Division of Mathematics and Science

CAPT K. Scott Pugh, USN
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Chemistry Department

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Chairman

The 2003-2004 academic year was an eventful yet productive one for research within the Naval Academy's Chemistry Department. During the summer of 2003, the Chemistry Department faculty moved into temporary offices in Preble Hall so that Michelson Hall could be renovated. While new chemistry lab spaces were being built in Michelson Hall, existing laboratories in the ground deck of Chauvenet Hall continued to operate. Nineteen 1/C midshipmen, including two Trident Scholars, began research projects at the start of the fall semester in the Chauvenet laboratories. Their work was abruptly halted on 18 September 2003 when a storm surge created by Tropical Storm Isabel sent 3-foot-deep brackish salt water throughout the ground decks of Michelson and Chauvenet Halls. All equipment, supplies, chemicals and records stored in the wooden laboratory benches were ruined. All floor-standing instrumentation, including the 400-MHz Nuclear Magnetic Resonance (NMR) spectrometer, the Electron Spin Resonance (ESR) spectrometer, the X-ray diffractometer and several lasers, was damaged beyond repair. In the two weeks after the storm's departure, the entire ground deck of Chauvenet Hall was permanently emptied of all academic activities. In spite of the tremendous obstacles of no longer having functional laboratories and not having operating chemical instrumentation, all but three of the student research projects continued. Some projects continued by modifying the goals and approaches of the projects. Some researchers found alternate work space at the Naval Research Laboratory (NRL) in Washington, D.C., at the National Aeronautics and Space Administration (NASA) campus in Greenbelt, Maryland, at the Johns Hopkins University in Baltimore, Maryland, and at the Walter Reed Army Institute for Research (WRAIR) in Washington, D.C. Temporary modular chemistry laboratories were designed and constructed in the late fall semester of 2003, and the Chemistry Department moved into them (from a warehouse storage facility) over the mid-semester break. During the spring semester of the 2004 academic year, thirty-four 1/C midshipmen researchers shared research space and salvaged instrumentation in the modular (and very temporary) chemistry laboratories. All thirty-four students presented the results of their research at end-of-semester poster sessions, via oral presentations in a department seminar course, and/or at regional and national scientific society meetings.

Research by Naval Academy Chemistry Department faculty also suffered from the loss-of-facility and instrumentation problems described above. Nevertheless, twenty faculty members continued on, conducting funded research on twenty-eight different projects. Funding came from fourteen different outside sources including the National Science Foundation (NSF), the Air Force Office of Scientific Research (AFOSR), the Army Research Office (ARO), the Office of Naval Research (ONR), the National Aeronautics and Space Administration (NASA), the Walter Reed Army Institute for Research (WRAIR), the Naval Research Laboratory (NRL), the Naval Surface Warfare Center at Indian Head (NSWC-IH), the Research Corporation and the Petroleum Research Fund (PRF). In addition, Chemistry Department faculty members pursued exploratory yet unfunded research projects (> 10) in their temporary laboratories at the Naval Academy. The significant time commitment and personal effort of the faculty and midshipmen, in less than ideal conditions, resulted in sixteen publications in refereed journals, one book chapter and forty presentations - including eleven presentations by students at regional, national and international (!) conferences.

Faculty members whose accomplishments are particularly noteworthy include the following. Associate Professor Christine Copper continued her long and productive collaboration with the Naval Research Laboratory collaborators, and together they published two papers on Navy-relevant analytical chemistry. Similarly, Associate Professor JudithAnn Hartman, Assistant Brian Rehill and LT Eric Welsh, USNR, each had two or more refereed publications. Professor Mark Elert supported a post-doctoral associate with whom he published one journal article and made five presentations on molecular dynamic simulations of shock waves. LCDR Greg Cotten, USNR, and Assistant Professor Clare Gutteridge also supported postdoctoral associates. Professor Judith Harrison continued to receive international recognition for her molecular dynamics studies of friction and wear. She was awarded a $1M, four-year grant as part of a multi-university collaboration to develop molecular modeling techniques useful over a wide range of length scales. Associate Professor Daniel O'Sullivan did field work as part of two ongoing projects: 1) Office of Naval Research-funded work on the aqueous chemistry of photochemically-produced peroxides and 2) a National Science Foundation-funded study of partially reduced oxygen species in the atmosphere. Associate Professor Christopher Kinter also received funding from two sources: 1) the Johns Hopkins University and 2) the Naval Surface Warfare Center at Indian Head. Professor Graham Cheek applied for a U.S. Patent on

the results of his project on "Low Temperature Refining and Formation of Refractory Materials." To support his work on novel organic photovoltaic materials, Associate Professor Craig Whitaker was awarded the Kinnear Fellowship which is funded through a private donation to the Naval Academy Alumni Association. Finally, Associate Professor Craig Whitaker and Assistant Professor Tammy Domanski served as project advisers and mentors for Midshipman 1/C Katharine Folz and Midshipman 1/C Daniel Bowers, respectively, who were appointed as 2004 Trident Scholars.

Sponsored Research

Effect of Chloride Concentration on Aluminum Oxide Characteristics

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

As part of an ongoing project involving aluminum corrosion, potentiodynamic (potential vs current) curves were used to obtain information about the passive layer on aluminum in NaCl solutions. For NaCl concentrations ranging from 3 mM to 3 M, the oxidation current through the passive layer was measured at various potential values relative to the pitting potential. Current values decreased with increasing chloride concentration from 3 mM to 0.1 M, after which current was constant. This behavior is consistent with the proposed role of chloride ion in replacing oxide ions in the aluminum oxide passive layer, thereby decreasing the current through the passive layer.

Separation of Chemical Warfare Agents by Capillary Electrophoresis

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

o-Phthalaldehyde (OPA) and its related compound, 2,3-naphthalenedicarboxaldehyde (NDA), are well recognized for their reaction with primary amines in the presence of an excess of cyanide or mercaptoethanol to form highly fluorescent isoindoles. These reactions have primarily been applied to the detection of amines and amino acids, although NDA or OPA can also be used in conjunction with an excess of amino acid, *e.g.,* taurine, to detect cyanide, as demonstrated by a number of flow injection schemes. Ion exclusion chromatography with postcolumn derivatization, capillary electrophoresis (CE) of blood samples and CE microchip of vapor and drinking water samples are all examples of techniques which have taken advantage of OPA or NDA for the separation and detection of cyanide. OPA is equally effective for the detection of thiols, as demonstrated by several liquid chromatographic applications. This research project, however, is the first application of OPA for the simultaneous separation of various structurally similar thiols and cyanide by CE. One motivating factor for developing a method that simultaneously examines thiols and cyanide is in monitoring for the potential contamination of drinking water supplies by chemical warfare (CW) nerve agents.

Detection and Quantification of Uranium (VI) in Building Materials

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

A method for detecting and quantifying uranium(VI) on concrete, Plexiglas, or steel surfaces is presented. Specifically, the uranium(VI) was removed from the building material surfaces using a low pH buffer rinse. The uranium(VI) in the wash solution was subsequently complexed with an organic chelating agent, arsenazo III, which allows concentration using C18 solid phase extraction. The amount of arsenazo III: uranium(VI) complex was detected using ultraviolet-visible spectroscopy at 654 nm. The method has a detection limit of 40 ng/L (5 ng/cm^2) and an overall extraction efficiency greater than 80% for each surface type. Methods to avoid interference by metal ions that are likely present on building materials are discussed.

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)

The development of new nanocomposite oxygen-reduction catalysts designed for high catalytic activity plus high electron and proton transport has been proposed. With this approach, it is anticipated that the oxygen-reduction reaction will be improved, increasing the efficiency of PEMFCs. Furthermore, the amount of platinum in fuel cell cathodes will be drastically reduced or eliminated, lowering the cost of the PEMFCs.

Reports have shown that Pt-Fe catalysts have up to 25 times the activity of Pt catalysts for oxygen reduction, and give weak evidence that this effect is due to a Pt-Fe alloy. Like the Pt-Ru system, it is likely that the active material is actually a nanocomposite of metals and oxides. Pt-Fe catalysts will resolve whether the active catalyst is a Pt-Fe alloy or Pt-FeOxHy composite. The stability of the Pt-Fe systems will also be examined in the acidic and oxidizing conditions of the PEMFC cathode.

Platinum-free nanocomposite catalysts were synthesized with a focus on the optimization of catalytic activity plus proton and electron transport. For instance, phosphate-based materials, such as vanadium phosphorous oxide, were used to enhance oxygen activity. These catalysts are traditionally used for high temperature partial oxidation reactions due to their ability to abstract hydrogen and store oxygen in their lattice. Like many phosphates, vanadyl phosphates are good proton conductors, and often exhibit semiconduction. By mixing with metallic perovskites, such as $CaMoO_3$ and $SrCrO_3$, the conductivity of the electrodes were not limited by electron transfer. The materials were evaluated for stability under acidic and oxidizing conditions.

These catalysts are being provided to the Department of Energy (DOE) fuel cell testing facility at Los Alamos National Laboratory (LANL) for characterization under fuel-cell operating conditions.

Environmental Stress Response in *Staphylococcus aureus*

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

The long-term objective of this study is to better understand the response of the bacterium *Staphylococcus aureus* (S. aureus) to environmental and host stresses, with a focus on particular proteins that are involved in survival under adverse conditions. From a clinical stand-point there is a distinct correlation between the ability of S. aureus to survive in adverse conditions and its capacity to cause disease. Historically, antibiotics have targeted the cell wall synthesis, transcription or translation. However, bacteria have developed resistances to these types of drugs relatively quickly with the first methicillin-resistant strains emerging in 1961. Identifying and targeting the mechanisms utilized by the bacterium for survival could result in the development of a novel class of drugs. The stress responses employed by *S. aureus* remain relatively undefined, leaving a noticeable gap between the gram-positive and gram-negative pathogens.

While a number of systems are activated during the virulence pathway of *S. aureus*, one family of proteins, the chaperone-linked (Clp) family of heat shock proteins, identified over a decade ago as a near-ubiquitous class of stress-induced proteins has only recently become a target of study in *S. aureus*. Clp proteins have also been found to be important for virulence in bacteria, and there is one study suggesting a role for ClpC in *S. aureus* virulence. Recently, ClpB from E. coli has been the focus of several research efforts that have provided information on the function of E. coli ClpB, the regulation of ClpB in E. coli, and the role of particular domains within the ClpB protein. In this study, the gene encoding *S. aureus* ClpB has been transferred into another bacteria, using molecular biological cloning techniques, to increase ClpB production. Purification of the ClpB protein has been conducted, suggesting that staphylococcal ClpB may be expressed in multiple forms. With the goal of analyzing the function of this protein, cloning of genes encoding proteins believed to interact with ClpB has been conducted.

Molecular Dynamics Simulations of Shock-Induced Chemistry in Anthracene

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

Computer simulations were conducted to analyze shock-induced chemical reactions in solid anthracene, a relatively large, aromatic, highly anisotropic hydrocarbon. Some experimental evidence indicates that anthracene undergoes dimerization upon shock wave impact, but no further details are known. Molecular dynamics simulations were carried out to investigate the kinetics, product distribution, and the orientation dependence of shock-induced chemistry in this material. The competition between fragmentation and polymerization processes in this large organic molecule was of particular interest.

Above a reaction threshold at a flyer plate impact velocity of 8 km/s, the dominant shock-induced reaction was found to be dimerization. However, "end-on" impacts resulting from shock wave propagation along the crystallographic c axis produced substantially more fragmentation than other shock wave directions. Higher oligomers of anthracene were also observed. The results are consistent with recent observations that amino acids can survive shock wave impacts in the same velocity range, such as those resulting from meteorite or cometary impact into earth's atmosphere, and can undergo polymerization reactions to form small protein fragments.

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)
Sponsor: 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 focused on ice processing by ion irradiation and described a number of radiation chemical products of N2-rich and H2O-rich ices containing CO or CH_4, including possible volatiles such as alcohols, acids, and bases. New IR spectra were reported for the 1-5 µm (NIR) region, along with band strengths for the stronger features of carbon suboxide, carbonic acid, the ammonium and cyanate ions, polyoxymethylene, and ethylene glycol. The new spectra will enable remote observers operating in the NIR to identify the presence of these species, and the band strengths will provide some measure of quantification. Spectra were also recorded for less volatile residues formed by reactions that occur during warming of the ion-irradiated ices. While these complicated residues could not be completely characterized in terms of molecular carriers, their general spectral features may also be of use in evaluating possible mechanisms for the evolution of terrains of varying IR response.

Antimalarial Chalcones

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

The aim of this project is to identify antimalarial chalcones with sufficient in-vitro potency to warrant in-vivo antimalarial testing. This will be achieved by exploring how varying the substitution pattern on the two rings of a chalcone influences antimalarial activity, with the aim of increasing in-vitro antimalarial potency.

One specific and potentially interesting class of antimalarial chalcones is one containing a 3-quinloline B-ring. Several examples were in the Walter Reed collection. However, the substituents present on such chalcones have not been optimized. Aldol condensations of various acetophenone and aldehydes were therefore used to synthesize the other analogs. Approximately 30 analogs targeted were successfully synthesized at the Naval Academy and then assayed at the Walter Reed Army Institute of Research for their abilities to inhibit the growth of Plasmodium falciparum, which is the causative agent

of malaria. The minimum concentration of each analog required to inhibit Plasmodium growth by 50% was determined.

Initially, a series of 3-quinoline-containing analogs bearing methoxy substituents was prepared. The synthesis and purification generally proceeded very smoothly. A series of 4-quinoline-containing analogs also bearing methoxy substituents was then prepared. Some of these syntheses proved more challenging than expected. Comparison of the data for the 3-quinoline analogs and the corresponding 4-quinoline analogs suggests that the latter are slightly more active. The synthesis of one analog has been scaled up to provide material for testing in mice infected with malaria.

The effect of halogen substitution on antimalarial activity was next explored. Data for the chloro- and fluoro-substituted compounds suggests that chloro substitution provides superior enhancement of antimalarial activity.

A series of analogs containing methoxy and fluoro substituents were then prepared. The synthesis of one analog was scaled up for testing in mice infected with malaria.

In conclusion, potent (submicromolar IC50) analogs have been discovered, along with trends in activity. This information will ultimately be used to design even better compounds.

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

Researchers: Dr. Guangtu Gao (AFOSR Post-doctoral Fellow) and Professor Judith A. Harrison
Sponsor: Air Force Office of Scientific Research (AFOSR)

Molecular dynamics simulations have been used to examine tribological and mechanical properties of amorphous carbon films, single-crystal diamond, and silicon-doped amorphous carbon films. In the past year, three sets of simulations were performed. The first set of simulations was designed to examine the effects of hydrogen concentration on the mechanical and tribological properties of amorphous carbon films. This set of simulations also examined the effect of the probe (or counterface) on the calculated friction. When an amorphous carbon film was used as a probe, adhesion (chemical reactions) between the probe and the film increased the friction markedly. When hydrogen-terminated probes are used, no reactions between the tip and the films were observed. In this case, surface roughness of the films governed the tribological behavior. The second set of simulations was inspired by our collaboration with Prof. Scott Perry at the University of Houston. These simulations examined the temperature dependence of the elastic constants of diamond, and the friction of both the (111) and the (100) surfaces. Both surfaces of diamond exhibited the same temperature dependence. That is, as the temperature increased the friction decreased. The friction of the (100) surface was less at a given load than it was on the (111) surface for each temperature examined. Lastly, we have begun to examine the effect of silicon doping in amorphous carbon films. Preliminary results indicate that progressively increasing the amount of Si from 0 to 20% causes a steady decline in the amount of sp2-hybridized carbon atoms, a slight decline in the sp-hybridized carbon atoms, and a slight increase in the amount of sp3-hybridized carbon atoms. Current simulations are focused on the examination of the effect of these hybridization changes on the elastic moduli of the films.

Molecular Dynamics Investigations of the Tribology of Diamond Surfaces and Films

Researchers: Dr. Ginger M. Chateauneuf (ONR Post-doctoral Fellow) and Professor Judith A. Harrison
Sponsor: Office of Naval Research (ONR)

In a series of complementary studies, the compression and friction of hydrocarbon monolayers were examined using molecular dynamics (MD). In one set of simulations, an amorphous carbon probe was used to examine C20H32 chains containing two triple bonds (or four sp-hybridized carbon atoms) attached to diamond (111) in a (2x2) arrangement. The sp-hybridized atoms were arranged so that the triple bonds were separated by one single bond. In one monolayer, the triple-bond region was on the ends of the chains and in the other it was in the middle of the chains. Simulations showed that polymerization between chains was induced by compression and sliding. When the triple-bond region was on the ends of the chains the friction was an order of magnitude larger. The degree of polymerization increased with increasing load and sliding distance. The cross-linked network of chains that results was irregular, unlike the cross-linked chains formed from exposure to UV radiation. The number of chemical reactions within the monolayer and between the monolayer and the probe was significantly reduced when a hydrogen-terminated diamond (111) probe was used. In addition, the friction at a given

load was smaller when the diamond (111) probe was used for both monolayers. Compression and sliding using the diamond (111) probe lead to an ordered interface. Previous MD simulations and AFM experiments have shown that more order leads to lower friction. Finally, the friction of monolayers composed of chains of different lengths (so-called mixed monolayers) was also examined. MD data show that mixed monolayers have higher friction than pure monolayers. Preliminary results indicate that the difference in friction may arise from differences in the local repulsive contacts at the interface.

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

Researcher: Professors Mark O. Robbins, Jean-Francois Molinari, Shiyi Chen, Dr. N. Bernstein, & Professor Judith A. Harrison

Sponsor: National Scientific Foundation (NSF) and The Johns Hopkins University

There are currently a number of theoretical techniques available to model a large number of phenomena. Continuum techniques, such as finite element methods, are used to model stress and strain in macroscopic sized objects, such as bridge components or automobile parts. Atomic-scale models, such as molecular dynamics simulations, can be used to model interactions that occur between atoms and molecules. For example, my research program at the Academy has focused on the modeling of atomic-scale friction and wear between two hydrocarbon surfaces in sliding motion. Lastly, electronic-structure techniques are generally used to examine the properties of single molecules. These methods are so computer intensive that typically only few 100 atoms can be modeled at one time. Each of these techniques is adequate when there is only one length scale in the problem of interest. However, these techniques break down when there is interaction between several length scales. The goal of this project, which is funded by the National Science Foundation, is to develop hybrid algorithms that can simultaneously model a range of length scales. Once developed, these algorithms will be used to examine fundamental problems in adhesion, friction, and nanofluidics.

This project has brought together a number of investigators with different areas of expertise. Chen and Molinari have extensive experience in developing continuum methods. Chen and coworkers have developed the Lattice Boltzman method [1] and Molinari and others have developed the SimuPak Finite Element code [2]. Robbins and Harrison have both done extensive research examining adhesion and atomic-scale friction using molecular dynamics techniques [3-4]. Harrison and coworkers developed an empirical potential energy function capable of modeling chemical reactions in all phases of hydrocarbon materials. Bernstein has experience in both continuum and atomic-scale modeling and has developed a multi-scale code for modeling crack propagation in silicon.

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. Our initial work has involved the study of aminopyridyl tripodal and linear ligands. In this study we are expanding our work to include the “softer” aminothiophene ligands.

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, Cu(II)DIPNEN-thio, and Ni(II)DIPNEN-thio complexes was isolated as a solid perchlorate salts. Magnetic susceptibility measurements, electronic spectra, UV-vis spectra, and electrochemistry were used to analyze the complexes.

Supramolecular Complexation of Dye Probes by Amylose: Fundamental Studies and Development of Device Applications

Researcher: Associate Professor William B. Heuer
Sponsor: 2003 Kinnear Fellowship

This project was conceived as a continuation of research initiated by research student Ben Visger last year. His results were intriguing and suggestive of some interesting and potentially useful changes in the acid-base properties of alkyl-substituted merocyanine dyes under supramolecular confinement by helical amylose. However, the purity level of some of the dye samples in that study were not adequately determined, and also there was also some question about the stability of the dyes under continuous irradiation. Accordingly, summer work was directed towards preparation of new, high-purity dye samples. This goal was achieved, and preliminary stability studies were underway when Isabel hit. Unfortunately, the dye samples were below the waterline, and so their purity was now again suspect. These samples are being re-purified in advance of restarting the stability studies this summer, however lack of on-site NMR capability has impeded this effort. A second, alternate project has also been developed during the interim period when the NMR and fluorimeter were not available. The latter project involves the synthesis of unsymmetrical mixed-ligand metal bis-dithiolene complexes for use as precursors to conductive and/or magnetic molecular crystals and also as potential non-linear optical materials.

In particular, we have found that incorporating dithiocroconate ligands into these complexes allows easy chromatographic separation of the desired mixed-ligand complexes from the byproduct symmetrical bis-complexes. Future work on this project will be directed towards preparation of a series of different unsymmetrical complexes and studies of their structural, spectroscopic and electrochemical properties.

New Synthetic Approaches to Geminal Difluoramino Compounds

Researcher: Associate Professor Christopher M. Kinter
Sponsor: Naval Surface Warfare Center, 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 (HNF2) 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. We previous explored the synthesis of gem-difluoramines through the preparation of gem-bisacetamides followed by reaction with elemental fluorine. However, this route suffered from the difficulties associated with the reliable production of the gem-bisacetamides and the unreliability of the reaction with fluorine. As such, alternate approaches for the production of organic compounds containing gem-difluoramino groups are currently being investigated including the reaction of diaziridines with selectfluor or diethylaminosulfur trifluoride (DAST), commercially available and widely applicable electrophilic and nucleophilic fluorinating agents, respectively.

Density Functional Calculations on the Reaction of Vanadium with Sulfur Dioxide

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

A computational study on the thermochemistry of the $V + SO_2 \rightarrow VO + SO$ reaction is reported. The objective of this work was to lay the ground work for the exploration of the potential energy surfaces of the reaction in question by first testing the theoretical method on the overall reaction. The method is density functional theory, which has been shown to be quite practical for transition metal systems when taking cost and accuracy into account.

Density Functional Theory (DFT) calculations are based on the notion that molecular properties can be determined from the electron probability density. The functionals take electron correlation into account explicitly. The Gaussian 03 suite of programs was used for the calculations. They were run on a Pentium IV personal computer.

Through previous work, it has been determined that on other transition metal (TM)/SO_2 systems, that the most practical basis sets are 6-311G(2d) for sulfur, 6-311G(d) for oxygen, and 6-311+G(d) for vanadium. These basis sets include polarization functions (d's) which allow the orbitals to change shape, and diffuse functions (+) which are important for TM atoms.

Geometry optimizations, frequency calculations, and population analysis were computed for SO_2, VO, and SO. The results compared well with accepted values. The energies, however, did not compare well for the reaction $V + SO_2 \rightarrow VO + SO$.

ΔH^oK(computed) = –37.64 kcal/mol and ΔH^oK(JANAF) = –20.33 kcal/mol. These results show that geometry optimizations and frequency calculations are not as sensitive to basis set size as energies are. The reactions $SO_2 \rightarrow SO + O$, $SO \rightarrow S + O$, and $SO_2 \rightarrow S + O + O$ were also studied at the same level of theory. Results (including energies) compared well with the literature. Computations involving transition metals, which have d-electrons and closely spaced energy levels, clearly require larger basis sets for increased accuracy in energies.

Future work includes potential energy surface scans, transition state optimizations, and reaction path following using the same basis sets (a total 125). Once transition state(s) and other stationary points have been found on the potential energy surface, single point energy calculations using larger basis functions may be performed. These jobs are significantly more expensive and they will have to be run on UNIX machines.

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 biological functions performed by ADARs are poorly understood and little is known about the regulation of this family of enzymes. Progress in these areas has been hampered by the lack of a simple and rapid method to measure the total amount of inosine in cellular mRNA. The goal of this project is to produce fluorescent RNA probes (called "beacon aptamers") that can detect inosine.

Beacon aptamers are RNA molecules that fluoresce upon binding to a selected ligand. A novel method for selecting beacon aptamers from a randomized pool of RNA has been developed. The method has been tested using the antibiotic tobramycin as ligand. Two unique RNA sequences resulted from this proof-of-principle experiment. Currently, experiments are being designed to test the ability of these RNAs to act as tobramycin beacon aptamers.

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 a cooperative agreement

The optical properties of surface seawater are impacted by the levels of chromophoric dissolved organic matter (CDOM). Photolysis of CDOM in surface waters leads to the destruction of the chromophore, potentially controlling the optical transparency of some surface waters. Coincident with the photolysis of CDOM is the production of a variety of oxygen radical species (OH, O^{2-}, HO_2 and RO_2) in surface waters, which lead to peroxide formation. A series of laboratory photolysis experiments and field measurements were performed to examine the relationship between peroxide formation and CDOM optical property changes. For each of the photolysis experiments, the peroxide concentrations were determined and several parameters to characterize changes in chromophoric dissolved organic matter were measured on each of the samples. In all the experiments changes in the absorption spectra for CDOM, (ad[λ]), were observed as well as changes in the synchronized fluorescence spectrum as a result of the irradiations. For some experiments samples were collected to characterize the change in dissolved organic carbon in the samples during the irradiation. Loss of absorbance or fluorescence indicated photobleaching of CDOM, while decrease in DOC indicated oxidation of DOC. These results were compared to production of peroxides. Our results suggest a substantial production of peroxides from waters containing abundant

terriginous C (humic substances), supporting the assertion that photochemically-mediated oxidation of DOM is a dominant mechanism for its removal in coastal waters. Quantum yield data for peroxide production were substantially different than for CDOM photobleaching for the same water samples. These results support the assertion that changes in optical properties and CDOM chemistry, while certainly being related, are separate processes, and that optical change in CDOM does not necessarily imply chemical change. Project work continues in cooperation with the Naval Research Laboratory, and has resulted in four presentations and one submitted paper.

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

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

The Rain in Cumulus over the Ocean Experiment (RICO) investigates trade wind cumulus clouds and the surrounding clear air to further understanding of shallow cumulus cloud microphysics and dynamics, larger-scale meteorological interactions, and climate forcing induced by cumulus cloud impacts on radiation and moisture budgets. RICO involves an international team of investigators employing in situ observations, remote sensing, and theoretical models. RICO traces the atmospheric physics and chemistry of particle evolution, from haze aerosol, to cumulus cloud droplet formation, alteration by clear-cloud air mixing and photochemistry, through to "warm-rain" precipitation development. In our collaborative sub-project of RICO, in situ chemical observations of gaseous hydrogen peroxide and methylhydroperoxide are made in clear and cloudy air in the marine boundary layer and lower free troposphere using the NCAR C-130 airborne platform. Observations of aqueous hydrogen peroxide and methylhydroperoxide condensed upon cloud size and larger droplets are also made using a counter-flow virtual impactor. The peroxide analytical instrumentation is capable of collecting a sample in 10 s and of analyzing a sample in 2 min. The sampling resolution is adequate to characterize clear air above and below cloud and bulk cloudy air. The peroxides are integral to understanding and predicting the temporal evolution of aerosol sulfate, cloudwater sulfate, and cloud condensation nuclei activity. The peroxides are the leading oxidants of sulfur dioxide dissolved in atmospheric water and sulfur dioxide oxidation is the principle chemical process by which aerosol dry mass increases. The RICO (Lesser Antilles in winter 2004-05) photochemical environment is favorable to the formation of hydrogen peroxide and methylhydroperoxide. Sulfur dioxide is expected to be present from oceanic sulfur gas emissions, episodic volcanism, and long-range transport of anthropogenic emissions. The in-cloud oxidation of sulfur dioxide is of the same time-scale as that of shallow cumulus cloud parcels and tractable by the suite of microphysical and chemical instruments on board the C-130. The USNA will participate in the field measurement phase and data analysis, as well as providing the organic peroxide standards. Methylhydroperoxide is not commercially available and will be synthesized and purified at the Naval Academy. The organic peroxide stock concentrations will be determined at the Naval Academy.

Measurement of Gas-Phase H_2O_2, CH_3OOH and CH_2O on the DC-8 during INTEX-A

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

H_2O_2, CH_3OOH, and CH_2O are primary and secondary photochemical products of naturally and anthropogenically emitted pollutants. These gases are active in odd-Oxygen and odd-Hydrogen photochemistry as reservoir species, and hence sources, of stronger oxidants like HO, HO_2, and CH_3OO. The latter two species, HO_2 and CH_3OO, along with NO are the necessary precursors for tropospheric O_3 production. The former species, HO, is a principal oxidant for most atmospheric material, controlling their transport time, distribution and deposition patterns. In the case of SO_2 (a primary precursor of aerosol sulfate), HO, H_2O_2, CH_3OOH, and CH_2O are all coupled to its oxidation through gas, aqueous, and heterogeneous reactions.

H_2O_2, CH_3OOH, and CH_2O concentrations are dependent upon the chemical environment; volatile organic carbon compounds (VOC's), oxygenated volatile organic carbon compounds (OVOC's), nitrogen oxides, ozone, and water vapor. They are also dependent upon the meteorological environment; advection and mixing processes and history, temperature, pressure, cloud and precipitation processes and history, and ultra-violet light. These dependencies make them tracers of chemical reaction mechanisms and of meteorological transport phenomena. As examples, CH_3OOH and CH_2O are relevant

to understanding methane oxidation and together with other OVOC's the oxidation pathways of other VOC's. H_2O_2 and CH_3OOH distributions can indicate strong convection or mixing events with associated cloud and precipitation processing. INTEX-A provides an opportunity to compare different H_2O_2 and CH_3OOH instrumental methods. We propose measurements using an established gas-to-aqueous collection method with wet chemical determination of H_2O_2 and CH_3OOH.

Plant Genetic Structure as a Controlling Factor in Community and Ecosystem Functioning: Studies Using Natural and Synthetic Hybrids of a Dominant Riparian Tree

Researchers: Assistant Professor Brian J. Rehill,
Dr. Richard Lindroth (University of Wisconsin at Madison),
and Dr. Thomas Whitham, Dr. Steven Hart, Dr. Gregory Martinsen,
and Dr. Phillip Keim (University of Northern Arizona)
Sponsor: National Science Foundation (NSF)

This project aims to elucidate the role of plant genetics in structuring associated ecological communities and the ecosystem processes of the surrounding landscape. The work focuses on the role of cottonwood trees, which dominate riparian habitats in the intermountain west of North America. Much of the research takes place in and around the Weber River in Utah, between the city of Ogden and the Wasatch-Cache National Forest. However, many other studies occur in suitable habitats along other rivers in the west, such as in Arizona, New Mexico, Utah, Colorado, Idaho, and Wyoming. The initial grant was part of the National Science Foundation's IRCEB (Integrated Research Challenges in Environmental Biology) program, with funding to be continued as part of the FIBR (Frontiers in Biological Research) program. The mandate of both funding imperatives is clear: to promote interdisciplinary research that investigates fundamental biological questions. As such, the project includes ecosystem, community, population, and chemical ecologists along with geneticists and chemists.

Dr. Rehill's as a postdoctoral research associate for 26 months (May 2001 through July 2003) in the laboratory of Dr. Richard Lindroth at the University of Wisconsin at Madison was to lead investigations related to plant chemistry and to chemical ecology. Manuscripts related to work in this system are in preparation, and multiple publications are anticipated as a result of this work. Furthermore, active research on this project continues, in collaboration with the other researchers.

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 Biophysics Department
Sponsors: Naval Academy Research Council (NARC) and
National Science Foundation (NSF) Research Opportunity Award

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 Staphylococcus nuclease. Intriguingly, the vast majority of resultant proteins were expressed in E. coli successfully. Of 25 amino acids mutated to lysine or aspartate, 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 □□G), and clear differences from the "wild-type" hyperstable proteins were observed. Two sets of mutants, in which residue 66 or 92 was converted to either lysine or aspartate, have been studied via

crystallography. 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.

Molecular Dynamics Studies of 1, 4-Polyisoprene

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

Among amorphous polymers, the dielectric and mechanical properties of 1,4-polyisoprene (PI) have been extensively studied. Although many workers have measured the local segmental and the normal modes, secondary relaxation of the Johari-Goldstein kind has not been reported previously. By using a high-resolution capacitance bridge, we are able to show a secondary relaxation in PI. Measurements were also carried out at lower temperatures which probe the local structure. Since both the secondary relaxation and local dynamics serve as precursors to structural relaxation, they are important to understanding the process of vitrification. We find evidence that the local dynamics of PI are manifested as a nearly constant loss (NCL) which has been reported in other glass-formers, both molecular and polymeric. Experimental results are consistent with theoretical predictions, and provide a basis for understanding glass transition behavior.

Synthesis and Characterization of Nanocomposite Materials for Impact Protection

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 U.S. Army is currently investigating the development of new synthetic polymers and nanocomposites for use in transparent armor and coatings applications. Novel synthesis procedures have been developed for a number of polymer systems based on polymethylmethacrylate and polycarbonate materials. 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 materials. Characterization studies of these new materials have included thermal analysis by differential scanning calorimetry (DSC) and molecular weight determinations by gel permeation chromatography (GPC) and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS). The goals of this project include synthesis and characterization of these new polymeric materials in hopes 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. 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 site-directed chemical labelling and electron paramagnetic resonance spectroscopy, we investigated the protein-protein interactions between SecB and its ligands.

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. Fluorescence spectroscopy, mass spectrometry and enzyme activity assays are being used to investigate the interactions between MsrA and oxidized proteins.

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

Researchers: Mr. Ronald R. Price, Naval Research Laboratory and LT Eric R. Welsh, USNR
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 underway with new formulations. Studies on the cross-linking system have yielded four peer-reviewed publications: two in *Biomacromolecules*; one in *Carbohydrate Polymers*, which derived from a collaborative effort with researchers at the National Institute on Standards and Technology (NIST) on chitosan hydrogels, and one in *Langmuir*.

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 goals of this research are to design, synthesize and characterize novel organic photovoltaic materials. Organic materials are attractive for photovoltaic devices primarily through the prospect of manufacturing ultra thin, flexible devices.

The initial objective for this project was the synthesis of high conductivity, high optical transparency conducting polymer films that incorporate 3,4-ethylenedixoythiophene (EDOT) monomers. The EDOT derivative 2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol was synthesized via a multi-step process starting from diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate. Triphenylamine (TPA) and oligo(*p*-phenylene vinylene) (OPV) units were also synthesized to be employed as light-harvesting groups. The OPV oligomer was a novel molecule with a maximum absorption wavelength in chloroform of 400 nm. When bonded covalently to a conducting polymer, this unit will increase the light-harvesting capability of the system. Such an increase would allow for the fabrication of more efficient photovoltaic devices.

The EDOT derivative 2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol was oxidatively polymerized in the presence of the OPV oligomer. The resulting polymers were then characterized with respect to conductivity and optical transparency. Once optimized, the materials will ultimately be used in organic-based photovoltaic devices.

Independent Research

Molecular Dynamics Simulations of the Bending of Filled Carbon Nanotubes

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

The overall goal of this project was to examine the mechanical properties of carbon nanotubes. Nanotubes are filled with CH4, C60, and Ne. Mechanical properties as a function of filling gas, tube length, and temperature have been examined. This collaboration resulted in a publication in *Physical Review Letters* and a second manuscript is under review.

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.

To date, some trial syntheses of 3-phenyl-3-cyclobutene-1,2-dione were conducted, and it was concluded that the published literature procedure being followed would not be a viable route. Extensive literature searching resulted in several possible alternate approaches. Continued research on this project during fall 2003 and spring 2004 was hampered due to the loss of laboratory spaces as a result of Tropical Storm Isabel in September 2003.

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

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

Solid state chemistry is important in electrochemical systems (batteries and fuel cells), catalysis and optics. 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 reactions 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, such as V_2O_5, 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 the SC364 Integrated Laboratory IV, we refined and extended the project. New difficulties with the PXRD presented themselves, and further refinement should lead to a journal publication. With the loss of PXRD capability a new approach to characterization using reflectance spectroscopy was suggested and implemented. Further improvements in synthesis and characterization of the compounds are ongoing.

Potential Energy Surface Scans of the Fe + SO_2 → $FeSO_2$ Reaction

Researcher: Associate Professor Roy E. McClean

The transition metals Cr - Ni react with SO_2 via a termolecular reaction mechanism; i.e., TM + SO_2 + Buffer → $TMSO_2$ + Buffer. The rate constants for these reactions depend on the electron configuration of the TM atoms. Cr, which has a $4s^1 3d^5$ configuration, is very reactive with SO_2 whereas the other TM atoms which have filled 4s subshells are not as reactive. The rate constants for the latter correlate with the s-d promotion energy, the energy required to promote an electron from the 4s orbital to a 3d orbital. In this work, we computed the most likely potential energy surface of the Fe + SO_2 association reaction, with the overall objective of obtaining additional information on the reaction mechanism.

The Gaussian 98 suite of programs was used for the computations. Because the jobs are quite costly, they were run on UNIX-based computers at U.S. Naval Academy. 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. A thorough investigation into the $FeSO_2$ was untaken. Once all the bugs were worked out on this system, the study was extended to other TM systems.

The η^2O,O complex of $FeSO_2$ was found to be the global minimum (24.4 kcal/mol below the Fe + SO_2 asymtote). It is of c2v symmetry and the Fe is bonded to the two O-atoms. PES scans along several collision axis were computed. The approach of Fe along the c2v axis of SO_2 (O-O end) was the most favorable energetically and was consistent with kinetic data. (The entire geometry was allowed to relax, but it remained approximately c2v.) The potential energy scan revealed a barrier of ≈1.4 kcal/mol. Further calculations on the population of the Fe atom indicate that it assumes a $4s^1 3d^7$ configuration at the barrier. Based on these observations, we conclude that the barrier to reaction is due to the energy required to promote a 4s electron to a 3d orbital.

Potential Energy Surface Scans of the TM + SO_2 → $TMSO_2$ Reactions, where TM = the 3d transition metals Cr - Ni

Researcher: Associate Professor Roy E. McClean

The transition metals Cr - Ni react with SO_2 via a termolecular reaction mechanism. The rate constants depend on the electron configurations and on the $4s^2 3d^{n-2} \rightarrow 4s^1 3d^{n-1}$ promotion energy (PE), where n is the number of valence electrons. Cr has a $4s^1 3d^5$ configuration and is very reactive with SO_2. The other 3d transition metal (TM) atoms are not as reactive and a correlation is observed between their rate constants and their PEs; the smaller the PE the larger the rate constant. In this work, we computed the most likely potential energy surfaces of the TM + SO_2 association reactions, with the overall objective of obtaining additional information on the association reaction mechanism of the 3d TM series.

The Gaussian 98 suite of programs was used for the computations. They were run on UNIX-based computers at the Naval Academy. 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 the TM atoms.

Previous theoretical work on $FeSO_2$ indicated that the barrier is related to the promotion energy. The PE of Cr, Ni, Co, Fe, and Mn are 0, 205, 3483, 6928, and 17052 cm-1, respectively. Therefore, one should see a corresponding increase in any computed barriers. The η^2O,O complex of the $TMSO_2$ complexes was found to be the global minimum. Results of PES scans along the c2v axis of SO_2 (O-O end) were found to be consistent with the experimental data and the PEs. The scans revealed no barriers for Cr (as expected), Ni, and Co. The PE is so small for Ni that presumably, it is the state at 205 cm-1 that reacts. The PE for Co is sufficiently small such that a barrier is not observed.

A barrier was computed for Fe, as presented earlier. Mn has a significantly larger PE and is unreactive, and the PES scan produces a completely repulsive surface along the c2v axis. Thus, experiment and theory are consistent.

Analysis of the Equilibrium Behavior of Peroxide Compounds and the Kinetics of Complex Formation between Titanium (IV) and Peroxide Compounds

Researchers: Associate Professor Daniel W. O'Sullivan PI, Assistant Professor Dianne J. Luning-Prak and Midshipman 1/C Michael Tyree, USN

Understanding the chemistry of hydrogen peroxide in the atmosphere is important for modeling pollutant formation. Measurement of hydrogen peroxide concentrations can be used to determine the concentration of hydroxyl radicals, which are involved in forming pollutants, and to predict the formation of acid rain by peroxide compounds. The objectives of this research are to quantify the equilibrium distribution of peroxide compounds and measure the rates of reaction of equilibrium mixtures with titanium (IV) oxysulfate.

Equilibrium concentrations will be determined using a high pressure liquid chromatograph equipped with a spectrofluorescence detector. Equilibrium mixtures have been prepared and various column conditions are being tested to optimize compound separation. Kinetic experiments will be done using a stop-flow injection technique. Initial experiments have quantified reaction rates for hydrogen peroxide and Ti(IV). Future work will examine the reaction rates for the equilibrium mixtures.

High-Pressure Crystal Structure of RDX

Researchers: Associate Professor Wayne H. Pearson and Dr. Suhithi M. Peiris, Naval Surface Warfare Center - Indian Head Division

Although the crystal structure of the RDX explosive has been determined at room temperature and pressure, there is essentially no information concerning structural changes that occur to the explosive at high pressure. This project, which is in the preliminary stages, is an attempt to determine the high pressure (> 1 GPa) crystal structure of RDX. Preliminary synchrotron data, provided by Dr. Peiris at Indian Head, had been obtained using a diamond anvil cell with X-ray radiation at approximately 0.30 Angstroms. A structure solution was obtained for these data and a model, with isotropic temperature factors, was refined to an R(F) = 17%. In spite of the uncertainty in unit cell measurements and a total lack of an absorption correction for the diamond anvil, this was a very favorable result. A full set of bond distances and angles were generated for analysis by the group at Indian Head.

Electron Density Mapping in Transition Metal Complexes

Researcher: Associate Professor Wayne H. Pearson

High quality, X-ray data from a series of compounds consisting of potassium chromate, potassium manganate, potassium ferrate and potassium sulfate have previously been examined using 2-dimensional Fourier analysis techniques. These techniques are quite limited in searching for electron density features that do not reside on a plane that can be defined by atom positions. The original data sets have now been examined and modified in format in order to be analyzed by the MaXus suite of software that is used for standard crystallographic modeling. Results for the planes defined by atomic positions are consistent with previous results obtained with older, 2-dimensional software. In addition, it is now possible to examine other orientations in real space that were impossible to define with the older software. This new, 3-dimenstional analysis allows for the determination of the height of the difference electron density features above and below a plane of atoms as well as planar slices at any angle to a plane of atoms.

Crystallization Studies of Mutant DNA-Binding Domains from the Heat Shock Transcription Factor of *Kluyveromyces lactis*

Researcher: Assistant Professor Jamie L. Schlessman

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 con-

sists 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, determination of the crystal structures of several of the DNA-binding domain mutants is being pursued. Once obtained, these atomic structures will be compared with that of the wild-type protein, and then 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 the Naval Academy. 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 Academy studies, single crystals of the wild-type protein were obtained. Successful candidate crystals will be taken to the School of Medicine at the University of Pennsylvania for X-ray diffraction analysis.

Biophysical Characterization of a Bifunctional Iron-binding Protein

Researcher: Assistant Professor Virginia F. Smith

Human cytoplasmic aconitase is a large (98 kDa) protein that contains a [4Fe-4S] center required for enzymatic activity. Under conditions of iron depletion, the iron-sulfur cluster disassembles and cytoplasmic aconitase assumes its alternate identity as human iron regulatory protein 1 (hIRP-1). By binding to iron responsive elements (IREs), hIRP-1 assists in the restoration of normal iron levels. the iron-sulfur cluster disassembles and the protein binds to iron-responsive elements Equilibrium thermal and chemical denaturation reactions monitored by intrinsic tryptophan fluorescence emission spectroscopy reveal that the protein has a complex unfolding mechanism that cannot be described by a two-state model. Furthermore, the urea- and thermally-denatured states have distinct spectroscopic properties, suggesting alternate unfolding pathways dependent on the method of denaturation. The enzymatic activity was measured over a range of temperature and urea concentrations that revealing that the enzyme activity is enhanced by low levels of urea (up to 1M) and persists to about 2M urea, the concentration at which the non-native baseline appears. Activity reaches a maximum at about 50°C, a value that was slightly higher than the apparent Tm of ~ 45°C in the absence of ligand, suggesting that the presence of substrate enhances protein stability. The apparent low thermal stability of cytoplasmic aconitase, combined with the relative robustness of the enzyme as measured by activity, suggest that the protein has a high degree of structural plasticity that may be required for its two functional roles and that this structure stabilized by the presence of its natural ligands.

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

Researcher: Associate Professor Joseph J. Urban

This project involves a systematic evaluation of the stereoelectronic effects that accompany fluoro and trifluoromethyl substitution in prototypical amine compounds. A variety of computational methods have been employed including molecular mechanics, semi-empirical, density functional, and *ab initio* methods. The effect of solvent is also being considered via a continuum solvation model. Specifically, the goals of this work are to characterize the energetic consequences of the stereoelectronic effects in terms of conformational preferences, and to characterize the changes in molecular geometry and charge distribution that accompany the stereoelectronic effects. Also, a comparison of results among the computational methods is being carried out and a comparison to minimal experimental data that is available. The results indicate that the stereoelctronic effects in these compounds can play a dominant role in determining the conformational preferences and are

often in opposition to simple sterics. Also, there are predictable changes in geometry that accompany the stereoelectronic effects. Finally, the molecular mechanics force fields that have been investigated thus far do a reasonable job of capturing the important trends when compared to high-level *ab initio* methods. The reliability of the semi-empirical methods seems much lower.

Trident Scholar Projects

Classification of Community-associated Strains of *Staphylococcus aureus* at the United States Naval Academy (Trident Report # 320)

Researcher: Midshipman 1/C Daniel L. Bowers, USN
Adviser: Assistant Professor Tammy L. Domanski

The genus staphylococcus was given its name by Sir Alex Ogston, a Scottish surgeon, in 1881 when he observed grape-like clusters of bacteria associated with clinical infections. Three years later, the German physician Anton Rosenbach isolated and grew these microorganisms in a pure culture. He named them *Staphylococcus aureus* because of their golden color. *S. aureus* remains one of the most important pathogens in clinical settings largely due to the rapidity of its evolutionary response to treatment. The first antibiotic-resistant strains of *S. aureus* were isolated only several years after penicillin was introduced commercially, and the subsequent history of antibiotics has been driven by the evolving emergence of antibiotic resistance.

Our ability to control the rate at which resistance develops and spreads is predicated on our understanding of the evolutionary biology of pathogens and the basic features of bacterial populations, and while hospital acquired strains of *S. aureus* have received a great deal of attention, the distribution and virulence (ability to cause infection) of community-associated strains of *S. aureus* are not well-defined and few studies have assigned isolates of the bacteria to known strains.

The objectives of this study were to collect, isolate and characterize samples of S. aureus from areas utilized by midshipman athletes at the United States Naval Academy and patients at the Naval Medical Clinic, Annapolis. These samples were classified in several steps including their gross morphology and determinative biochemical activities. Finally, a multilocus sequence typing (MLST) scheme was used to unambiguously characterize the isolates and analyze significant evolutionary trends in the population. The sequences of internal fragments of seven genes were obtained for 36 *S. aureus* isolates and assigned a unique allelic profile. These profiles, like fingerprints, were used to assign the isolates to known strains or to identify them as novel strains via publicly accessible MLST databases. The genetic information provided by MLST was used not only to distinguish between unrelated strains, but to predict relationships in the causes, distribution, and control of infection in populations.

Detailed environmental studies are the first and most important step in delineating the population biology of community associated bacteria and will contribute to a viable long term strategy for the treatment of infectious disease.

Synthesis and Characterization of Novel Organic Conducting Polymers (Trident Report # 322)

Researcher: Midshipman 1/C Katharine E. Folz, USN
Adviser: Associate Professor Craig M. Whitaker

The last two years have seen an extraordinary growth of interest in photovoltaic (PV) cells made from organic conducting polymers. Such attention stems primarily from the prospect of using organic materials in manufacturing ultra thin, flexible devices. Polymeric photovoltaic cells also present a tantalizing possibility for producing coatings that function as sunlight-harvesting paints or even for developing fabrics to produce electricity from sunlight. The U.S. Navy developed an interest in electroactive polymeric research because of these specific potential applications for such devices and the materials from which they are based. The Office of Naval Research is currently probing new opportunities to convert energy into useful power sources, motivated by its interest in the development of an electric Navy for future years.

The technical objectives for this project were the synthesis and characterization of high conductivity, high optical transparency conducting polymer films that incorporate 3,4-ethylenedixoythiophene (EDOT) monomers. Initially, the EDOT derivative 2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol was synthesized via a multi-step process starting from diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate. Triphenylamine and oligo(p-phenylene vinylene) units were also synthesized to be employed as light-harvesting groups.

Midshipman Research Course Projects

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 Nicholas S. Cardillo, USN
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.

The properties of TREN-based podands to design an easily synthesized "pre-organized" ligand have been studied. The initial work has involved the study of aminopyridyl tripodal and linear ligands. In this study, the initial work is being expanded to include the "softer" aminothiophene ligands.

The following series of aminothiophene ligands were synthesized and characterized: TREN-thio (tris(2-((2-thiop hene)amino)ethyl)amine), EN-thio (1,7-bis(2-thiophene)-2,6-diazaheptane), DIEN-thio (1,9-bis(2-thiophene)-2,5,8-triaza-nonane), 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, Cu(II)DIPNEN-thio, and Ni(II)DIPNEN-thio complexes was isolated as a solid perchlorate salts. Magnetic susceptibility measurements, electronic spectra, UV-vis spectra, and electrochemistry were used to analyze the complexes.

Molecular Modeling Studies of Fluoroolefin Peptide Mimetics

Researcher: Midshipman 1/C W. A. Cronin, USN
Adviser: 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 results indicate that the fluoroalkene moiety is a reasonable mimic of the peptide bond in terms of geometry but that it has a much smaller separation of charge than the native peptide. For the simplest model compounds, the fluoroolefin is also less well hydrated than the natural peptide but follows the same trend in terms of the relative hydration of the cis and trans conformers. For larger systems (ala-ala and ala-pro), there are significant differences in the conformational preferences that are related to the differences in the hydrogen bonding capability of the fluoroalkene group relative to that of a natural peptide.

Illustrating the Concept of Sparingly Soluble Salts Using Various Copper Salts: A Classroom Demonstration

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

Many students in general and advanced chemistry courses have difficulty understanding differences in solubility by inspecting changing values of the solubility product constants for the sparingly soluble salts. In this demonstration, the concept of differing solubility of sparingly soluble salts is illustrated visually. Utilizing bathocuproinedisulfonic acid in a mixed reducing reagent to complex copper (I), it is possible to demonstrate (to the naked eye) changes in copper (II) concentrations resulting from the dissolution of a variety of sparingly soluble copper salts. The actual concentration of copper (II) in solution can be determined using this visual demonstration in combination with a spectrophotometer. This demonstration visually confirms changes in copper (II) concentration in the range of 1×10^{-3} to 1×10^{-6} M. The range of observable solubility can be extended to higher concentrations using ammonia as a complexing agent. The experimentally determined solubility product constants compare favorably with the theoretical values.

Synthesis of Nucleotide Diphosphonate Analogues with Potential Antiviral Activity

Researcher: Midshipman 1/C David T. Fleischmann, USN
Adviser: Associate Professor Debra K. Dillner

This study involved preparing diphosphonate nucleotide analogues as possible antiviral agents. Potentially, incorporation of these specific molecules into new viral genetic material will lead to unstable or nonfunctional viral RNA or DNA. To develop compounds whose conformational isomers will be similar to those of natural nucleotides, computer modeling was undertaken. A symmetrical arrangement of two phosphonate functional groups places one phosphonate in an active site of DNA/RNA polymerase, while another phosphonate rests outside the active site. The target compounds were prepared from simple dihalides. After completing their synthesis, the compounds were considered for antiviral activity.

Exploration of the Structure of Human Iron Response Protein – 1 through Sequence Analysis, Molecular Modeling and Protein Analysis

Researcher: Midshipman 1/C Kristina N. Melendez, USN
Adviser: Assistant Professor Virginia F. Smith

Iron response protein 1 (IRP-1) is the mammalian iron responsive element (IRE) binding protein. When cellular levels of iron are low, IRP-1 binds to IRE on mRNA, and participates in the production of proteins that are involved in iron production. Once the cellular level of iron is restored, IRP-1 loses its affinity for IRE and changes conformation, becoming cytoplasmic aconitase. Cytoplasmic aconitase has a similar primary structure to mitochondrial aconitase, yet its three-dimensional (3-D) structure and conformation are not fully known.

A sequence alignment was performed between the amino acid sequence of human iron response protein 1 (hIRP-1) and mitochondrial aconitase from Sus scrofa using molecular alignment software. The results of this alignment were used to mutate the sequence of Sus scrofa using Swiss-Pdb Viewer 3.7, and the resultant structure was analyzed. Further exploration of the conformation changes cytoplasmic aconitase undergoes due to pH and temperature changes was also explored through the use of ultraviolet (UV)-spectroscopy.

Low Temperature Infrared (IR) Spectroscopy of Water and Ammonia Ices

Researcher: Midshipman 1/C Jason N. Stone, USN
Adviser: Professor Robert F. Ferrante
Sponsor: NASA/Goddard Space Flight Center

Water- and ammonia-ices have been observed or postulated as important components of the icy surfaces of planetary satellites in the outer solar system, such as Pluto and its moon Charon. Significant gaps exist in our knowledge of the spectra and behavior of such mixtures under astrophysical conditions. Samples were prepared by direct deposition of pure gases or

gas mixtures of ammonia and water onto a low-temperature surface maintained by a closed-cycle helium refrigerator. The resulting ices were examined by low temperature (10 K - 160 K) FT-IR spectroscopy before and after thermal processing (accomplished by warming the samples to various temperatures appropriate for the astrophysical systems) or radiation processing (achieved by exposing the samples to a beam of 1 MeV protons generated by a van de Graaff accelerator). Changes in the spectra were indicative of formation or destruction of chemical compounds, or phase changes of the components. The experiments were mainly focused on two stable hydrates of ammonia, NH_3:H_2O and $2NH_3$:H_2O, and the effects of initial gas composition, temperature, thermal- and radiation-processing on the spectra. Special emphasis was placed on the near-IR region, which is most accessible to ground-based observations. These studies were designed to supply laboratory data that might aid in interpretation of astronomical observations, and provide for better modeling of the surfaces of these icy bodies. New features in the near-IR were reported for the two hydrates, and short-term radiation effects, modeling up to a few million years of solar system irradiation, were quantified for the first time. Early results were reported at the 227th National Meeting of the American Chemical Society in Anaheim in March 2004. Work is continuing with two specific aims: observing the third stable hydrate (NH_3:$2H_2O$), which may be important in terrains with relatively higher amounts of water, and quantifying long-term radiation effects, to model the 4+ billion years of the life of the solar system.

Antimalarial Activity of Halomethoxylated Quinoline-Containing Chalcones

Researcher: Midshipman 1/C Darshan S. Thota, USN
Adviser: Assistant Professor Clare E. Gutteridge

a) Purpose: To identify antimalarial chalcones with sufficient in vitro potency to warrant in vivo antimalarial testing.

b) Objectives: To understand how varying the substitution pattern on the two rings of quinoline-containing chalcones influences antimalarial activity, with the aim of increasing in vitro antimalarial potency.

c) Method of Investigation: One potentially interesting class of antimalarial chalcones is one bearing a quinoline B-ring. However, the analogs described in the literature have not been optimized on the A-ring. Using aldol condensation of various acetophenone and aldehydes, the synthesis of the four analogs in Figure 5 was planned to explore the relationship between molecular structure and antimalarial activity in this class of compound.

d) Results: The analogs targeted were successfully synthesized at USNA, then assayed for their ability in inhibit the growth of Plasmodium falciparum, the causative agent of malaria at WRAIR. The minimum concentration of each analog required to inhibit cell growth by 50% is shown in Figure 5 under its corresponding structure (IC50 values). Potent single-digit micromolar inhibitors were produced, and trends in activity were established which will be useful in designing more potent compounds.

e) Status: Complete. The results of this project were presented in a seminar by Midshipman 1/C Darshan Thota at the Eastern Colleges Science Conference on 3 April 2004.

Antibacterial Chalcones

Researcher: Midshipman 1/C Cera B. Tillett, USN
Adviser: Assistant Professor Clare E. Gutteridge

a) Purpose: To identify chalcones able to selectively inhibit the growth of Staphylococcus aureus and simultaneously develop a research-based laboratory program, suitable to complement an upper-level medicinal chemistry lecture course.

b) Objectives: To develop syntheses and assays suitable for use in an upper-level laboratory course that can be used to teach the principles of drug discovery, while simultaneously gaining an understanding of how the presence of substituents on a chalcone influences its antibacterial activity.

c) Method of Investigation: Develop a Minimum Inhibitory Concentration (MIC) assay then use a known antibiotic (chloramphenicol) to validate it. Then synthesize and test chalcone antibacterials.

d) Results: The assay was developed using culturing S. aureus in Mueller-Hinton broth and dosing drug in DMSO (to a final concentration of 1%). The MIC determined for chloramphenicol match that reported and that from an E-test assay, thus validating the assay.

e) Status: Two of the dihydroxylated chalcones were synthesized by an aldol condensation (15 min at 55°C in aqueous KOH, followed by HCl neutralization) and then purified by silica column chromatography. The other compounds were synthesized in a similar manner.

Bimolecular Rate Constant for the Recombination Reaction $CH_3 + C_2H_5 \rightarrow C_2H_6$ at T = 298 K and 202 K

Researcher: Midshipman 1/C Eric H. Twerdahl, USN
Adviser: Professor Mark L. Campbell
Sponsor: NASA/Goddard Space Flight Center

The recent detection of alkyl free radicals in the atmospheres of Saturn and Neptune provides the impetus for this study. The disagreement between observed and calculated levels of CH_3 in these atmospheric systems has led to suggestions that current models greatly underestimate the loss of CH_3 due to poor knowledge of the self reaction $CH_3 + CH_3 + M \rightarrow C_2H_6 + M$ and the analogous reaction $CH_3 + C_2H_5 + M \rightarrow C_3H_8 + M$ at the relevant low temperature and pressure conditions. The kinetics of the CH_3 self reaction have been previously reported at low temperature and pressure. In this study, a method for determining the bimolecular rate constant for the reaction $CH_3 + C_2H_5 \rightarrow C_3H_8$ has been shown using the discharge-flow kinetic technique coupled with mass spectrometric detection at T = 202 and 298 K and P = 0.4 – 2.0 Torr He. To date, we cannot accurately report the bimolecular rate constant for any set of temperature and pressure conditions studied. The fundamental assumption of the pseudo-first order analysis ($[C_2H_5] = [C_2H_5]_0$) has been found invalid in each case by a mass spectroscopic measurement of C_2H_5 signal decay over the reaction interval. C_2H_5 signal was measured as the result of product analysis that suggested the formation of butane from $C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$. Further experiments are required to assess a possible remedy for the apparent departure from first order behavior.

Analysis of the Kinetics of Complex Formation between Ti(IV), Hydrogen Peroxide, and Hydroxymethylhydroperoxide

Researcher: Midshipman 1/C Michael G. Tyree, USN
Adviser: Associate Professor Daniel W. O'Sullivan

The kinetics of the formation of the titanium-peroxide ($[TiO_2^{2+}]$) complex from Ti(IV), hydrogen peroxide, hydroxymethylhydroperoxide (HMP) were studied in this project. This was done in order to determine whether Ti(IV) can be used to distinguish between hydrogen peroxide and HMP. The kinetics of the system were studied though both standard UV/Visible and stop flow spectroscopy at 405 nm at various temperatures. The molar absorptivity of the $[TiO_2^{2+}]$ was measured from its formation in standard hydrogen peroxide solutions. The ε of the complex was found to be 654.44 cm-1M-1. The rate constant for the reaction between peroxide and Ti(IV) was found to be 575.99 min-1 at 25°C. In addition, it was determined that the formation of the $[TiO_2^{2+}]$ complex can be used to distinguish between hydrogen peroxide and HMP.

Synthesis and Field Testing of Elastomeric Materials in Repair of Radford Terrace

Researcher: Midshipman 1/C Elizabeth A. Yatko, USN
Adviser: Associate Professor Maria J. Schroeder

Elastomers have served in a wide variety of applications, ranging from tires to o-rings to bungee cords. Not surprisingly, elastomeric materials have been employed in many construction applications due to their unique physical properties and weather resistance. In this project, elastomers were examined as a unique and inexpensive solution to the failing paver tile system of Radford Terrace located on the grounds of the U.S. Naval Academy. Every few months, the grout between the cement pavers and cement supports deteriorates causing instability of the pavers and consequently the system must be replaced. It was theorized that a rubber pad acting as a gasket between the pavers and supports could provide protection from deterioration and serve as a cushion absorbing the loading stresses. Therefore, a variety of elastomeric pads were

synthesized in the laboratory and characterized. Various recipes of rubber materials and additives were investigated as well as different curing conditions. Three different elastomeric materials were installed on the terrace and tested under actual usage conditions in an attempt to evaluate their performance. After two months of field testing, an elastomeric material (based on a deproteinized natural rubber) proved to be most resistant to wear and showed the greatest potential for solving the paver problem.

Midshipmen Capstone Projects

Organic Small Molecule Additives for the Crystallization of Proteins

Researcher: Midshipman 1/C Daniel S. Cabrales, USN
Advisers: Assistant Professor Shirley Lin and Assistant Professor Jamie L. Schlessman

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

Synthesis of Octakis(pentafluorophenyl)tetraazaporphyrin as Potential Oxygen Activation Catalyst

Researcher: Midshipman 1/C Jeanne H. Cameron, USN
Adviser: Professor Jeffrey P. Fitzgerald

The goal of this experiment was to synthesize octa-pentafluorophenyl-tetraazaporphyrin. The target molecule was successfully synthesized through three reaction steps and purified mainly via pressure and gravity column chromatography. Compounds were characterized by IR, 19F NMR, UV-Vis, GC-MS, MALDI-TOF MS and X-ray crystallography. Further experimentation may provide results on whether metal derivatives of octapentafluorophenyltetraazaporphyrin can be successfully used as molecular oxygen activation catalysts, in the hopes of providing more efficient means to oxidize alkanes and alkenes to alcohols. Such a catalyst could have a variety of beneficial uses, including more efficient decontamination of equipment and personnel exposed to chemical warfare agents, along with safer, and more ecologically sound means of cleaning up oil spills.

Laboratory Development: Detection of 2,4,6-Trinitrotoluene in Soil Samples using a Fluorescent Immunoassay Technique

Researcher: Midshipman 1/C Brian J. Cummings, USN
Adviser: Associate Professor Maria J. Schroeder

The demilitarization, testing, and storage of military weapons have led to explosives contamination of the soil and groundwater in certain areas. As a result, several traditional methods for detection of 2,4,6-Trinitrotoluene (TNT) have been used. However a new technique developed by military researchers shows promise as a faster, more sensitive alternative. This research was the basis for the development of a new laboratory experiment for the Integrated Laboratory Program at the U.S. Naval Academy. The experiment involves the analysis of soil samples for TNT using a fluoroimmunoassay technique. In this technique, a fluorescently-labeled TNT analog pre-bound to an anti-TNT antibody is reacted with TNT. The TNT and the analog undergo a competitive immunoassay and the ability of the analog to undergo fluorescence is based on the displacement by TNT. Concentrations in the ppb range can be detected in soil samples by monitoring the fluorescence decrease when TNT competes with the fluorescent analog for binding to the antibody. Based on this technique, a student experiment was written and tested, and the results were determined to be suitable for undergraduate chemistry majors. The experiment is well suited for the Integrated Laboratory Program because of its interdisciplinary nature, combining aspects of biochemistry, analytical chemistry, and environmental chemistry, as well as involving a military application that would be interesting to midshipmen.

Cloning of the Gene Encoding Rubredoxin from the Psychrophile *Aquaspirillium arcticum* using Degenerate Primers

Researcher: Midshipman 1/C Janine E. Curcio, USN
Advisers: Assistant Professor Tammy L. Domanski and Assistant Professor Jamie L. Schlessman

Aquaspirillium arcticum is a psychrophilic bacterium that optimally grows at 4ºC. Associated with the low growth temperature of psychrophilic organisms is a decreased thermostability of the constituent proteins, which allows for protein function at low temperatures. Not much is known about the cause of decreased thermostability. To gain a better understanding of this phenomenon, the electron-transfer protein, rubredoxin, was chosen to represent a general cold adaptation mechanism. Since *A. arcticum*'s rubredoxin sequence was not known, a DNA sequence alignment of known degenerate oligodeoxyribonucleotide primers was created and used to create the primers used for the DNA amplification of a portion or the *A. arcticum* genome. Following amplification, DNA was then ligated, transformed into host *Escherichia coli* cells, and later sequenced. While rubredoxin was the protein targeted for study, a portion of a different protein, possibly a carboxyltransferase, was sequenced instead. This may have resulted from a small submitted sample.

Computational Investigations of Difluoramine-containing Compounds as Models for High Energy Materials

Researcher: Midshipman 1/C Sean M. Driscoll, USN
Adviser: Associate Professor Joseph J. Urban

This project investigated the abilities of numerous computational models to properly calculate the structure and electronic distribution of simple difluoramine-containing compounds, notably CH2(NF2)2. The interest in these compounds is derived from the fact that the difluoramine group (NF2) has recently come into favor as an alternative to the nitro group (NO2) for incorporation into materials with potential application as explosives and/or propellants. In this work, good agreement between ab initio and molecular mechanics approaches was found in terms of conformational properties and geometries for small model compounds. However, the semiempirical methods produced results that were not in agreement. In comparing the NO2 group to NF2, the general trend that was observed was that the NO2 group is slightly more electron withdrawing which could perhaps be attributed to its trigonal planar, sp2 configuration as opposed to the pyramidal, sp3 nature of the NF2 group. In addition, the project was extended to the much larger system HNFX and a conformational analysis was carried out using Monte Carlo (with minimization) approach. The preliminary results produced a very diverse array of conformers and indicate that up to 20 could be populated under room temperature conditions. Further studies are needed to validate the force fields used for general application to NF2-containing compounds.

Metal Binding Studies of Calmodulin

Researcher: Midshipman 1/C Adesina O. Ekundayo, USN
Advisers: Assistant Professor Jamie L. Schlessman and Assistant Professor Virginia F. Smith

Calmodulin is a Ca^{2+}-sensing protein that is expressed in all eukaryotic cells. From organism to organism, calmodulin's amino acid sequence is highly conserved. It is an essential protein to many pathways that regulate and are regulated by Ca^{2+}. Calmodulin participates in pathways that are involved in signaling as well as growth and proliferation. The presence of calcium has significant effects on the function and structure of calmodulin. The apo-protein will not bind to substrate proteins. Increases in Ca^{2+} concentration allow apo-calmodulin to bind Ca^{2+} and under a conformational change, thereby affording the protein the special spatial arrangement necessary to perform its function. While Ca^{2+} is the primary metal ion for calmodulin function, the enzyme has been shown to bind other divalent cations with substantial affinity. The effects of two other divalent metal ions, Pb^{2+} and Mg^{2+}, on the structure of calmodulin were of interest. As a first step, complexes of calmodulin and Ca^{2+}, Pb^{2+} and Mg^{2+} were prepared. Complex formation was monitored using MALDI-TOF methods. In addition, atomic coordinates for calmodulin bound to Ca^{2+} or Pb^{2+} were analyzed to identify similarities and differences in metal ion ligation or protein conformation.

Hydrogen Bonded Networks in Metal Ammonium Phosphates and Their Analogues

Researcher: Midshipman 1/C Graham T. MacDonald, USN
Adviser: Associate Professor Wayne H. Pearson

The hydrogen-bonded network in metal ammonium phosphates is known to be essential to the stability of the crystal structures. The multiple equilibria that exist in such systems make the syntheses of these salts quite a challenge. We have attempted to grow a series of metal ammonium phosphates by systematically altering the stoichiometric composition of the starting solutions as well as the pH. Products have been characterized by IR spectroscopy and X-ray crystallography. X-ray data were collected at the X-ray facility at WRAIR in Silver Spring, MD. The initial target compound, struvite ($MgNH_4PO_4 \bullet 6H_2O$), was never obtained. However, newberyite ($MgHPO_4 \bullet 3H_2O$), was prepared and a very good quality X-ray data set was collected. The structure was refined to a final R(F) of 4.79%. An interesting side project will be the investigation of the coordination sphere around the Mg ion in newberyite. Bond distances indicate some degree of covalency in the bonding of waters and monohydrogenphosphates to the magnesium with some indications of a pi interaction. The quality of the crystal and the interesting coordination sphere make this a prime target for a complete electron density analysis via X-ray diffraction. This project will continue in future years to an attempt to completely characterize the conditions that are favorable for growth of these minerals.

Recognition of Methionine Oxidation in Staphylococcal Nuclease by Peptide Methionine Sulfoxide Reductase

Researcher: Midshipman 1/C Christy A. Pachall, USN
Adviser: Assistant Professor Virginia F. Smith

Aerobic respiration creates highly reactive oxygen species, which attack and damage proteins. One amino acid residue in proteins, in particular, that is sensitive to oxidation is methionine. Methionine oxidation, in the form of sulfoxide groups, has been implicated in a wide variety of human diseases. Fortunately, methionine oxidation can be reversed through the enzyme, MsrA. MsrA reduces methionine sulfoxide back to methionine, restoring the activity to the damaged protein. The protein Staphylococcal nuclease was chosen to serve as a model substrate for the study of the MsrA repair mechanism. The effects of methionine sulfoxidation on Staph nuclease were measured by enzyme activity assays and inspection of the mass by MALDI-TOF mass spectrometry. It was found that sulfoxidation reduces enzyme activity, which suggests either a modification to the active site of the enzyme or an overall denaturation of the protein that renders the protein inactive. Because of the difficulty of detecting such a small mass changes on a 17 kDa protein (each sulfoxidation increased the mass by only 16 Da), a method was developed to cleave Staph nuclease into peptide fragments using the proteolytic enzyme trypsin. Further optimization of the method is necessary in order to assign modifications to a specific protein fragment.

Prediction of ^{13}C NMR Chemical Shifts of Carbonyl-Containing Compounds

Researcher: 1/C Stephanie L. Patterson, USN
Advisers: Assistant Professor Shirley Lin, Associate Professor Debra K. Dillner,
and Dr. Daniel Traficante (Naval Academy Preparatory School)

The ability to predict ^{13}C NMR shifts of organic compounds is useful in the determination of chemical structure. The prediction of the ^{13}C chemical shifts of carbonyls, a common functional group, has not been as fully developed as the methods chemical shift prediction for other functional groups such as alkanes, alkenes, and benzenes. A searchable database of benzaldehyde carbonyl chemical shifts has been created and from this a table of substituent increments for various electron-donating and electron-withdrawing substituents has been developed. This research demonstrated that the ^{13}C NMR shift of the carbonyl can be predicted for many di- and tri-substituted benzaldehydes through simple additivity of the substituent increments.

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

Researcher: Midshipman 1/C Stephen J. Raulli, USN and Midshipman 1/C Drew F. Thomas, USN
Adviser: Associate Professor Joseph F. Lomax

The goal of this project is to find ion exchange membranes which are thermally table at temperatures above 150 °C. This goal represents a fuel cell membrane able to operate at expected temperatures for multiple purposes, which will not degrade during function. Two complementary lines of layered zirconium phosphonate /phosphate research converge in this project 1) the thermal stability and conductivity of zirconium phosphonates substituted with acidic functional groups, and 2) the ability to create pillared α-$Zr(O_3P\text{-}R\text{-}PO_3)$ compounds, varying the pillar length by varying the R radical. The pillaring holds the Zr-phosphate-like layers together thus preventing the swelling and contracting which prevented previous acid-substituted phophonates from making an effective electrochemical separator. By separating the functions of ion conductivity and pillaring, the synthesis of the compound is simplified while maintaining thermal and mechanical stability (from the pillar) and high ion conductivity (from the substituted phosphonate). This approach has been successful in making other mixed phosphonate/diphosphonate zirconium layered compounds. The important part is to match the size of the diphosphonate and the substituted phosphate and to choose the proper functional group on the phosphonate. The two-part thrust of the research deals with first, the synthesis of different phosphonate and diphosphonate compounds and second, taking the resulting phosphonate and diphosphonate compounds and reacting them with a Zr^{4+} salt.

Plebe Laboratory Experiment Development: Kinetics Lab

Researchers: Midshipman 1/C Daniel Reinhardt, USN and Midshipman 1/C Joseph R. Petkus, USN
Adviser: Professor Boyd A. Waite

Currently, a significant portion of the laboratory work in the plebe (freshman) chemistry course is confined to an expository lab approach that leaves students feeling distant and withdrawn from the basic concepts being taught. New lab methods are necessary that will fulfill the course requirement but also introduce more student critical thinking, a better overall understanding of the concept being explored, and an interest in the chemistry major. As such, a new kinetics lab was developed using the guided inquiry format, which may replace the traditional iodine clock kinetics laboratory.

Synthesis and NMR Spectral Characterization of Menthol Derivatives

Researcher: Midshipman 1/C Ryan D. Restrepo, USN
Adviser: 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 NMR assignments published by other groups. Details of these spectral assignments will be 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 have been synthesized, extensive NMR spectral data will be collected. Complete assignment of all peaks and coupling constants of these compounds and their synthetic precursors are underway.

Shock Wave Dynamics in Naphthalene

Researcher: Midshipman 1/C Shannon M. Revell, USN
Adviser: Professor Mark L. Elert

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.

Shock-induced chemistry in naphthalene, $C_{10}H_{14}$, was studied as a complement to previous studies of methane and anthracene, which are respectively much smaller and much larger hydrocarbons. This was done to contribute to a more complete understanding of size effects on reactivity.

When shock waves were produced in the material by simulated impact of two crystal segments at high relative velocity, naphthalene was found to have a threshold impact velocity for the onset of chemical reactivity in between that of methane and anthracene. Its density at the reaction threshold is the same as anthracene but the higher impact velocity in naphthalene causes the temperature at the impact zone to be much higher. The products are also different for the two simulations. The primary reaction channel for naphthalene is fragmentation, whereas anthracene forms a considerable number of dimers.

Lewis Acid Interactions with Fluorenone in a Room-Temperature Ionic Liquid

Researcher: Midshipman 1/C Eli W. Sanders, USN
Adviser: Professor Graham T. Cheek

Room-temperature ionic liquids have been receiving much attention in recent years, one application being solvents for reactions of organic compounds. In the present work, the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMI{\cdot}BF_4$) was used as solvent, and results were compared to those obtained in acetonitrile. The interaction of fluorenone with Lewis acids was studied by cyclic voltammetry. The reduction of fluorenone in this melt involves two successive one-electron transfers, similar to behavior seen in most nonaqueous solvents. Addition of boron trifluoride etherate caused another reduction peak at -0.85V to appear, indicating complexation of the carbonyl oxygen by BF_3. An analogous study in acetonitrile gave similar results. Addition of aluminum chloride to the melt gives rise to an oxidation peak at +1.00V, indicative of chloride ion. Chloride ion is apparently formed by interaction of aluminum chloride with tetrafluoroborate ion.

Time Resolved Measurements of Al-Oxygen Chemistry in Detonating Enhanced Blast Formulations Performed Under Controlled Atmospheres

Researcher: Midshipman 1/C Patrick Sneed, USN
Adviser: Professor Mark L. Elert
Sponsor: Naval Surface Warfare Center, Indian Head

The energy release rate in the late-time metal combustion of detonating aluminized formulations is dependent on the chemical processes occurring between the explosives and the ambient atmosphere. Recently, the role of added oxidizers in the formulation was shown to modulate the energy release through changes in the metal combustion kinetics. We now present results on measurements designed to elucidate the role of atmospheric oxidizers to late-time metal combustion. We observed spectral emissions from transient species in combustion after detonation of PBXIH-135 in both ambient (oxygen containing) and inert (oxygen deprived) atmospheres through time resolved streak spectroscopy. Distinctly different chemical transients and processes were observed in the first 50 microseconds, indicating that metal combustion is modified even at early times by the atmospheric oxidizers. These results, together with modeling efforts are critical in our understanding of the phenomenology of enhanced blast explosives.

Publications

Journal (Refereed) Manuscripts

COPPER, C.L., Associate Professor, "Separation of Thiol and Cyanide Hydrolysis Products Of Chemical Warfare Agents by Capillary Electrophoresis," *Electrophoresis*, Vol. 25, (2004), p.897.

The fluorescence derivatizing agent, o-phthalaldehyde (OPA), has been applied to the separation and detection of cyanide and several structurally similar thiols by capillary electrophoresis (CE) laser induced fluorescence (LIF). Of particular interest to this investigation was the separation of 2-dimethylaminoethanethiol, 2-diethylamino-ethanethiol, and cyanide, each of which are hydrolysis products or hydrolysis product simulants of the chemical

warfare (CW) agents VX, R-VX, and tabun (GA). Other structurally similar thiols simultaneously resolved by this method include 1-pentanethiol and 2-mercaptoethanol. Instrumental parameters were probed and optimum values for capillary length (50 cm) and inner diameter (75 μm), injection time (30 s) and field strength (15 kV) were determined. Sample stacking methods enabled detection limits of 9.3 μg/L for cyanide, 1.8 μg/L for 2-diethylaminoethanethiol, 35 μg/L for 2-dimethylaminoethanethiol, 15 μg/L for 2-mercaptoethanol, and 89 μg/L for 1-pentanethiol. The linearity of the method was verified over an order of magnitude and the reproducibility was found to be 3.0%.

COPPER, C.L., Associate Professor, "Analysis of Intermediates from Polycyclic Aromatic Hydrocarbon Biodegradation," *J. Separation Science*, Vol. 26, (2003), p.1683.

A major difficulty in assessing bioremediation in hydrocarbon impacted field sites is the determination of the extent and products of contaminant biodegradation. Previously, various analytical techniques, including mass spectrometry and chromatography, have been used to characterize components in mixtures resulting from biodegradation. In this work, the applicability of capillary electrophoresis (CE) to this area of research is demonstrated. CE methods were optimized for analysis of compounds that are known metabolites of polycyclic aromatic hydrocarbon (PAH) biodegradation.

ELERT, Mark L., Professor, (co-author), "Molecular Dynamics Study Of Shock-Induced Chemistry in Small Condensed-Phase Hydrocarbons," *J. Chem. Phys*., 118, pp. 9795-9801 (2003).

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.

FERRANTE, Robert F., Professor, (co-author), "Radiation Products in Processed Ices Relevant to Edgeworth-Kuiper Belt Objects," *Earth, Moon and Planets*, Vol. 92, pp. 291-306, 2003.

Near the inner edge of the Edgeworth-Kuiper Belt, EKB, are Pluto and Charon, which are known to have nitrogen (N_2)- and water (H_2O)-dominated surface ices, respectively. Such non-polar and polar ices, and perhaps mixtures of these, also may be present on other trans-Neptunian objects. Pluto, Charon and all EKB objects reside in a weak, but constant UV-photon and energetic ion radiation environment that drives chemical reactions in their surface ices. Effects of photon and ion processing include changes in ice composition, volatility, spectra, and albedo, and these have been studied in a number of laboratories. This paper focuses on ice processing by ion irradiation and is aimed at understanding the volatiles, ions, and residues that may exist on outer solar system objects. We summarize radiation chemical products of N_2-rich and H_2O-rich ices containing CO or CH_4, including possible volatiles such as alcohols, acids, and bases. Less-volatile products that could accumulate on EKB objects are observed to form in the laboratory from acid-base reactions, reactions promoted by warming or reactions due to radiation processing of a relatively pure ice (e.g. $CO \rightarrow C_3O_2$). New IR spectra are reported for the 1-5 μm region, along with band strengths for the stronger features of carbon suboxide, carbonic acid, the ammonium and cyanate ions, polyoxymethylene, and ethylene glycol. These six materials are possible contributors to EKB surfaces and will be of interest to observers and future missions.

HARTMAN, J. R., Associate Professor, Kammier, A.L., Spraklin, R.J., PEARSON, W. H., Associate Professor, Combariza, M. Y., and Vachet, R.W., "A Comparison Of The Gas, Solution, And Solid State Coordination Environments For The Cu(II) Complexes Of A Series Of Aminopyridine Ligands With Varying Rations Of 5- And 6-Membered Chelate Rings," *Inorg Chim. Acta*., Vol. 357 (2004) pp. 1141-1151.

The synthesis and characterization of the copper(II) complexes of a series of tetradentate, pentadentate and hexadentate aminopyridine ligands that contain ethylenediamine and/or propylenediamine groups are described. The ligands include: 1,12-bis(2-pyridyl)-2,5,8,11-tetraazadodecane, TRIEN-pyr; 1,13-bis(2-pyridyl)-2,5,9,12-tetraazatridecane, DIEN-PN-pyr; 1,14-bis(2-pyridyl)-2,6,9,13-tetraazatetradecane, DIPN-EN-pyr; 1,15-bis(2-pyridyl)-2,6,10,14-tetraazapentadecane, TRIPN-pyr; 1,9-bis(2-pyridyl)-2,5,8-triazanonane, DIEN-pyr; 1,11-bis(2-pyridyl)-2,6,10-triazaundecanenane, DIPN-pyr; 1,6-bis(2-pyridyl)-2,5-diazahexane, EN-pyr; and 1,7-bis(2-pyridyl)-2,6-diazaheptane, PN-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 electrospray ionization mass spectrometry. An X-ray structure was determined for the DIPN-pyr complex. The solid state structures were all found to be monomeric Cu(II) complexes with the coordination number set by the denticity of the ligand while the solution structures of all of the complexes except those with TRIPN-pyr and DIPN-pyr were found to be square pyramidal or elongated octahedral. The TRIPN-pyr and DIPN-pyr complexes showed considerable trigonal bipyramidal distortions. The gas phase data showed that the substitution of 6-membered for 5-membered chelate rings helped the ligand span more coordination sites. The TRIEN-pyr complex was 4- or 5-coordinate compared to the 5- or 6-coordination seen with the other three hexadentate ligands, and the DIPN-pyr complex was weakly 5-coordinate as compared to the 4-coordinate DIEN-pyr complex. The preferred structures of the ligands were consistent with their electrochemical behavior which showed that the stability of the Cu(II) complex decreased in the order: DIPN-EN-pyr , TRIEN-pyr , DIEN-PN-pyr > DIEN-pyr > DIPN-pyr > TRIPN-pyr > PN-pyr > EN-pyr.

HARTMAN, J. R., Associate Professor, Combariza, M. Y., and Vachet, R.W., "A Comparison Of The Gas, Solution, And Solid State Coordination Environments For The Ni(II) Complexes Of A Series Of Aminopyridine Ligands With Accessible Ni(III) Oxidation States," *Inorg Chim. Acta*., Vol. 357 (2004) pp. 51-58.

The synthesis and characterization of the nickel(II) complexes of a series of pentadentate and hexadentate aminopyridine ligands that contain ethylenediamine and/or propylenediamine groups are described. The ligands include: 1,12-bis(2-pyridyl)-2,5,8,11-tetraazadodecane, TRIEN-pyr; 1,13-bis(2-pyridyl)-2,5,9,12-tetraazatridecane, DIEN-PN-pyr; 1,14-bis(2-pyridyl)-2,6,9,13-tetraazatetradecane, DIPN-EN-pyr; 1,15-bis(2-pyridyl)-2,6,10,14-tetraazapentadecane, TRIPN-pyr; 1,9-bis(2-pyridyl)-2,5,8-triazanonane, DIEN-pyr; and 1,11-bis(2-pyridyl)-2,6,10-triazaundecane, DIPN-pyr. The following methods were used to determine the binding geometries of the nickel(II) complexes in the solid, solution, and gas phases: magnetic susceptibility measurements, absorption spectroscopy, EPR spectroscopy, electrochemistry, and electrospray ionization mass spectrometry. All of the ligands form 6-coordinate compounds in the solid, liquid, and gas states, with the exception of the TRIEN-pyr, DIEN-PN-pyr(partially), DIPN-pyr, and DIEN-pyr ligands which form 5-coordinate species in the gas state. All of the complexes could be oxidized to Ni(III) species electrochemically, although the Ni(III) complexes of TRIPN-pyr and DIPN-pyr were much less stable than the other four ligands. EPR spectra of the frozen solutions showed the low spin d7 Ni(III) complexes of TRIEN-pyr and DIPN-EN-pyr to be similar to those that have been found for poly-aza macrocyclic compounds.

MORSE, Daniel P., Assistant Professor, "Identification of Substrates for Adenosine Deaminases that Act on RNA," *Methods Mol Biol*., Vol. 265, pp. 199-218, (2004).

Adenosine deaminases that act on RNA (ADARs) are RNA-editing enzymes that convert adenosine to inosine in double-stranded RNA. This chapter provides a detailed protocol for identifying inosine-containing RNAs. Candidate ADAR substrates are identified by cleaving poly (A)+ RNA specifically after inosine and using differential display to detect cleaved molecules. To confirm the presence of inosine, each individual candidate substrate is amplified by reverse transcriptase polymerase chain reaction (RT-PCR) and the PCR product is directly sequenced. Sites that contain inosine at the RNA level appear as a mixture of adenosine and guanosine in the cDNA. The relative peak areas provide an estimate of the extent of editing at each site.

O'SULLIVAN, Daniel W., Associate Professor, (co-author), "Airborne Tunable Diode Laser Measurements of Formaldehyde during TRACE-P: Distributions And Box Model Comparisons," *Journal of Geophysical Research-Atmospheres*, 108, D20, (2003), Art. No. 8798, September 2003.

Airborne measurements of CH2O were acquired employing tunable diode laser absorption spectroscopy during the 2001 Transport and Chemical Evolution Over the Pacific (TRACE-P) study onboard NASA's DC-8 aircraft. Above similar to 2.5 km, away from the most extreme pollution influences and heavy aerosol loadings, comprehensive comparisons with a steady state box model revealed agreement to within +/- 37 pptv in the measurement and model medians binned according to altitude and longitude. Likewise, a near unity slope (0.98 +/- 0.03) was obtained from a bivariate fit of the measurements, averaged into 25 pptv model bins, versus the modeled concentrations for values up to similar to 450 pptv. Both observations suggest that there are no systematic biases on average between CH2O measurements and box model results out to model values similar to 450 pptv. However, the model results progressively underpredict the observations at higher concentrations, possibly due to transport effects unaccounted for in the steady state model approach. The assumption of steady state also appears to contribute to the scatter observed in the point-by-point comparisons. The measurement-model variance was further studied employing horizontal flight legs. For background legs screened using a variety of nonmethane hydrocarbon (NMHC) tracers, measurement and model variance agreed to within 15%. By contrast, measurement variance was similar to 60% to 80% higher than the model variance, even with small to modest elevations in the NMHC tracers. Measurement-model comparisons of CH2O in clouds and in the lower marine troposphere in the presence of marine aerosols suggest rather significant CH2O uptake by as much as 85% in one extreme case compared to expectations based on modeled gas phase processes.

REHILL, B. J., Assistant Professor, (co-author), "Enhanced Invertase Activities in the Galls of Hormaphis Hamamelidis," Journal of Chemical Ecology, Vol. 29, pp. 2703-2720 (2003).

Invertases are sucrose hydrolyzing enzymes often associated with plant tissues acting as physiological sinks, and plant galls are physiological sinks. We investigated several types of invertase and their potential benefits in galls of the aphid Hormaphis hamamelidis. Invertase activities in galls differed from those in leaves throughout the growing season. Vacuolar invertase activities were always greater in galls than leaves. In contrast, cell wall invertase activities started low in galls, but increased with time and were greater than those in leaves after 1 month. Gall growth was most closely related to vacuolar invertase activity, whereas leaf growth was correlated with both vacuolar and cell wall invertase activities. In separate correlational studies of aphid fecundity and invertase activities, cell wall invertase activity per gall accounted for 15 - 21% of the variation in offspring per gall. Gall dry weight explained more of the variation in offspring per gall (34.2%) than did gall volume (17.8%), indicating the importance of sink strength over the life of the gall. Increased invertase activity probably underlies the enhanced sink strength commonly observed in galls. Overall, Hormaphis hamamelidis fundatrices appear to maximize reproductive output by eliciting multiple beneficial responses from their hosts.

REHILL, B. J., Assistant Professor, (co-author), "Genetically Based Trait in a Dominant Tree Affects Ecosystem Processes," *Ecology Letters*, Vol. 7, pp. 127-134 (2004).

Fundamental links between genes and ecosystem processes have remained elusive, although they have the potential to place ecosystem sciences within a genetic and evolutionary framework. Utilizing common gardens with cottonwood trees of known genotype, we found that the concentration of condensed tannins is genetically based and is the best predictor of ecosystem-level processes. Condensed tannin inputs from foliage explained 55-65% of the variation in soil net nitrogen (N) mineralization under both field and laboratory conditions. Alternative associations with litter lignin, soil moisture or soil temperature were relatively poor predictors of litter decomposition and net N mineralization. In contrast to the paradigm that the effects of genes are too diffuse to be important at the ecosystem-level, here we show that plant genes had strong, immediate effects on ecosystem function via a tight coupling of plant polyphenols to rates of nitrogencycling.

REHILL, B. J., Assistant Professor, (co-author), "Beavers as Molecular Geneticists: A Genetic Basis To The Foraging of An Ecosystem Engineer," *Ecology*, Vol. 85, pp. 603-608 (2004).

Ecological genetics is increasingly recognized as critical to understanding interactions among organisms and ecosystem processes. Using a common garden with pure and hybrid cottonwood trees of known genotype, two years of field surveys, and a cafeteria feeding experiment, we link introgression of Fremont genetic markers, condensed tannins (a genetically based plant trait), and foraging by beavers. These data support two major arguments. First, hybridization is an important mechanism for the transmission of ecologically functional traits. Second, links between a genetically based plant trait in a dominant riparian-forest tree species and the foraging behavior of beavers, an ecosystem engineer, emphasize that genetically based plant traits can directly and indirectly link population, community, and ecosystem processes.

SCHROEDER, Maria J., Associate Professor, (co-author), "Evolution Of The Dynamics In 1,4-Polyisoprene From A Nearly Constant Loss To A Johari-Goldstein β-Relaxation To The α-Relaxation," *Macromolecules*, 37(7), 2630-2635.

The Johari-Goldstein (JG) secondary relaxation, presumed to be universal, has never been seen in 1,4-polyisoprene (PI) by dielectric spectroscopy, despite many measurements extending over the past half-century. By using a high-resolution capacitance bridge, we are able to show the existence of a secondary relaxation in PI that has properties of the JG process. Measurements were also carried out at lower temperatures, which probe the dynamics of chain units "caged" by neighboring segments compromising the local structure. The caged dynamics precede by decades of time the JG relaxation and, from general physical principles, are also expected to be a property of all glass-forming materials. Collectively, the caged dynamics and JG relaxation serve as precursors to structural relaxation (*i.e.,* the glass transition) and thus are of central importance to understanding vitrification. The present data show that the dynamics of caged PI repeat units are manifested as a nearly constant loss (NCL). This NCL has been found in other glass-formers, both molecular and polymeric, and its temperature dependence in PI is similar to that for these other materials. The experimental results are consistent with the predictions from the coupling model.

WELSH, Eric R., Lieutenant, (USNR), (co-author), "In Situ Cross-Linking of Alternating Polyelectrolyte Multilayer Films," *Langmuir*, Vol. 20, pp. 1807-1811 (2004).

A water-soluble, blocked diisocyanate was proven to support stable growth of bilayers with branched poly(ethylenimine), bPEI, in a layer-by-layer (LBL) technique. QCM and ellipsometry were employed to measure bilayer formation and infrared spectroscopy of LBL deposited films of hexamethylene-1,6-di-(aminocarboxysulfonate), HDACS, and bPEI revealed in situ cross-linking between successive layers. Erratic film growth with poly(diallyldimethylammonium chloride), PDDA, with which covalent linkage was not possible, and film stability in high salt and diethanolamine (DEAM) solutions also supported cross-linking. Silica beads coated with alkaline phosphatase (ALP)-bPEI bilayers were capped with the cross-linking agent and loss of enzymatic activity and less dissolution of active ALP were observed, relative to uncapped or alternately caped assemblies. Consequently, such a cross-linking agent alone or diluted with other polyanions, like PSS, might prove useful in controlling network and dissolution properties of LBL films having a variety of biologic and other functions, such as for controlled release.

WELSH, Eric R, Lieutenant, (USNR), (co-author), "Chitosan Crosslinking with a Water-Soluble, Blocked Diisocyanate. 2. Solvates and Hydrogels," *Biomacromolecules*, Vol. 4, pp. 1357-1361 (2003).

A water-soluble, blocked diisocyante was used to cross-link chitosan under various degrees of solvation, including hydration to form hydrogels. Thermal cross-linking of films cast from various amounts of organic cosolvents was found to increase with increased level of cosolvent up to a solvation level of 17% (w/w) and to be more efficient than for films prepared without cosolvent. Rheological studies revealed that gel modulus increased and gel time decreased with increasing cross-linker content and that gelation kinetics were consistent with a process having an activation energy of 103 kJ/mol. Swelling of hydrogels indicated that, even at high levels of hydration, the increased molecular mobility of reactants allowed for efficient network formation in a concentration-dependent manner. The extent of solvation via equilibrium swelling correlated well with degradative properties of chitosan networks in the presence of Chitinase (E. C. 3.2.1.14) from Streptomyces griseus, with stability increasing with decreasing swelling (i.e. increased cross-linking).

WELSH, Eric R., Lieutenant, (USNR), (co-author), "Reaction Kinetics and Gel Properties of Blocked Diisocyanate Crosslinked Chitosan Hydrogels," *Carbohydrate Polymers*, Vol. 54, pp. 193-199 (2003).

Cure kinetics and network properties of hydrogels prepared by the reaction of chitosan and a water-soluble blocked diisocyanate cross-linker have been measured using swelling experiments and rheometry. The gel time measured by two different rheological methods, the rate equivalence of the change in modulus as a function of reaction time (G′G″ crossover) and the critical gel via the Winter-Chambon approach, were comparable. The reaction rate increased with increased temperature following Arrhenius behavior, from which apparent activation energies were determined. The network moduli were tailored by adjusting the ratio of chitosan to cross-linker or the solution concentration. This allowed for the formation of processable, chemically cross-linked chitosan hydrogels with controlled cure kinetics and mechanical properties.

WELSH, Eric R., Lieutenant, (USNR), (co-author), "Endotheilial Cell Adhesion to the Fibronectin CS5 Domain in Artificial Extracellular Matrix Proteins," *Biomaterials*, Vol. 24, pp. 4245-4252 (2003).

This study examines the spreading and adhesion of human umbilical vein endothelial cells (HUVECS) on artificial extracellular matrix (aECM) proteins containing sequences derived from elastin and fibronectin. Three aECM variants were studied: aECM 1 contains lysine residues periodically spaced within the protein sequence and three repeats of the CS5 domain of fibronectin, aECM 2 contains periodically spaced lysines and three repeats of a scrambled CS5 sequence, and aECM 3 contains lysines at the protein termini and five CS5 repeats. Comparative cell binding and peptide inhibition assays confirm that the tetrapeptide sequence REDV is responsible for HUVEC adhesion to aECM proteins that contain the CS5 domain. Furthermore, more than 60% of adherent HUVEC were retained on aECM 1 after exposure to physiologically relevant shear stresses (<100 dynes/cm2). Finally, the levels of thrombogenic markers (tissue plasminogen activator and plasminogen activator inhibitor-1) secreted by HUVEC monolayers on aECM 1 were found to be similar to those secreted by HUVEC monolayers cultured on fibronectin. These characteristics, along with the physical strength and elasticity of crosslinked films prepared from these materials, make aECM proteins promising candidates for application in small-diameter vascular grafts.

Book Chapter

HARRISON, J. A., Professor, "The Friction Of Model Self-Assembled Monolayers," *Encyclopedia of Nanoscience and Nanotechnology*, Vols. 3, ed. H. S. Nalwa, American Scientific Publishers, Los Angeles, CA, pp. 511-527., 2004.

This book chapter is a comprehensive overview (containing 139 references) of the potential energy functions and modeling that has examined the structure and friction of self-assembled monolayers.

Presentations at Professional Meetings and Conferences

BOWERS, Daniel L., Midshipman 1/C (USN) and DOMANSKI, Tammy L., Assistant Professor, "Isolation and Characterization of Environmental *Staphylococcus aureus* Samples at the U.S. Naval Academy," 14th European Congress for Clinical Microbiology and Infectious Diseases, Prague, Czech Republic, 1-4 May, 2004.

BURNS, Rebecca, Midshipman 1/C (USN) and MORSE, Danny P., Assistant Professor, "Fluorescent RNA Probes for Detecting Small Molecules," Eastern Colleges Science Conference, Tarrytown, NY, April 2004.

CARDILLO, Nicholas S., Midshipman 1/C (USN) and HARTMAN, JudithAnn R., Associate Professor, "Cu(II) and Ni(II) Complexes of Novel Aminothiophene Ligands," Eastern Colleges Science Conference, Tarrytown, NY, April 2004.

COPPER, C.L., Associate Professor, and Collins, G.E, "A Comparison of Capillary Electrophoretic Methods for the Detection of Cyanide," Eastern Analytical Symposium, Atlantic City, NJ, November 2003.

COPPER, C.L., Associate Professor, and Collins, G.E., "Separation of Thiol and Cyanide Hydrolysis Products of Chemical Warfare Agents by Capillary Electrophoresis," 227th National American Chemical Society Meeting, Anaheim, CA, March 2004.

CROUCH, Collier, Midshipmen 1/C (USN), and O'SULLIVAN, Daniel W., Associate Professor, "Illustrating the Concept of Sparingly Soluble Salts using Various Copper Salts: A Classroom Demonstration," 227th National American Chemical Society Meeting, Anaheim, CA, March 2004.

DOMANSKI, Tammy L., Assistant Professor, "Isolation and Characterization of Environmental *Staphylococcus aureus* Samples at the U.S. Naval Academy," American Society for Microbiology 104th General Meeting, New Orleans, LA, 23-27 May 2004.

ELERT, Mark L., Professor, "Shock-Induced Chemistry in Aromatic Hydrocarbons," American Physical Society Conference on Shock Compression of Condensed Matter, Portland, OR, 20-25 July 2003.

ELERT, Mark L., Professor, "Molecular Dynamics Study of Non-reacting Shock Waves in Anthracene," American Physical Society Conference on Shock Compression of Condensed Matter, Portland, OR, 20-25 July 2003.

ELERT, Mark L., Professor, "Molecular Dynamics Studies of Orientation Dependence of Shock Structure in Solids," American Physical Society Conference on Shock Compression of Condensed Matter, Portland, OR, 20-25 July 2003.

ELERT, Mark L., Professor, "Molecular Dynamics of Shock Waves and Detonation," U.S. Naval Academy Sigma Xi Chapter, Annapolis, MD, 5 December 2003.

ELERT, Mark L., Professor, "Orientation Dependence of Reactive and Nonreactive Shock Waves in Anthracene by Molecular Dynamics," American Physical Society National Meeting, Montreal, Quebec, Canada, 22-26 March 2004.

FERRANTE, Robert F., Professor, (co-author), "Formation and Stability of Radiation Products in Europa's Icy Shell," Europa 2004 Workshop, Lunar and Planetary Institute, Houston, TX, February 2004.

FERRANTE, Robert F., Professor, (co-author), "Low Temperature IR Spectroscopy of Water and Ammonia Ices," 227th National American Chemical Society Meeting, Anaheim, CA, March 2004.

FLEISCHMANN, David T., Midshipman 1/C (USN) and DILLNER, Debra K., Associate Professor , "Synthesis of Nucleotide Diphosphonate Analogues with Potential Antiviral Activity," Eastern Colleges of Science Conference, Tarrytown, NY, April 2004.

Gittis, A., Karp, D., SCHLESSMAN, J., Assistant Professor, Dolan, M., Stites, W., Lattman, E. and García-Moreno B., "Crystallographic Study of Water Penetration and Internal Hydration in Mutants of Staphylococcal Nuclease with Internal Ionizable Residues," Biophysical Society Meeting, Baltimore, MD, 14-18 February 2004.

GREENE, Philip, Midshipman 1/C (USN), Berv, D., COPPER, C.L., Associate Professor, Collins, G.E., and Ramsey, J., "Detection and Quantification of Uranium (VI) in Building Materials," 227th National American Chemical Society Meeting, Anaheim, CA, March 2004.

HARRISON, Judith A., Professor, "Compression- and Shear-Induced Polymerization in Model SAMs," 227th National American Chemical Society Meeting, Anaheim, CA, 28 March – 1 April 2004.

HARRISON, Judith A., Professor, "Molecular-Scale Tribology in Model SAMs," American Physical Society Meeting, Montreal, Quebec, Canada, 22-26 March 2004.

HARRISON, Judith A., Professor, "Multiscale Modeling of Contacts between Self-Affine Surfaces,"American Physical Society Meeting, Montreal, Quebec, Canada, 22-26 March 2004.

HARRISON, Judith A., Professor, "Contact Stresses in Nanoscale Contacts: Comparison of Simulations and Continuum Predictions," The Materials Research Society, Boston, MA, 1-5 December 2003.

HARRISON, Judith A., Professor, "Molecular-Scale Tribology in Amorphous Carbon Films and Model SAMs," Naval Research Laboratory, Washington, D.C., 24 November 2003.

HARRISON, Judith A., Professor, "Molecular-Scale Tribology in Model SAMs and Amorphous Carbon Films," American Vacuum Society 50th International Symposium, Baltimore, MD, 2-7 November 2003.

HARRISON, Judith A., Professor, "Filling Carbon Nanotubes: Mechanics and Nanofluidics," NASA-Ames Research Center, Moffett Field, CA, 11 August 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, 12 August 2003.

MacDONALD, Graham T., Midshipman 1/C (USN) and PEARSON, W.H., Associate Professor, "Hydrogen Bonded Networks in Metal Ammonium Phosphates and Their Analogues," Eastern Colleges Science Conference, Tarrytown, NY, April 2004.

McCLEAN, Roy E., Associate Professor, "Fe + SO2: Kinetic and DFT Study," 226th National American Chemical Society Meeting, New York, NY, 10 September 2003.

O'SULLIVAN, Daniel W., Associate Professor, "Peroxide Measurement Component of RICO," RICO Science Team Workshop, Boulder CO, 24-26 February 2004.

O'SULLIVAN, Daniel W., Associate Professor, (co-author), "Transport and Photochemical Degradation of Chromophoric Dissolved Organic Matter in the Mackenzie River-Delta System," American Geophysical Union, Ocean Sciences Meeting, Honolulu, HI, February 2004. (SS1.01 SS5.08)

O'SULLIVAN, Daniel W., Associate Professor, "Quantum Yields for the Photochemical Production of Hydrogen Peroxide and Methylhydroperoxide in Coastal Waters," 227th National American Chemical Society Meeting, Anaheim, CA, March 2004.

PATTERSON, Stephanie, Midshipman 1/C (USN), DILLNER, Debra K., Associate Professor, and LIN, Shirley, Assistant Professor, "Prediction of Benzaldehyde C-13 NMR Chemical Shifts," Eastern Colleges of Science Conference, Tarrytown, NY, April 2004.

REHILL, Brain J., Assistant Professor, "Potential Ecological Consequences of Developmental Trajectories in the Phytochemistry of a Dominant Riparian Tree," Gordon Research Conference on Plant-Herbivore Interactions, Ventura, CA, 2 March 2004.

SCHROEDER, Maria J., Associate Professor and BROWNING, Colin M., Midshipman 1/C (USN), "Using Polydimethylsiloxanes in the Classroom," Gordon Research Conference on Elastomers, New London, NH, 2 July 2003.

SMITH, Virginia F., Assistant Professor, "Effects of Ligands on the Stability of Human Cytoplasmic Aconitase," 48th Annual Meeting of the Biophysical Society, Baltimore, MD, 14 February 2004.

THOTA, Darshan, Midshipman 1/C (USN) and GUTTERIDGE, Clare E., Assistant Professor, "Antimalarial Activity of Halomethoxylated Quinoline-Containing Chalcones," Eastern Colleges Science Conference, Tarrytown, NY, April 2004.

TILLET, Cera, Midshipman 1/C (USN) and GUTTERIDGE, Clare E., Assistant Professor, "Antibacterial Chalcones," Eastern Colleges Science Conference, Tarrytown, NY, April 2004.

TYREE, Michael, Midshipmen 1/C (USN) and O'SULLIVAN, Daniel W., Associate Professor, "Analysis of the Kinetics of Complex Formation Between Ti(IV), Hydrogen Peroxide, Hydroxymethylhydroperoxide," 227th National American Chemical Society Meeting, Anaheim, CA, March 2004.

URBAN, Joseph J., Associate Professor, and CRONIN, William A, Midshipman 1/C (USN), "Fluorinated Peptide Mimetics: A Computational Study," 227th National American Chemical Society Meeting, Anaheim, CA, March 2004.

WHITAKER, Craig, Associate Professor, (co-author), "New Approaches to Organic Materials for Photovoltaic Applications," Office of Naval Research Review for Optics and Electronics, Arlington, VA, 4 May 2004.

YATKO, Elizabeth A., Midshipman 1/C (USN), and SCHROEDER, Maria J., Associate Professor, "Synthesis and Field Testing of Elastomeric Materials in Repair of Radford Terrace," Eastern Colleges Science Conference, Tarrytown, NY, April 2004.