. The active filter results are compared to ion chromatographic (IC) analyses.

COPPER, Christine L. Associate Professor and O'SULLIVAN, Daniel, Associate Professor, "Evaluating Active Learning," *Journal of College Science Teaching*, 32 (2003), pp. 448-452.

A group of faculty developed and tested active learning strategies in a freshman chemistry course. Their students showed significant improvement in performance relative to students experiencing a lecture course during the first semester of the study. For three of the four semesters examined, the active learning sections showed evidence of enhanced performance.

ELERT, Mark L., Professor (co-author), "Orientation Dependence of Shock-Induced Chemistry in Diamond," *Phys. Rev. B (Rapid Comm.)*, 66, 2002, pp. 220102-1(R) – 220102-4(R).

Molecular dynamics simulations employing a reactive empirical bond order potential are used to study the orientational dependence of shock-induced chemistry in diamond. Even for strong shock waves the mechanism of bond breaking and shock-induced transition to amorphous carbon is found to depend crucially on the direction of shock wave propagation. For <110> oriented shock waves, high rate shear deformation causes the formation of layered carbon structures while <111> shock waves favor the formation of diamond micrograins separated by amorphous carbon inclusions.

ELERT, Mark L., Professor (co-author), "Molecular Dynamics Study of Shock-Induced Chemistry in Small Condensed-Phase Hydrocarbons," *J. Chem. Phys*., June 2003, in press.

Molecular dynamics simulations using an empirical bond order potential have been performed to investigate shock-induced chemistry in solid acetylene, ethylene, and methane. Acetylene was found to undergo significant polymerization reactions for flyer plate impact speeds above 10 km/s. These conditions are similar to those which would be experienced upon planetary impact of comets, which are known to contain condensed-phase acetylene. Ethylene exhibits similar reactivity above 15 km/s. Methane undergoes hydrogen abstraction reactions at flyer plate impact speeds of 16 to 20 km/s and produces hydrocarbon chains at higher impact speeds. The latter results are significant for elucidating the fate of atmospheric methane upon cometary or meteor impact, and for predicting the initial reaction steps in the reactivity of methane ices in the high-pressure, high-temperature interiors of Neptune and Uranus.

GUTTERIDGE, Clare E., Assistant Professor, De Laszlo, S.E., Kamenecka, Mccauley, T.M.,Van Riper, E.G., Mumford R.A., Kidambi U., Egger, L.A., Tong, X., and Hagmann, W.K., "*N*-(3-Phenylsulfonyl-3-Piperidinoyl)-Phenylalanine Derivatives as Potent, Selective VLA-4 Antagonists," *Bioorganic and Medicinal Chemistry Letters*, 2003, Vol. 13, pp. 885-890.

The relationship between the structure of a series of amide-containing ligands and their affinity for the VLA-4 integrin is described (integrins are receptors involved in cellular adhesion and are important in various inflammatory diseases). This effort resulted in the identification of a potent, selective VLA-4 antagonist, a molecule which when present at only picomolar concentrations is able to inhibit the binding of $\alpha4\beta1$ ($\alpha4\beta1$ is the natural ligand of VLA-4) (IC_{50} = 90 pM). The series of molecules described were patented by the authors prior to this publication, since they may prove to be clinically useful for the treatment of various inflammatory diseases.

HARRISON, Judith A., Associate Professor, GAO, G. (Post-doctoral Fellow), and MIKULSKI, P.T. (USNA Physics Department), "The Molecular-Scale Tribology of Amorphous Carbon Coatings: Effects of Film Thickness, Adhesion, and Long-Range Interactions," *J. Am. Chem. Soc.,* 124 (2002) pp. 7202-7209.

Classical molecular dynamics simulations have been conducted to investigate the atomic-scale friction and wear when hydrogen-terminated diamond (111) counterfaces are in sliding contact with diamond (111) surfaces coated with amorphous, hydrogen-free carbon films. Two films, with approximately the same ratio of sp^3-to-sp^2 carbon, but different thicknesses, have been examined. Both systems give a similar average friction in the load range examined. Above a critical load, a series of tribochemical reactions occur resulting in a significant restructuring of the film. This restructuring is analogous to the ``run-in'' observed in macroscopic friction experiments and reduces the friction. The contribution of adhesion between the probe (counterface) and the sample to friction was examined by varying the saturation of the counterface. Decreasing the degree of counterface saturation, by reducing the hydrogen termination, increases the friction. Finally, the contribution of long-range interactions to friction was examined by using two potential energy functions that differ only in their long-range forces to examine friction in the same system.

HARRISON, Judith A., Associate Professor, MIKULSKI, P.T. (USNA Physics Department), Ni, B., and Sinnot, P.T., "Compression of Carbon Nanotubes Filled with C_{60}, CH_4, or Ne: Predictions from Molecular Dynamics Simulations," *Phys. Rev. Lett.,* 88 (2002) 205505-1-205505-4.

The effects of filling nanotubes with C_{60}, CH_4, or Ne on the mechanical properties of the nanotubes were examined. The approach was classical molecular dynamics using the reactive empirical bond order (REBO) and the adaptive intermolecular REBO potentials. The simulations predict that the buckling force of filled nanotubes can be larger than that of empty nanotubes, and the magnitude of the increase depends on the density of the filling material. In addition, these simulations demonstrate that the buckling force of empty nanotubes depends on temperature. Filling the nanotube disrupts this temperature effect so that it is no longer present in some cases.

HARTMAN, JudithAnn R., Associate Professor, Vachet, R.W., PEARSON, W.H. Associate Professor, WHEAT, R. Jeremy, Midshipman 1/C (USN) and Callahan, J.H., "A Comparison of the Gas, Solution, and Solid State Coordination Environments for the Copper(II) Complexes of a Series of Aminopyridine Ligands of Varying Coordination Number," *Inorg Chim Acta,* 343 (2003), pp.119-132.

The synthesis and characterization of the copper(II) complexes of a series of aminopyridine ligands that range from tri- to heptadentate is described. The ligands include the tripod ligand tris(2-((2-pyridylmethyl)amino)ethyl)amine, TREN-pyr, and the following linear ligands: (2-pyridylmethyl)(2-((2-((2-((2-pyridylmethyl)amino)ethyl)amino)ethyl)amine,TRIEN-pyr;bis(2-((2-yridylmethyl)amino)ethyl)amine, DIEN-pyr; (2-pyridylmethyl)(2-((2-pyridylmethyl)amino)ethyl)amine, EN-pyr; bis(2-pyridylmethyl)amine, AM-pyr; and methyl(2-((-pyridylmethyl)amino)ethyl)amine, MeEN-pyr. The following methods were used to determine the binding geometries of the copper(II) complexes in the solid, solution, and gas phases: magnetic susceptibility measurements, absorption spectroscopy, epr spectroscopy, electrochemistry, and analyzing the gas phase ion-molecule reactions in a mass spectrometer. The solid state structures for the TRIEN-pyr and DIEN-pyr complexes were determined by x-ray crystallography. [Cu(TRIEN-pyr)](BF4)2 crystallized in the octahedral system, space group Pbca, with a=9.4107(7) Å, b=17.536(13) Å, c=30.132(6) Å, and Z=8 (R=0.064, Rw=0.060). [Cu(DIEN-pyr)](BF4)2 crystallized in the octahedral system, space group Pbca, with a=29.137(5) Å, b=14.829(3) Å, c=9.850(1) Å, and Z=8 (R=0.071, Rw=0.066). The coordination numbers of the Cu(II) complexes in this study are dependent on the denticity of the ligand. The complexes with AM-pyr, MeEN-pyr and TRIEN-pyr appear to be 6-coordinate, DIEN-pyr to be 5-coordinate and the EN-pyr to be 4-coordinate in the solid state. The TREN-pyr complex was isolated as a dimer in the solid state but appears to be a tetragonally distorted monomeric complex in the solution and gas phases. For all of the complexes except DIEN-pyr, the coordination sphere appears to be independent of the phase of the complex. The Cu(II) DIEN-pyr complex appears to be 5-coordinate in the solid phase, a mixture of 4- and 5- coordinate in the solution phase, and predominately 4 coordinate in the gas phase.

HEUER, William B., Associate Professor (co-author), "Bipolar Behavior Revealed by Chromophores Bearing Dithienothiophene (DTT) as π-Center in Redox and LE Properties" *Chem. Phys Lett.,* 2002, 364, pp. 432-437.

A series of D/D^- and D/A pair conjugated chromophores based on dithienothiophene, DTT, as conjugated linker

(π-center) were synthesized (D-π-D and D-π-A) and their optical and electrochemical properties studied. Unusual bipolar behavior was observed for members of the D-π-D series, which exhibited redox properties similar to those of the D-π-A analogues. Single layer light-emitting (LE) devices fabricated with such electronically dissimilar oligomers exhibited a close resemblance in their diode characteristics that are commonly observed with bipolar LE materials.

LOMAX, Joseph F., Associate Professor, DILLNER, Debra K., Associate Professor, and TEICHERT, Melonie A., Capt, USAF, "Web-Based Data Analysis and Feedback for General Chemistry Laboratory: Improving Analysis with Timely, Distance Feedback," *Mat. Res. Soc. Symp. Proc*., 760E, (2003), JJ4.4.1-.6.

In a general chemistry course, while the hands-on experience of the laboratory is important, the goals of the laboratory are not fulfilled until the calculations and analysis are complete. Quite often students are capable of following laboratory instructions and generating excellent data, only to fail in the data analysis, which rarely occurs in the confines of the laboratory or the presence of the instructor. All too often, students are unable to learn important information from the interpretation of experimental results and draw correct conclusions because they make calculational errors, which are most often discovered by the instructor in the grading process. There is an opportunity for distance learning to help bridge the gap between collection of data and its correct analysis. At the United States Naval Academy (USNA), we have developed a Web-based system where the students input their data and calculational results into a web form with immediate feedback. The students are then allowed to correct their errors and resubmit. This system has been in successful use for 5 years. A description of a typical experiment is described, along with an assessment of student and faculty satisfaction with the program.

LUNING-PRAK, Dianne J., NRL Post-doctoral Fellow and Pritchard, Parmely H., "Solubilization of PAH Mixtures in Micellar Solutions of Nonionic Surfactants," *Water Research*, 36 (34), pp. 3463-3472.

This study sought to examine the solubilization of mixtures of the polycyclic aromatic hydrocarbons (PAHs) in solutions of the nonionic surfactants: Tween 20, Tween 80, Triton X-100, Brij 35, and Brij 58. When pyrene (PYR), fluoranthene (FLA), and phenanthrene (PHE) were solubilized from two-PAH mixtures, the PAH concentrations and molar solubilization ratios (MSRs) deviated very little from those as found in the single-PAH systems. When these PAHs were solubilized from three-PAH mixtures, however, not all three PAHs reached their single-PAH solubilities. When the PAHs were added sequentially to surfactant solution, the PAH added last reached its single-PAH solubility, while the concentration of the other two PAHs were lowered by 14 to 45%. When the PAHs were added simultaneously to the surfactant solution, the composition of the solid phase influenced which PAH reached its single-PAH solubility. For solids containing equal mole fractions of all three PAHs, FLA and PHE dissolved in surfactant solution to a lesser extent than the single-PAH systems. In similar systems containing no surfactant, only FLA solubility decreased. As the mole fraction of a PAH in the solid phase increased, its solubility in the micelle phase (and in the aqueous phase) increased up to the solubility limit. Based on these studies, both PAH-PAH interactions and micelle-PAH interactions should be taken into account when predicting the concentrations of PAH mixtures in micellar surfactant solutions. This should be done because PAH-PAH interactions can influence aqueous solubility and micelle-PAH interactions can affect the distribution of PAHs in the micellar phase, which may change as solid mixture composition changes.

SCHROEDER, Maria J., Associate Professor, BENDLER, John T., Associate Professor (USNA Physics Department), Boyles, David A., and Filipova, Tsvetanka S., "Synthesis of 1,1-Dichloro-2,2-bis[4'-(4-hydroxyphenyl)phenyl]ethene and its Incorporation into Homo- and Heteropolymers," *Polymer Preprints*, 44 (2003), pp. 753-754.

Polycarbonates synthesized from 1,1-dichloro-2,2-bis-(4-hydroxyphenyl)ethylene (BPC) are a highly flame-resistant family of engineering thermoplastics. The role of the phenyl rings in the structural and physical properties of BPC polycarbonates has often been postulated but it remains unknown. It is therefore of significant interest to prepare BPC polycarbonates with two additional rings in the structure of the BPC monomer since this may lead to improved ductility and heat-resistant polycarbonates. In this study, an efficient synthesis of the new monomer

1,1-dichloro-2,2-bis[4'-(4-hydroxyphenyl)-phenyl]ethene, TA-BPC, has been achieved in three steps with high purity and an overall yield of 45-50%. The structure has been confirmed by IR and ^{1}H NMR. Using pure tetraaryl and diarylaromatic diols, bisphenol A, bisphenol C, hexafluorobisphenol, and sulfonylbisphenol, solution polycondensation of these monomers with triphosgene was successful. The molecular weight distributions of these polymers were determined by gas-phase chromatography.

SCHROEDER, Maria J., Associate Professor; BENDLER, John T., Associate Professor (USNA Physics Department), Boyles, David A., and Filipova, Tsvetanka S., "Synthesis of Bis[4'-(4-hydroxyphenyl)phenyl]propane and Novel Polycarbonates Prepared Therefrom," *Polymer Preprints*, 44 (2003), pp. 771-772.

Polycarbonates are a class of high-performance engineering resin. Increasing interest has been directed towards the preparation of new ductile, high-heat polycarbonates for aircraft, automotive, electronic and medical applications. Ductile polycarbonates from bis[4'-(4-hydroxyphenyl)-phenyl]alkanes having glass transition temperatures typically 30-40°C higher then those of bisphenol A polycarbonates have been reported. In this study, a new three-step route for the synthesis of the monomer bis[4'-(4-hydroxyphenyl)-phenyl]propane was developed. The synthesis utilized a Suzuki aryl coupling reaction which resulted in a high purity product and an overall yield of 72-75%. The structure was confirmed by IR and ^{1}H NMR. Using the pure tetraaryl monomer and diarylaromatic diols, bisphenol A, bisphenol C, hexafluorobisphenol, and sulfonylbisphenol, solution polycondensation of these monomers with triphosgene was successful and good conversion of the monomer into the polymer was evidenced by GPC analysis.

WHITAKER, Craig M., Associate Professor, BURKHOLDER, Garrett, ENS (USNR), SMITH, Sandra, ENS (USNR), Naciri, Jawad, Weslowski, Brian and Shashidhar, Ranganathan, "Synthesis and Characterization of Laterally Substituted Bis(alkoxybenzoyloxy)hydroquinones," *Liquid Crystals* 2003, 30 (5), pp. 617-621.

A new series of laterally substituted (alkoxybenzoyloxy) hydroquinone molecules have been synthesized and their mesomorphic properties studied. A number of hydroquinone compounds were synthesized which possess terminal n-alkoxy chains ranging from butyl to decyl. Additionally, lateral substituents ranging from n-butyl to n-octyl were incorporated through esterification at the remaining unsubstituted phenolic oxygen atoms. By optimizing the combination of the end-group and lateral moieties we were able to tailor the molecular structure to form different liquid crystalline phases.

Conference Proceedings

CHEEK, Graham T., Professor, "Passive Film Characterization on Aluminum by Impedance Spectroscopy," Electrochemical Society Proceedings, Volume PV2002-24, pp. 257 – 266.

Impedance spectroscopy has been used to study the characteristics of the aluminum in 0.10 M NaCl solution at potentials below the pitting potential (-1.50 V_{SCE} to -0.70 V_{SCE}). Two impedance semicircular features have been identified over this range of potentials. The impedance is observed to increase monotonically as potential increases up to a point where metastable pitting begins to occur. Using information obtained from earlier XPS and XANES investigations, a correlation is 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 the 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.

CHEEK, Graham T., Professor, "Electrochemical Impedance Characterization of Passivity Breakdown on Aluminum," Electrochemical Society Proceedings, Volume PV 2002-24, pp. 445 – 456.

The impedance analysis of pure aluminum in deaerated 0.10 M NaCl during passive film breakdown shows a single capacitive feature, ending with an inductive loop at low frequencies. This response can be modeled with two serial R/CPE combinations, one combination having positive values and the other negative values. The first process (positive values of R / CPE) is taken as characteristic of the unpitted metal surface. The critical frequency value for this first process shows a continual increase as potential is increased. This behavior is ascribed to the increasing conductivity of the surface oxide. The critical frequency value for the second impedance feature is constant with applied potential, indicating that the time constant of the pitting process (pit activation time) is independent of applied potential. Current – time transients show that a transition to metastable pitting is observed at –700 mV, whereas stable pitting is observed above –700 mV.

ELERT, Mark L., Professor (co-author), "Atomistic Modeling of Orientation Dependence of Shock Wave Properties in Diamond," in Shock Compression of Condensed Matter – 2001, M. D. Furnish, N. N. Thadhani, and Y. Horie, eds., AIP Press, New York, 2002, pp. 355–358.

A series of molecular dynamics (MD) simulations using a reactive empirical bond order (REBO) potential for carbon were performed to study the orientation dependence of elastic-plastic shock wave structures in a single diamond crystal. The calculated Hugoniot relation between shock and piston velocities shows reasonable agreement with experimental results. The mechanism of shock-induced plasticity for shock waves propagating along the <110> and <111> directions is quite different. In the <110> case non-equality of transverse components of the stress tensor stimulates formation of layered carbon structures n the shock layer, while the <111> shock reveals bulk martensitic-like deformation with formation of diamond micrograins separated by amorphous carbon inclusions.

ELERT, Mark L., Professor (co-author), "Molecular Dynamics Modeling of Impact-Induced Shock Waves in Hydrocarbons," in Shock Compression of Condensed Matter – 2001, M. D. Furnish, N. N. Thadhani, and Y. Horie., eds., AIP Press, New York, 2002, pp. 1406–1409.

We use nonequilibrium molecular dynamics (MD) simulations to study the behavior of hydrocarbons under shock compression and spallation processes in shock compression and rarefaction waves generated by the high-velocity impact of a flyer plate into a target material. The interatomic forces were introduced using a recently modified reactive empirical bond order (REBO) potential with intermolecular interactions, termed the adaptive intermolecular REBO potential (AIREBO). This potential allows us to simulate as many as ten thousand molecules on a single processor, providing a relatively large cross-section at the shock front in hydrocarbon solids. We performed plane-wave impact experiments with different flyer velocities and observed the chemical dissociation of methane and acetylene molecules in the shock layer, followed by polymerization into carbon chains for certain flyer velocities. The hydrocarbon oligomers survive into the rarefaction region, indicating that stable molecular products have been formed. These results may be significant for the understanding of shock-induced chemical reactions resulting from meteorite impact in planetary atmospheres and methane ice surfaces.

SMITH, V.F. Assistant Professor, De Long, Hugh C., Trulove, Paul C. and Sutto, Thomas E., "Nonenzymatic Synthesis of Peptides in an Ionic Liquid," *Proceedings of the Electrochemical Society, PV 2002-19, Molten Salts XIII*: pp. 268-275.

Amino acids, the monomers that comprise proteins, are abundant in nature and have even been found in environments that do not support life, such as meteorites. The origin of proteins, however, is mysterious because the condensation reaction that forms the peptide bond linking two amino acids is thermodynamically disfavored in the aqueous solutions that are required for life. Ionic liquids, which are polar but non-aqueous and which are stable over a wide temperature range, are an ideal medium for testing whether peptide bonds could form spontaneously between amino acids in the absence of water. We have demonstrated that peptides can form non-enzymatically in the molten salt 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF6) by incubation of various solid amino acids at temperatures above 100 C. Incubation at temperatures below 100 C did not produce peptides, even when performed under vacuum.

Book Chapters

HARRISON, Judith. A., Associate Professor (co-author), "Contributions of Molecular Modeling to Nanometer-Scale Science and Technology," in Nanoscience, Engineering, and Technology Handbook, eds., W. Goddard, D. W. Brenner, S. Lyshevski, and G. Iafrate, CRC Press, (2002) pp. 24-1 through 24-28.

Molecular modeling has played a key role in the development of our present understanding of the details of many chemical processes and molecular structures. Molecular modeling has played a central role in developing and evaluating new concepts related to nanometer-scale science and technology. Indeed, molecular modeling has a long history in nanotechnology of both leading the way in terms of what in principle is achievable in nanometer-scale devices and nanostructured materials, and in explaining experimental data in terms of fundamental processes and structures. The first goal of this chapter is to educate scientists and engineers who are considering using molecular modeling in their research, especially as applied to nanometer-scale science and technology, beyond the "black box" approach sometimes facilitated by commercial modeling codes. The second goal of this chapter is to discuss some examples of systems that have been modeled, and the type of information that has been obtained from these simulations.

HARRISON, Judith. A., Associate Professor, MIKULSKI, P.T. (USNA Physics Department), Stuart, S.J., and Tutein, A.B., "Dependence of Frictional Properties of Hydrocarbon Chains on Tip Contact Area," in *Nanotribology: Critical Assessment and Research Needs*, ed. S. M. Hsu, Kluwer Academic Publishers, Norwell, MA, (2002) pp. 55-62.

A number of groups have examined the frictional properties of alkanethiols on Au and alkylsilane monolayers on various substrates using the atomic force microscope (AFM).[1-6] Such kinds of monolayers may be useful in the construction of MEMS with low friction, reduced stiction, and the desired wear properties. In addition, the frictional properties of related systems, such as Langmuir-Blodgett films, have also been investigated.[7,8] Complementary work described here uses classical molecular dynamics (MD) simulations to study monolayers of *n*-alkanes that are chemically bound to diamond substrates. Other MD simulations have examined the structure[9-12] and compression of *n*-alkanethiols on Au.[13,14] In this work, two kinds of probes with different contact areas are utilized to study the effects of chain length on mechanical and frictional properties. The probes are a nanotube, which penetrates into the monolayers (Figure 1, left), and a countersurface, which compresses the monolayers (Figure 1, right).

HARRISON, Judith. A., Associate Professor, ELERT, Mark L., Professor, ZYBIN, Sergey (Post-doctoral Fellow), and White, C.T., "Atomistic Modeling of Orientation Dependence of Shock Wave Properties in Diamond," in *Shock Compression of Condensed Matter,* eds. M. D. Furnish, et al., AIP Press, New York, (2002) pp. 355-358.

A series of molecular dynamics (MD) simulations using a reactive empirical bond order (REBO) potential for carbon were performed to study the orientation dependence of elastic-plastic shock wave structures in a single diamond crystal. The calculated Hugoniot relation between shock and piston velocities shows reasonable agreement with experimental results. The mechanism of shock-induced plasticity for shock waves propagating along the <110> and <111> directions is quite different. In the <110> case non-equality of transverse components of the stress tensor stimulates formation of layered carbon structures n the shock layer, while the <111> shock reveals bulk martensitic-like deformation with formation of diamond micrograins separated by amorphous carbon inclusions.

Patent

Adams, Alan D., Bouffard, Aileen, Dropinski, James F. , GUTTERIDGE, Clare E., Assistant Professor, Jones, A.Brian, Lui, Weiguo, Ondeyka, John George, and Singh, Sheo Bux, "Therapeutic Compounds for Treating Dyslipidemic Conditions," U.S. 20030125357.

This patent was filed to protect the results of a medicinal chemistry project performed by the authors at Merck Research Laboratories in 2001. The other co-authors had substantial roles in the research.

The patent describes a series of molecules based upon the natural product podocarpic acid, potentially useful for the treatment of various diseases where lipid levels are affected. Since the patent will not publish for several months a more detailed abstract cannot be provided.

Presentations at Professional Meetings and Conferences

BROWNING, Colin M., Midshipman 1/C (USN), and SCHROEDER, Maria J., Associate Professor, "Polydimethylsiloxane: A Versatile Polymer for Teaching in the Laboratory," 225th National Meeting of the American Chemical Society, New Orleans, LA, 24 March 2003.

COPPER, Christine L., Associate Professor, and Callahan, J.H., "Capillary Electrophoresis as a Method for Ozone Determination in Atmospheres," Frederick Conference on Capillary Electrophoresis, NCI-Frederick, Frederick, MD, October 2002.

Lyons, K.S., Stanley, J.A., COTTEN, G.B., Lieutenant Commander (USNR), Dmowski, W., and Egami, T. "Low-Platinum Oxide-based Electrocatalysts for Oxygen Reduction in Proton Exchange Membrane Fuel Cells," 224th American Chemical Society National Meeting, 18-22 August 2002.

Bouwman, P. J., Stanley, J.A., COTTEN, G.B. Lieutenant Commander (USNR), Dmowski, W., Egami, T. Lyons, K.S., "Low Platinum Oxide-based Electrocatalysts for Oxygen Reduction in Proton Exchange Membrane Fuel Cells," Gordon Conference (Electrochemistry), Ventura Beach, CA, January 2003.

ELERT, Mark L., Professor, "Modeling of Shock Wave Effects in Carbon and Hydrocarbon Systems," Gordon Research Conference on Energetic Materials, Tilton, NH, 16-21 June 2002.

ELERT, Mark L., Professor, "Modeling Shock-Induced Chemistry in Carbon and Hydrocarbon Systems with a Reactive Empirical Potential," European Centre for Atomic and Molecular Computations (CECAM) Workshop, "Upscaling from *ab initio* to Molecular Dynamics: Interatomic Potentials and Hybrid Methods," Lyon, France, 8-12 July 2002.

ELERT, Mark L., Professor, "Orientation Dependence of Shock-Induced Plasticity and Chemistry in Diamond," TMS Annual Meeting, San Diego, CA, 2-6 March 2003.

ELERT, Mark L., Professor, "Oscillatory Structure of Elastic Precursor in Shocked Crystalline Solids: A Molecular Dynamics Study," American Physical Society National Meeting, Austin, TX, 3-7 March 2003.

ELERT, Mark L., Professor, "Shock-Induced Plasticity and Chemistry in Diamond: Orientation and Shock Strength Dependence," American Physical Society National Meeting, Austin, TX, 3-7 March 2003.

GUTTERIDGE, Clare E., Assistant Professor, "Synthesis of Biologically-Active Molecules with Potential for Therapeutic Application: Azadirachtin, Eleutherobin and VLA4-Antagonists," Walter Reed Army Institute of Research, Silver Spring, MD, 10 September 2002. (Invited seminar)

HARRISON, Judith A., Associate Professor, "Molecular-Scale Tribology in Model SAMs and Amorphous Carbon Films,"

The Johns Hopkins University, Baltimore, MD, 14 May 2003.

HARRISON, Judith A., Associate Professor, "Atomic-Scale Investigation of Friction at Amorphous Carbon Interfaces via Molecular Dynamics Simulations," The International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, 28 April - 2 May 2003.

HARRISON, Judith A., Associate Professor, "Atomic-Scale Investigations of Friction at Amorphous Carbon Interfaces," 225th American Chemical Society National Meeting, New Orleans, LA, 23-27 March 2003.

HARRISON, Judith A., Associate Professor, "The Molecular Dynamics Examination of Indentation- and Friction-Induced Polymerization," 225th American Chemical Society National Meeting, New Orleans, LA, 23-27 March 2003.

HARRISON, Judith A., Associate Professor, "Analysis of Compression- and Shear-Induced Polymerization in Model SAMs," 225th American Chemical Society National Meeting, New Orleans, LA, 23-27 March 2003.

HARRISON, Judith A., Associate Professor, "The Atomic-Scale Investigation of Friction at Hydrocarbon Interfaces via Molecular Dynamics Simulations," ASIATRIB 2002, International Conference, JeJu Island, South Korea, 21-24 October 2002.

HARRISON, Judith A., Associate Professor, "Theoretical Investigation of Atomic-Scale Friction and Wear in Hydrocarbon Containing Systems," 10th Foresight Conference on Molecular Nanotechnology, Bethesda, MD, 10-12 October 2002.

HARRISON, Judith A., Associate Professor, "Atomic-Scale Investigation of Friction at Amorphous Carbon Interfaces," Gordon Research Conference, Bristol, RI, 4-9 August 2002.

HARRISON, Judith A., Associate Professor, "Analysis of Polymerization in SAMs under Compression and Shear," Gordon Research Conference, Bristol, RI, 4-9 August 2002.

HARTMAN, J. R. Associate Professor, and O'BRIEN, Richard L., Jr., Associate Professor, (USNA Weapons and Systems Engineering Department), "Assessment at the Naval Academy, Communication, Geopolitical Awareness, and Critical Thinking; Annual Conference of the Middle States Commission on Higher Education, Washington, D.C., 16-17 December 2002.

HEUER, William B., Associate Professor (co-author), "Supramolecular Complexation of a Merocyanine Dye by Helical Amylose," American Chemical Society 225th National Meeting, New Orleans, LA, 22-27 March, 2003.

KINTER, Christopher M., Associate Professor (co-author), "Synthesis and Binding Studies of Ligands Selective for Delta Opioid Receptors: Radioiodinated (*E*)- and (*Z*)-N1'-(3-Iodoallyl) Naltrindole," 15th International Symposium on Radiopharmaceutical Chemistry, Sydney, Australia, 10-14 August 2003. J Labelled Compds Radiopharm 46: S36, 2003.

LOMAX, Joseph F., Associate Professor, DILLNER, Debra K., Associate Professor, and TEICHERT, Melonie A., Captain (USAF), "Web-Based Data Analysis and Feedback for General Chemistry Laboratory: Improving Analysis with Timely, Distance Feedback," Materials Research Society Meeting, Abstract, JJ.4.4, Boston, MA, 2-4 December 2003.

MCCLEAN, Roy E., Associate Professor, "Thoughts on Education and Science," University of the Virgin Islands, St. Croix, U.S. Virgin Islands, 14 March 2003.

MORSE, Daniel P., Assistant Professor, Aruscavage, J., Tonkin, L.A., Saccomanno, L., Brodigan, T., Krause, M., and Bass, B.L., "Biological Roles for A to I Conversion in Untranslated Regions of mRNAs," 12th International Beyond the Identification of Transcribed Sequences: Functional, Expression, and Evolutionary Analysis Workshop, Vienna, VA, 25-28 October 2002.

Pollack, Steven and WHITAKER, Craig M., Associate Professor, "4-Mercaptostyrene Polymers and Block Copolymers Through Trimethylsilyanylethyl Protected Monomers," 224th American Chemical Society National Meeting, Division of Polymer Chemistry, Boston, MA, 18-22 August 2002.

SCHROEDER, Maria J., Associate Professor; DILLNER, Debra K., Associate Professor; FERRANTE, Robert F., Professor;

FITZGERALD, Jeffrey P., Professor; and HEUER, William B., Associate Professor; "The Integrated Laboratory Curriculum at the U.S. Naval Academy," 225th National Meeting of the American Chemical Society, New Orleans, LA, 23 March 2003.

SCHROEDER, Maria J., Associate Professor, BENDLER, John T., Associate Professor (USNA Physics Department), Boyles, David A., and Filipova, Tsvetanka S., "Synthesis of Bis[4'-(4-hydroxy-phenyl)phenyl]propane and Novel Polycarbonates Prepared Therefrom," 225th National Meeting of the American Chemical Society, New Orleans, LA, 25 March 2003.

SCHROEDER, Maria J., Associate Professor, BENDLER, John T., Associate Professor (USNA Physics Department), Boyles, David A., and Filipova, Tsvetanka S., "Synthesis of 1,1-Dichloro-2,2-bis[4'-(4-hydroxyphenyl)phenyl]ethene and its Incorporation into Homo- and Heteropolymers," 225th National Meeting of the American Chemical Society, New Orleans, LA, 27 March 2003.

SMITH, Virginia F., Assistant Professor, "Exploring the Equilibrium Folding Properties of Human Cytoplasmic Aconitase," 47th Annual Meeting of the Biophysical Society, San Antonio, CA, 3 March 2003.

TEICHERT, Melonie A., Captain (USAF), and LUNING-PRAK, Dianne J., Assistant Professor, "Effects of Pre-class Preparation and Reading Quizzes on Student Study and Learning," American Chemical Society 225th National Meeting, Chemical Education Research Symposium, New Orleans, LA, 23-27 March 2003.

VISGER, Benjamin F., Midshipman 1/C (USN) and HEUER, William B., Associate Professor, "Supramolecular Complexation of a Merocyanine Dye by Amylose," National Conference on Undergraduate Research (NCUR), Salt Lake City, UT,13-15 March, 2003.