Division of Mathematics and Science

CAPT K. Scott Pugh, USN
Director

Chemistry Department

Professor Jeffrey P. Fitzgerald
Chair

The 2001-2002 Academic Year was another productive year for research within the Chemistry Department. Eighteen faculty members conducted funded research on twenty-four different projects. Funding came from fifteen different outside sources including the prestigious Camille and Henry Dreyfus Foundation, the Air Force Office of Scientific Research (AFOSR), the National Aeronautic and Space Administration (NASA), the Office of Naval Research (ONR), the Naval Research Laboratory (NRL) and the Petroleum Research Fund (PRF). Six additional faculty members carried out unfunded research in their laboratories at the Naval Academy. In addition, fourteen 1/C and 2/C midshipmen participated in one or more semesters of research and several of these presented their findings at regional and national meetings of scientific societies.

Faculty members whose accomplishments are particularly noteworthy include Associate Professor Judith Harrison, who continues to develop an international reputation in the emerging field of tribology. Professor Harrison supported two post-doctoral associates and published four papers this year including one in the premier chemistry journal, the *Journal of the American Chemical Society*. Professor Mark Elert also hosted a post-doctoral associate, studying molecular dynamic simulations of colliding crystals. Professor Mark Campbell continued his research in picosecond kinetics of gas phase reactions as a Henry Dreyfus Teacher/Scholar (one of five nation-wide each year). Major Kevin Pitzer, USA, received a U.S. Patent (6284772) for a new series of organic heterocycles useful in the treatment of malaria. Associate Professor Joseph Urban was awarded the Kinnear Fellowship through the Naval Academy Alumni Association in support of his work on conformational analysis of fluoro-substituted organics. Assistant Professor Daniel O'Sullivan did field work in the South Pacific as part of his NASA-funded research on atmospheric chemistry. Finally, Professor Jeffrey Fitzgerald and Assistant Professor Virginia Smith served as advisors for Midshipman 1/C Peter Huffman, USN and Midshipman 1/C Pritha Mahadevan, USN, respectively, two of the fourteen 2001-2002 Trident Scholars at the Naval Academy.

Other research interests of the faculty include 1) synthesis of solid-state electrolytes for methanol-based fuel cells, 2) bioremediation of polycyclic aromatic hydrocarbons, 3) impedance studies at single crystal and polycrystalline electrodes, 4) molten salt electrochemistry and synthesis, 5) spectroscopic studies of molecules/ions trapped in ices related to comets, 6) transition metal coordination chemistry of new tripodal ligands, 7) synthesis and study of radio-labeled neurotransmitters, 8) charge-transfer complexes as sensors, 9) development of a fluorescence assay for inosine in messenger RNA, 10) polydimethylsiloxane network polymers and 11) self-assembly approaches to molecular electronic devices.

Sponsored Research

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

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

The objective of this research is to determine the rate constants for reactions of ground state and low-lying excited state transition metal atoms in the gas phase with oxygen-containing oxidants as a function of temperature and pressure. In particular, three projects are in varying stages of completion: (1) reactions of transition metals with N_2O, (2) reactions of ground state and low-lying excited states of niobium and tantalum with several oxidants, and (3) reactions of zirconium and hafnium with water. By obtaining Arrhenius parameters for these reactions, geometric factors and energy barrier effects will be determined. The experimentally measured rate constants and barriers will be analyzed to determine if a relationship exists between these values and the physical properties of the transition metals and reactants. Results for the reactions with N_2O will be compared to the

calculated values from a theoretical model developed by Fontijn and co-workers. The reactions of niobium and tantalum will indicate the importance electronic effects have on the reaction rate. The reactions of zirconium and hafnium with water will yield a better understanding of chemical reactions that may occur during accidents in nuclear reactors. Completion of this research will greatly enhance our understanding of transition metal chemical reactions.

Isolation and Characterization of Metabolic Intermediates from Polycyclic Aromatic Hydrocarbon Biodegradation

Researcher: Associate Professor Christine L. Copper
Sponsor: Naval Research Laboratory (NRL)

The Navy is inherently interested in methods which will help clean up petroleum-based contaminants in their shipyards. The cheapest and most natural way to do this is through bioremediation. Bacteria already present in the environment can breakdown larger organic molecules into smaller, less harmful byproducts. One important aspect in evaluating bioremediation as a viable method for environmental clean up is to identify the byproducts produced by the bacteria so that their environmental impact can be assessed. In this work, several metabolites produced from biodegradation of a representative component of petroleum (phenanthrene) by the bacterium Pseudomonas paucimobilis were identified using several analytical techniques. These techniques included capillary electrophoresis, liquid chromatography, and gas chromatography/mass spectrometry.

Capillary Electrophoresis as a Method for Ozone Determination in Atmospheres

Researcher: Associate Professor Christine L. Copper
Sponsor: Dr. John H. Callahan, Section Head/Research Chemist,
Chemical Dynamics and Diagnostics Branch (code 6110), Naval Research Laboratory (NRL)

Capillary electrophoresis (CE) is used to quantify nitrate and nitrite extracted from nitrite-impregnated glass fiber filters (IGFF) that are used to monitor ozone in atmospheres. The amount of nitrate produced from conversion of nitrite in the filters is directly related to the amount of ozone passed over the filter. The effect of the excess nitrite in the IGFF on the limits of detection is discussed. Results from CE analyses of both active and passive filters are presented. The active filter results are compared to ion chromatographic (IC) analyses. This method is a novel approach to the analysis of submarine atmosphere composition. A publication reporting this project is in the review process at this time.

Impedance Studies of Aluminum Electrodes in Chloride Media

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

Research efforts on this project have involved impedance spectroscopy of aluminum electrodes in aqueous chloride systems. Emphasis has been placed on the type of aluminum electrodes used in the investigations. Studies began with polycrystalline aluminum electrodes in 0.10 M NaCl electrolyte, scanning a frequency range of 100 kHz to 0.001 Hz in the impedance studies. Continuing efforts have involved the use of single-crystal electrodes having orientations 111, 110, and 100.

Polycrystalline electrodes were prepared from Al foil by sanding with 600 grit paper and masking with electrographic tape. It was found that low-frequency impedances (at 0.001 Hz) increased from 10 kΩ at a polarization of -1.50 V to approximately 1 MΩ at -0.750 V *vs* SCE. These results have been interpreted as evidence for an increasing thickness of oxide on the surface as polarization potential is made more positive. Further work in this regard involved running the impedance scans in more concentrated chloride solutions (0.60 M NaCl), producing impedance values somewhat less than those in 0.10M NaCl.

The single crystal results have proven to be somewhat more complex. For Al<111> electrodes initially polarized at -1.50 V (as above), the impedances at 0.001 Hz were much higher than those at polycrystalline electrodes under the same conditions, implying that the oxide film on the single crystal electrodes is somehow much more resistive than that on the polycrystalline electrodes. These impedances increased from 1 MΩ at -1.50 V to 10 MΩ at -0.75 V. When Al<111> electrodes were initially polarized near the open-circuit potential (-1.10 V), however, the impedances observed as potential were stepped to

-0.70 V actually decreased. This is not the case for polycrystalline electrodes, for which the initial polarization potential makes no difference in the observed impedance values.

Continuing studies during the academic year have involved work at Al rod electrodes, the surface area of which is larger than that of the foil electrodes. The resulting impedance data have improved noise characteristics and allow one to observe that an additional frequency response becomes evident at potentials between –0.90 V and –0.70 V.

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

Researcher: Lieutenant Gregory B. Cotten, USN, Ph.D., P.E.
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, we anticipate 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-FeO_xH_y 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 will be 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, will 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 will not be limited by electron transfer. The materials will be evaluated for stability under acidic and oxidizing conditions. These catalysts will be provided to the DOE fuel cell testing facility at LANL for characterization under fuel-cell operating conditions.

Investigations into Electrodeposition Processes in Room –Temperature Molten Salts: August 1995 – Present

Researchers: Dr. John Mitchell (ASEE Post-Doctoral Fellow),
Major Hugh C. De Long, USAF (Assistant Professor at USNA, PI),
Lieutenant Colonel Paul C. Trulove, USAF (AFOSR),
Dr. Patrick Hagans and Dr. William O'Grady (NRL)
Professor Graham T. Cheek (USNA)
Sponsor: Air Force Office of Scientific Research (AFOSR)

Aluminum alloys with enhanced resistance to chloride-induced pitting corrosion have been produced using solute elements such as Ti, Cr, Mn, Cu, Zr, Nb, Mo, Ta, and W. These "stainless" aluminum alloys are of interest both for use as bulk deposits and as coatings over existing structural aluminum alloys. Producing improved corrosion resistance in the aluminum alloys often requires solute concentrations (up to 50 atom percent, a/o) that are far in excess of the equilibrium solubility limit (ca. 1 a/o). Consequently, nonequilibrium methods such as sputter deposition, melt spinning, and ion implantation have been employed to prepare these metastable single-phase aluminum alloys. Unfortunately, these techniques are of limited commercial utility because of their high inherent cost and the difficulty associated with their application to large structures. Electrochemical deposition is an alternative method for producing nonequilibrium aluminum alloys that generally does not suffer from the cost and applicability disadvantages of the above methods.

Room-temperature molten salts provide some unique properties which make them ideal for studying the deposition of aluminum and aluminum alloys. Aluminum can be reversibly electrodeposited from acidic melt compositions. The molten salts readily solubilize both ionic and molecular species, they possess a wide electrochemical window, they have high intrinsic conductivities, and they are thermally stable over a very wide temperature range.

We have demonstrated the deposition of Al-Mn, Al-Co, Al-Ni, Al-Nb, and Al-Cr from the molten salts. Characterization of these deposits shows them to be non-equilibrium alloys with solute concentrations up to 80 a/o. Aqueous corrosion studies indicate significant improvement in the chloride pitting potential over unalloyed aluminum.

Investigations of Ionic Liquid-Polymer Gel Electrolytes

Researchers: Dr. Thomas E. Sutto (ASEE Post-Doctoral Fellow)
Major Hugh C. De Long, USAF (Assistant Professor at USNA, PI),
Lieutenant Colonel Paul C. Trulove, USAF (AFOSR),
Professor Graham T. Cheek (USNA, co-PI)
Sponsor: Air Force Office of Scientific Research (AFOSR)

Room-temperature ionic liquids composed of perfluoroanions and 1,3- dialkylimidazolium and 1,2,3-trialkylimidazolium cations possess a number of unique properties that make them ideal electrolytes for compact power sources. In particular, they are nonflammable, nonvolatile, and chemically inert, and they display wide electrochemical windows, high inherent conductivities, and wide thermal operating ranges. Also, unlike room-temperature ionic liquids based on chloroaluminate anions, these perfluoroanion electrolytes are not moisture sensitive.

For manufacturing and design optimization, solid-state electrolytes with high ionic conductivities are preferred to liquid electrolytes. In this research program we are investigating the generation of solid-state electrolytes that incorporate perfluoroanion ionic liquids into a poly(vinylidene fluoride)-hexafluoropropylene copolymer. These free-standing rubbery electrolytes appear to retain much of the desirable properties of the perfluoroanion ionic liquids. In this project we are investigating the physical and electrochemical properties of these gel electrolytes using thermal mechanical analysis, differential scanning calorimetry, imbedded microelectrode techniques, AC-impedance, and luminescent probe molecules. In addition this project evaluates graphite intercalation anodes and cathodes with the ionic liquid-polymer gel electrolytes in solid-state cells employing the dual intercalating molten electrolyte (DIME) concept.

Investigations of Novel Nanocomposites Using Room Temperature Molten Salts

Researchers: Dr. Thomas E. Sutto (ASEE Post-Doctoral Fellow)
Major Hugh C. De Long, USAF (Assistant Professor at USNA, PI),
Lieutenant Colonel Paul C. Trulove, USAF (AFOSR), and Dr Jeffrey Gillman (NIST, co-PI)
Sponsor: Air Force Office of Scientific Research (AFOSR)

Room-temperature ionic liquids composed of perfluoroanions and 1,3- dialkylimidazolium and 1,2,3-trialkylimidazolium cations possess a number of unique properties that make them ideal electrolytes for nanocomposite work. In particular, they are nonflammable, nonvolatile, and chemically inert, and they intercalate into layered materials, which makes them ideally suitable for our nanocomposites using clays. Also, unlike room-temperature ionic liquids based on chloroaluminate anions, these perfluoroanion electrolytes are not moisture sensitive. In this program, we are investigating the preparation and analysis of mica-type clays nano-dispersed in polymers. These “nanocomposites” exhibit the unusual combination of reduced flammability, in the form of lower peak heat release rates, and improved physical properties. The most significant aspect of the nanocomposite approach is the combined improvement in both flammability properties and physical properties. The key to successful generation of fully dispersed polymer-clay nanocomposites is the organic treatment used to prepare the clay silicate layers. Chemical compatibility of the organic treatment with the polymer is critical to producing fully optimized nanocomposites. In addition, the high thermal stability of these organic treatments is essential if melt processing methods are to be employed. In this program, we are developing novel organic treatments for clay-polymer nanocomposites. We are synthesizing unique imidazolium based salts, which possess both high temperature stability and tailorable polymer compatibility. We are using standard, modern analytical methods, such as TEM, SEM, X-ray diffraction, NMR, TGA, TMA, and cone calorimetry, to characterize the physical and chemical properties of the salts, the treated clays, and the polymer nanocomposites.

Molecular Dynamics Simulations of Shock-induced Chemistry in Hydrocarbons

Researcher: Professor Mark L. Elert
Sponsor: Naval Research Laboratory (NRL), Code 6189

The chemistry of hydrocarbons subjected to shock impact may be relevant to our understanding of the composition and evolution of planetary atmospheres and to the formation of life. In addition to its possible cosmological interest, shock wave impact on hydrocarbons may provide a unique environment for the synthesis of organic compounds under novel kinetically-controlled conditions. Shock-induced chemistry in hydrocarbons was investigated by carrying out molecular dynamics simulations on two representative systems, using a Reactive Empirical Bond Order potential which can accurately predict bond-breaking and bond-forming activity in hydrocarbons. Shock impact studies on solid methane and acetylene were carried out by simulating the impact on crystals of the subject hydrocarbon with a flyer plate of the same material. Acetylene was found to readily form hydrocarbon polymers at impact speeds which are modest on a planetary scale, whereas methane is unreactive up to much higher flyer plate velocities. Although acetylene polymerization is thought to lead eventually to the formation of polycyclic aromatic hydrocarbons (PAHs) in interplanetary dust particles and large solar system objects, the present study indicates that PAHs are not the initial products of shock impact on acetylene.

Spectroscopic Studies of Ion-Irradiated N_2-Rich Ices

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

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

Molecular Dynamics Investigations of the Friction and Tribology of Solid Lubricants

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

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

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

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

Molecular Dynamics Investigations of the Tribology of Diamond Surfaces and Films

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

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

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

Atomic force microscope (AFM) measurements have examined the friction of spiroalkanedithiols and a single structurally related normal alkanethiol chains bound to Au surfaces. Various surface science techniques were used to ascertain the order of the monolayers. These studies clearly show that the more ordered monolayer (more tightly packed) has lower friction measured with the AFM. We have used our re-fit potential energy function to examine the friction of n-alkane chains on diamond with different packing densities. (This potential energy function has been published in *The Journal of Chemical Physics*.) Simulations show that the tightly packed monolayers (or more ordered) have lower friction than the loosely packed (less ordered) monolayers in agreement with the experimental trend. The origin of this difference in friction appears to be related to differences in carbon-carbon bond-length distributions. This work was published in *The Journal of the American Chemical Society*. An analysis of other system properties that are related to friction appeared in *Tribology Letters*.

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

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

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

Department of Defense (DoD) Reactive Atomic-Scale Potential Molecular Dynamics (RASP-MD) for Computation and Prediction of Materials Properties

Researchers: Dr. John W. Mintmire and Dr. Carter T. White (NRL),
Dr. Brad L. Holian (Los Alamos National Laboratory)
Dr. Daniel H. Robertson (IUPUI), Professor Mark L. Elert (USNA),
Dr. Steven J. Stuart (Clemson University), and Associate Professor Judith A. Harrison
Sponsor: Common HPC Software Support Initiatives

The overall goal of this project is to develop a scalable and portable suite of programs for Molecular Dynamics (MD) simulations of materials of critical Department of Defense interest using chemically realistic potentials. The planned software suite will be developed as a main set of MD programs that interface with the empirical potential routines via a custom application programming interface (API). A set of auxiliary routines will be constructed that implement the NRL-developed REBO and ES+EAM potentials and the USNA-developed AIREBO potential using API. Currently, a parallel version of the REBO code is in alpha testing. We will receive this code soon to do the beta testing.

Investigations into the Effects of Tripodal Ligands on Transition Metal Environments

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

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

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

Synthesis and Characterization of Extended Donor-Acceptor Molecules With Conducting Polymer Bridges

Researcher: Associate Professor William B. Heuer
Sponsor: Dr. O. K. Kim, Research Chemistry, Naval Research Laboratory (NRL)

The objective of this research is to prepare novel types of materials for use in electroluminescent, photovoltaic, or electrochemical sensors applications. We are specifically seeking to prepare photochemically-or redox-active guest species for inclusion into the hydrophobic cavity of helical amylose. These host-guest complexes will then be deposited as thin films onto conductive substrates. Work continues to focus on synthesis of tris-bipyridine ruthenium(II), ($Ru(bipy)_3^{2+}$) derivatives. The excited triplet state of this complex is a strong electron donor, and can transfer an electron to an acceptor group, such as 4,4'-bipyridinium dication ("viologen"), which is covalently attached via a bridging group to the $Ru(bipy)_3^{2+}$ cation, a process which mimics the first step in photosynthesis. The lifetime of the charge-separated state arising from this transfer is largely determined by the rate of back electron transfer from the reduced viologen back to the oxidized Ru(III) complex. We are investigating whether formation of amylose inclusion complexes of these donor-bridge-acceptor molecules might greatly increase the lifetime of the charge-transferred state. We are also looking at the possible role that the electronic conductivity of the bridging group itself may play in this system.

Synthesis of Radiotracers for the Study of the Nicotinic Acetylcholine Receptor

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

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

New Synthetic Approaches to Geminal Difluoramino Compounds

Researcher: Associate Professor Christopher M. Kinter
Sponsors: Office of Naval Research (ONR)
and Naval Surface Warfare Center (NSWC), Indian Head Division

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

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

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

A Kinetic Study of the Association Reaction of Iron with Sulfur Dioxide

Researcher: Associate Professor Roy E. McClean
Sponsor: 2001 Kinnear Fellowship

The gas phase reaction kinetics of ground state Fe with SO_2 are reported. The objective of this work was to measure the rate constants as a function of total pressure from 10 – 600 Torr. Such data provides information on the efficiency of 1:1 adduct formation in transition metal/SO_2 systems. Rate constants were also measured as a function of temperature to determine the presence of any barrier to reaction.

The laser photolysis/laser-induced fluorescence (LP/LIF) technique was used in this work. In brief, a stainless steel reactor contained ferrocene, SO_2, and N_2. Fe atoms were produced by the laser photodissociation of ferrocene. N_2 served as the bath gas. Reactions were carried out under pseudo-first order conditions where the concentration of Fe atoms was much less than the concentration of SO_2. Relative concentrations of Fe atoms were monitored by LIF as a function of time.

Experimental data were collected at 294, 345, 398, and 498 K. At each temperature, rate constants were measured as a function of total pressure. At a given temperature, the rate constants increased with increasing total pressure, an indication of an association reaction:

$$Fe + SO_2 \rightarrow FeSO_2 + N_2$$

The measured third order rate constant at 294 K is $k_o = (2.94 \pm 0.13) \times 10^{-32}$ cm^6 molecule^{-2} s^{-1}. Over the temperature range 294 – 498 K, k_o is given by:

$$k_o(T) = (2.96 \pm 0.97) \times 10^{-30} \exp[-(2.68 \pm 0.28) \text{ kcal/mol}] \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

The results presented here indicate that the Fe + SO_2 reaction is inefficient. (For comparison, Cr + SO_2 at room temperature has $k_o = 2.68 \times 10^{-28}$ cm^6 molecule^2 s^{-1}.) The activation energy is attributed to the filled 4s subshell of Fe; in general, the orbital occupancies of transition metal atoms in complexes is s^1. Additionally, the relatively large spatial extent of the filled 4s-subshell causes repulsion on Fe – SO_2 collisions.

This project is complete. However, its submission for publication is on hold until extensive theoretical calculations are completed. Calculations are currently being performed on the $FeSO_2$ adduct to gain fundamental information (structure, frequencies, relative energies) on its isomers.

Gas Phase Measurements Of Hydrogen Peroxide, Methylhydroperoxide, and Formaldehyde During TRACE-P

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

We performed measurements of gas-phase hydrogen peroxide, methylhydroperoxide, and formaldehyde on board the NASA DC-8 aircraft as part of the NASA/GTE TRACE-P mission during the spring of 2001. These chemical compounds are involved in the chemical reactions leading to tropospheric oxidants and ozone formation in the lower troposphere. These species act as sources of odd-hydrogen and odd-oxygen radicals, as reservoirs of these radicals, and as conductors in their loss. The target species are coupled to the gas-phase and, more significantly, to the heterogeneous chemistry of sulfur dioxide and its oxidation to sulfuric acid. The species to be measured provide mechanistic insight and chemical constraints to chemical model simulations and provide an additional measure of confidence in their results. Multi-dimensional space-time models suggest that atmospheric motions, the vertical transport and mechanical redistribution of the hydroperoxides, may have a profound effect on odd-O and odd-H chemistry in the upper troposphere. The hydrogen peroxide, methylhydroperoxide, and formaldehyde measurements added needed information on transport, chemical redistribution, and scavenging by cloud and precipitation systems. The data collected during the field phase of this project were finalized and submitted to the NASA GTE data archive in December 2001. The data became available to the public through the NASA GTE archive in January 2002. Measurement distributions

and correlations with other species are being examined with respect to air mass characterization and cloud processing. Analysis and interpretation of our measurements with respect to tropospheric oxidants, net oxidant production, and sulfur gas oxidation is underway and will be performed collaboratively with other members of the science team using our own and more sophisticated meteorological transport and photochemical models.

Dielectric and Mechanical Properties of Polydimethylsiloxane Networks

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

Silicones are utilized in a variety of applications ranging from elastomers to lubricating oils to adhesives. Characterizing the behavior of these materials can lead to improvements in their preparation and application. End-linked polydimethylsiloxane (PDMS) networks were prepared by the reaction of vinyl-terminated linear PDMS with a tetrafunctional silane crosslinking agent and a platinum catalyst. Linear PDMS polymers ranging in molar mass from 186 to 28000 g/mol were used to create networks of varying crosslink density and hence different levels of molecular constraint. A tetrafunctional crosslinker allows four PDMS chain attachments per crosslink and results in a well-defined, model network system. Dielectric a-relaxation spectra, thermal expansivities, and elastic moduli were obtained for these networks. From the crosslink density at which marked changes occur in the segmental relaxation times and the T_a-scaled temperature dependence (fragility), a characteristic length for the a-relaxation was determined. The result, 14 Å at T_a, is quite close to the length scale associated with constraint of crystallization in similar PDMS networks. Crosslinking also affects the thermal expansion and elastic modulus, although these properties exhibit a more modest variation with crosslink density.

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

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

Chaperone proteins are a general class of proteins that perform a vital function in the cell by preventing improper interactions between proteins that might lead to degradation and aggregation. Many of these chaperone proteins work according to relatively well-understood mechanisms that require cleavage of the chemical energy molecule adenosine triphosphate (ATP). However, less is known about the chaperone protein SecB of *Escherichia coli*, which does not require ATP in order to perform its job. We exploited our knowledge of the three-dimensional structure of SecB to obtain information about the mechanism by which SecB recognizes the proteins it binds to and determine how it prevents them from aggregating or becoming degraded. Using chemical crosslinking and high-resolution separation techniques, we investigated the ligand-binding mechanism of SecB in order to obtain a detailed picture of the protein-protein interactions that confer protection.

Self-Assembly Approaches to Molecular Electronic Devices

Researcher: Associate Professor Craig M. Whitaker
Sponsors: Office of Naval Research (ONR), Naval Research Laboratory (NRL)
and Defense Advanced Research Projects Agency (DARPA)

1) Continued collaboration with a research group at the Naval Research Laboratory
2) Third year of an Office of Naval Research grant
3) Patent consultant for the synthesis of molecular electronic molecules through the MITRE Corporation, Dr. James Ellenbogen, McLean, Virginia, Summer 2001.
4) DARPA grant via the Naval Research Laboratory

This project focuses on the design and requirements for molecular computer circuits that incorporate gain-producing elements. The researcher serves as the team leader for the synthetic portion of the project through the Naval Research Laboratory that includes collaboration between many different institutions (Cornell University, the Scripps Research Institute, the University of South Carolina, the University of North Texas and the MITRE Corporation). Organic molecules are being created, based on a phenylacetylene architecture that can be self-assembled on a highly symmetric virus. The virus nanoblocks can then be used to construct the elements required to produce the desired computer circuits.

Independent Research

Electrodeposition of Aluminum from Neutral Buffered Melts

Researcher: Professor Graham T. Cheek

The electrodeposition of aluminum from neutral buffered melts has been studied at vitreous carbon electrodes. At 77°C, deposition at – 1.30 V produced a porous dark film on the electrode surface; however, removal of this loose deposit revealed a dendritic deposit as observed in scanning electron microscope (SEM) studies. The peak potentials for aluminum stripping processes were found to depend on the time during which the potential is held at the deposition potential (-1.40 V) before beginning the positive-going sweep. This behavior is apparently due to diffusion of chloride ions, produced during the deposition process, away from the electrode surface during the potential hold period.

Molecular Dynamics Simulations of the Bending of Filled Carbon Nanotubes

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

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

Synthesis of Acidic Substituted Diphosphonic Acids

Researcher: Associate Professor Joseph F. Lomax

Phosphonic acids can be considered phosphoric acid with one of the –OH groups substituted with an organic group, R-(P=O)$(OH)_2$. If this organic group has two phosphonic acid groups, it would be a diphosphonic acid and if it has yet another acidic group, such as a sulfonic acid, R-(S(=O)$_2$(OH), or sulfate ester, R-O-(S(=O)(OH), this would be the title compound, acidic substituted diphosphonic acid. All three of the above mentioned groups are quite electronegative and a synthetic challenge to incorporate into a molecule, especially in a short (three to seven carbons) chain. The reason for wishing to synthesize such a challenging series of molecules is to provide starting materials for a mixed organic/inorganic material which would maintain the acid quality of the sulfur containing acid while utilizing the basic character of the conjugate base of the diphosphonic acid (the diphosphonate) to react with a highly acidic metal. Diphosphonates have two reactive sites to form insoluble, yet well defined structures. Proper reaction conditions and stoichiometries should allow formation of ion conductors, solid state acidic catalysts with tunable size exclusion properties, sequestering agents for toxic metals, ion exchange materials for incorporation of optically interesting transition and lanthanide metals, etc. Once the organic acidic substituted diphosphonic acid is synthesized, a myriad of metal/organic matrices should be able to be formed and then tested for interesting conductive, catalytic, and optical properties.

A Kinetic Study of the Reaction of Vanadium with Sulfur Dioxide

Researcher: Associate Professor Roy E. McClean

The temperature dependence of the reaction of ground state V with SO_2 in the gas phase is reported. The objective of this work was to experimentally determine the Arrhenius parameters.

The laser photolysis/laser-induced fluorescence (LP/LIF) technique was used in this work. In brief, a stainless steel reactor contained VCl_4, SO_2, and Argon. The V atoms were produced by the laser photodissociation of the VCl_4. Argon served as the bath gas. Reactions were carried out under pseudo-first order conditions where the concentration of V atoms was much less than the concentration of SO_2. Relative concentrations of V atoms were monitored by LIF as a function of time.

Experimental data were collected at 296, 351, 401, 472, 522, and 571 K. Rate constants were also measured as a function of total pressure at each temperature. The rate constants were found to be independent of total pressure, an indication that the association reaction

$$V + SO_2 + Ar \rightarrow VSO_2 + Ar$$

was not important under the experimental conditions. The measured rate constant at 296 K is $k = 3.44 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^1. The uncertainties on the rate constants are estimated at ±25%. The rate constant increased with increasing temperature and can be given by $k(T) = (2.33 \pm 0.57) \times 10^{-10} \exp[-(1.14 \pm 0.19)$ kcal/mol] cm^3 $molecule^{-1}$ s^{-1} where the uncertainties for k(T) represent $\pm 1\sigma$ in precision.

The positive activation energy and the absence of total pressure dependence are indications of an abstraction reaction. The most likely abstraction channel is

$$V + SO_2 \rightarrow VO + SO$$

This conclusion is based on the energetics and types of all possible reaction channels. (e.g., Concerted reactions are not expected to be as efficient as the O-atom abstraction channel.)

The experimental part of this project is complete. Theoretical calculations will be performed in the future to explore the nature of the potential energy surface.

A Density Functional Theory (DFT) Study on Sulfur Dioxide

Researcher: Associate Professor Roy E. McClean

A computational study on SO_2 using density functional theory (DFT) is reported. The objective of this work was to determine how accurate the calculations are for SO_2 and to lay the groundwork for the use of DFT calculations in transition metal/SO_2 systems. DFT has been shown to be quite practical for transition metal systems when taking cost and accuracy into account.

DFT is 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 98 suite of programs was used for the calculations. They were run on a Pentium III personal computer and on superaero, a unix-based computer in the Division of Engineering and Weapons at the Naval Academy.

Several methods are available in DFT. They differ in the way correlation and exchange are treated. The well-documented, popular B3LYP was used in this work. This method is a hybrid of Hartree Fork theory and DFT. The hybrid functions are generally more accurate than the pure DFT methods. (Another common method, mPW1PW91, was also used for a few geometry calculations; results were not superior to the B3LYP method.)

The effect of basis set size on geometry, vibrational frequencies, dipole moment, and energies was investigated. The basis sets ranged from the minimal (termed STO-3G) to the very large basis set 6-311+G(3df). The STO-3G basis set for SO_2 contains 19 functions (sulfur has one *1s*, one *2s*, three *2p*'s, etc.) and the 6-311+G(3df) has 125 functions. Larger basis sets,

which contain two or more functions for each valence orbital, allow the orbitals to change size. Larger basis sets may also include polarization and diffuse functions. Polarization functions allow the orbitals to change shape and diffuse functions allow the orbitals to occupy a larger region of space. It is worth mentioning here that the (3df) represents polarization functions and the "+" represents diffuse functions.

In terms of geometry, the DFT results on SO_2 were not overly sensitive to the size and quality of the basis sets above ≈ 40 functions. However, fairly large basis sets were needed to adequately reproduce the dipole moment and ΔH for the reaction: $SO_2 \rightarrow SO + O$. It was determined that the most practical basis sets are 6-311G(2d) for sulfur and 6-311G(d) for each oxygen. This gives a total of only 67 functions. Note that two *d* polarization functions are used for S and only one *d* function for O. *d* orbitals are not as important for bonding in oxygen atoms as they are for sulfur atoms. This is no surprise since oxygen and sulfur are in the 2nd and 3rd rows of the periodic table, respectively. Diffuse functions were unimportant for SO_2.

This project is complete. Information gathered here will be used for the transition metal/SO_2 calculations.

Biochemical and Structural Studies of the Nitrogen-fixation Regulatory Proteins, NifA and NifL

Researcher: Assistant Professor Jamie L. Schlessman

Biological nitrogen fixation is the process by which relatively inert dinitrogen (N_2) is reduced to metabolically usable ammonia (NH_3) by a small group of microorganisms that produce the metalloenzyme nitrogenase. Expression of the active nitrogenase enzyme exacts a significant cost in protein synthesis from nitrogen-fixing bacteria: more than 30 proteins are involved in nitrogenase assembly and function, and more than 10% of the total protein content of a nitrogen-fixing organism may be nitrogenase enzyme. In addition, the nitrogenase enzyme is swiftly inactivated by oxygen, yet many nitrogen-fixing bacteria are aerobes. To combat these potential hazards of nitrogen fixation, bacteria have evolved a tightly-regulated system for transcribing the *nif* (nitrogen-fixing) genes that lead to nitrogenase production: the multi-domain proteins NifA and NifL. NifA positively regulates transcription of *nif* genes, while NifL negatively regulates *nif* transcription based on environmental stimuli. Together, NifA and NifL function as an unusual two-component regulatory system to maintain optimal expression of nitrogenase. As an initial attempt towards a structural understanding of the regulatory mechanism of nitrogen fixation, the researcher is expressing single functional domains of NifA and NifL from two bacterial sources, *Azotobacter vinelandii* and *Klebsiella pneumoniae*. The corresponding DNA sequences will be cloned from the bacteria into plasmids using recombinant DNA techniques. The protein domains will be expressed recombinantly in Escherichia coli and purified to homogeneity. The domains will be tested for secondary structure using circular dichroism spectroscopy, and crystallization attempts will be initiated on individual domains.

Purpose: to understand the regulatory mechanism of nitrogen-fixation using single functional domains of the proteins NifA and NifL

Objectives:

1) Clone single domains of *nifA* and *nifL* from *Azotobacter vinelandii* or *Klebsiella pneumoniae*, for overexpression in *Escherichia coli*,
2) Develop protein expression protocols and initial purification strategies for the *nif* regulatory domains, and
3) Initiate crystallization of a single *nif* regulatory domain.

Methods of Investigation: Recombinant DNA technology; recombinant protein expression and purification; X-ray crystallography.

Enzymatic Repair of Proteins Damaged by Oxidation

Researcher: Assistant Professor Virginia F. Smith

Although oxygen is essential for life, too much oxygen can be disastrous. Modification of proteins, DNA and lipid molecules by certain oxygen-containing molecules (*e.g.*, superoxide, hydrogen peroxide, the hydroxyl ion, and water) has been shown to contribute to human disease and the aging process. Although most of these changes are irreversible, certain modifications can be repaired by enzymes present in our body. One such repair enzyme is methionine sulfoxide reductase (MsrA). Although MsrA is an essential protein – it has been found in the genome of every organism sequenced to date – we are just beginning to understand how it works. In this project, protein folding methods are being used to answer fundamental questions about MsrA and biological oxidation by observing how this interesting enzyme folds to its three-dimensional form, how it recognizes damaged proteins and how it then repairs them.

Biophysical Characterization of a Bifunctional Iron-Binding Protein

Researchers: Assistant Professor Virginia F. Smith
and Midshipman 1/C Pritha Mahadevan, USN

Iron is crucial for a variety of physiological processes, however, it is present in very low abundance in the environment and is difficult for the cell to obtain. One way that nature has devised to ensure sufficient levels of iron is through the iron-responsive element protein-1 (IRP-1). The manner in which IRP-1 maintains intracellular iron levels is fascinating: When iron levels are low inside the cell, IRP-1 causes the levels of iron to rise by either increasing the production of proteins that bring in iron from outside or by causing iron-storage proteins to release the iron they were holding, making it available for other purposes. Once the iron concentration is restored to normal levels, IRP-1 becomes an iron-containing enzyme called aconitase that participates in energy production. In this project, protein folding techniques are being used to learn how IRP-1/aconitase can exist in two functionally distinct forms and how it is able to convert between these two forms reversibly and efficiently. The experimental methods used include ultraviolet and visible spectroscopy, fluorescence spectroscopy and enzyme assays performed under various environmental conditions.

Nonenzymatic Synthesis of Peptides in an Ionic Liquid

Researchers: Assistant Professor Virginia F. Smith
Major Hugh C. De Long, USAF, Lieutenant Colonel Paul C. Trulove (USAF)
and Dr. Thomas E. Sutto (ASEE Post-Doctoral Fellow)

Amino acids, the monomers that comprise proteins, are abundant in nature and have even been found in environments that do not support life, such as meteorites. The origin of proteins, however, is mysterious because the condensation reaction that forms the peptide bond linking two amino acids is thermodynamically disfavored in the aqueous solutions that are required for life. In nature, elaborate and energetically costly enzymatic methods for synthesizing proteins have evolved to overcome this thermodynamic limitation. However, all these methods require proteins, which begs the question of where the first proteins came from. Ionic liquids, which are polar but non-aqueous and which are stable over a wide temperature range, are an ideal medium for testing whether peptide bonds could form spontaneously between amino acids in the absence of water. We have demonstrated that peptides can form non-enzymatically in the molten salt butyl, methyl imidazole-PF6 (BMI-PF6) by incubation of various solid amino acids at temperatures above 100°C. Analysis of an aqueous extract of the mixture by reversed-phase high-pressure liquid chromatography (HPLC) revealed the presence of condensation products. Incubation at temperatures below 100°C did not produce peptides, even when performed under vacuum.

An Evaluation of the Midshipman Online Lab System (MOLS)

Researchers: Captain Melonie A. Teichert, USAF, (Assistant Professor at USNA),
Associate Professor Joseph F. Lomax and Associate Professor Debra K. Dillner

This project was an evaluation of the Midshipman Online Laboratory System (MOLS). MOLS is a web-based system that allows students to input their numerical data and analysis for laboratory exercises. Any calculation error is visually indicated by an error flag to give the students direct and immediate feedback. The instructors can use the input values to evaluate the student work. The purpose of this research was to improve the program as well as to provide information about the effectiveness of its use in Plebe Chemistry. Data was collected via online student surveys, student end of course evaluations, and instructor surveys. Preliminary data analysis indicates that a majority of the students use the program, find it useful, and would like to see it used for more lab experiments. This project is currently in the stages of more detailed data analysis, and we plan to submit for publication within a few months.

The Effects of Pre-class Preparation on Student Study and Learning

Researcher: Captain Melonie A. Teichert, USAF (Assistant Professor at USNA)

This project was designed to study the effect of a new approach to teaching Plebe Chemistry. The most important way that instructors can impact student achievement is in their use of class time. Using valuable class time to lecture on material exactly as it is covered in the text is not productive. However, instructors often must do this because students do not read the text or prepare in any way before attending class. The goal of this study was to require students to read the textbook to prepare for class so that class time can be spent on more cognitive activities. Instructors ensured advanced preparation by giving daily quizzes on the text readings. Class time was spent on group activities and problem solving, class discussions, and lectures to explain more complex topics and to model problem solving. The hypothesis was that using class time on more cognitive activities will enhance learning and will help poor-performing students, such as those in summer school courses, develop valuable study techniques, such as preparing for class ahead of time. To evaluate the effect of this approach to teaching Plebe Chemistry, the researcher analyzed course materials (such as in-class quizzes and exams), surveys of student study habits and attitudes, and instructor surveys. Baseline data was collected from the spring Chemistry II course to determine how many students prepared for class ahead of time without explicit requirements to do so. This project is in the midst of data analysis with projected completion by December 2002. A treatment-control study to determine the effects on course performance and grade may be implemented in the fall Chemistry I course.

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

Researcher: Associate Professor Joseph J. Urban

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

The goal of this work is to develop a consistent set of accurate data that will allow for a quantification of the magnitude of the fluoro substituent effects and the role played by the surrounding solvent medium. These calculations also offer a qualitative description of the underlying causes of the effects. The results gleaned from the model compounds will lead to the further investigations of more complicated systems of biological significance.

Research Course Projects

Isolation and Characterization of Metabolic Intermediates from Polycyclic Aromatic Hydrocarbon Biodegradation

Researcher: Midshipman 1/C Rory Kipper, USN
Adviser: Associate Professor Christine L. Copper
Sponsor: Naval Research Laboratory (NRL)

The Navy is inherently interested in methods which will help clean up petroleum-based contaminants in their shipyards. The cheapest and most natural way to do this is through bioremediation. Bacteria already present in the environment can breakdown larger organic molecules into smaller, less harmful byproducts. One important aspect in evaluating bioremediation as a viable method for environmental clean up is to identify the byproducts produced by the bacteria so that their environmental impact can be assessed. In this work, several metabolites produced from biodegradation of a representative component of petroleum (phenanthrene) by the bacterium Pseudomonas paucimobilis were identified using several analytical techniques. These techniques included capillary electrophoresis, liquid chromatography, and gas chromatography/mass spectrometry.

Effects of Hyperbaric Oxygen on Glutamate Transporters

Researcher: Midshipman 1/C Leslie Gregory, USN
Adviser: Associate Professor Christine L. Copper
Sponsors: Dr. Suzan Nadi, Navy Medical Research Center (NMRC)
and Office of Naval Research (ONR)

In an effort to understand hyperbaric oxygen (HBO) toxicity, researchers at the Navy Medical Research Center (NMRC) have modeled seizures under conditions of HBO. HBO, or oxygen exposure at increased pressures, is the condition found in Navy divers, who are breathing pure oxygen at depth. HBO exposure increases the release of the excitatory neurotransmitter glutamate. Throughout the semester of research, experiments were performed in order to find the effects of HBO on the glutamate uptake system, in which glutamate is cleared from the synaptic cleft by uptake into the glial and neuronal cells. Experiments were intended to determine the optimal conditions at which to carry out uptake assays and the effects of HBO on the glutamate transporters.

Synthesis of Substituted Cyclopentanes from a Bicyclic Precursor

Researcher: Midshipman 1/C Jonathan D. McDivitt, USN
Adviser: Associate Professor Debra K. Dillner

This project investigated the use of a rigid bicyclo[3.3.0]octane ring system as a template for introducing substituents onto a cyclopentane ring with enhanced stereoselectivity. Such substituted cyclopentanes are a common feature of many terpenes, including some with anticancer activity. The template was easily synthesized in four steps in 50% overall yield. The first experiments conducted were alkylations at the bridgehead position. Exact conditions for the production of excellent yields of specific alkylation products have been developed. Production of a single product indicates that the stereospecificity desired has been achieved. Second, reduction studies were conducted to investigate the selectivity of the ketone versus the lactone ring and the stereospecificity of various reducing agents. Investigations show that substituents highly influence the product created. All products were fully characterized using NMR, IR and GC/MS. Further studies are being conducted on conversion of the bicyclic compounds to cyclopentanes.

Synthesis of Radiotracers for the Study of the Nicotinic Acetylcholine Receptor

Researcher: Midshipman 2/C Justin Popso, USN
Adviser: Associate Professor Christopher M. Kinter
Sponsor: Division of Nuclear Medicine and Radiation Health Sciences,
The Johns Hopkins University

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

Determination of the Solubility of Hydrogen Peroxide and Short Chain Organic Peroxides in Surface Waters of the Chesapeake Bay

Researcher: Midshipman 1/C Jennifer L. Everson, USN
Adviser: Assistant Professor Daniel W. O'Sullivan

Hydrogen peroxide (H_2O_2), methylhydroperoxide (CH_3OOH), other organic hydroperoxides (ROOH), and formaldehyde (CH_2O) participate in gas phase chemical reactions affecting the distribution of many important atmospheric species such as ozone, sulfur dioxide, and nitrogen species. The hydroperoxides are intimately involved in the odd-oxygen and odd-hydrogen chemistry of the atmosphere. The hydroperoxides are important reservoirs for odd-hydrogen (e.g., hydroxyl, perhydroxyl, methylperoxyl) and odd-oxygen (e.g., atomic oxygen, ozone, perhydroxyl, nitrogen dioxide), as they are produced through the dismutation of peroxyl radicals. Hydroxyl radical is the principal cleansing agent in the atmosphere. In the remote marine atmosphere, the photolysis of H_2O_2 and CH_3OOH and that of CH_2O contributes between 10 and 40% of the gross odd-hydrogen production in the lower troposphere and from 50 to 80% of this production in the upper troposphere, with the balance of odd-hydrogen production primarily due to the photolysis of ozone in the presence of water vapor. Hence, H_2O_2, CH_3OOH, and CH_2O concentrations will reflect the activity of these radical species in the atmosphere. To fully characterize the activity of the radical species, an excellent understanding of the sources and sinks of the hydroperoxides is necessary. We performed several experiments to determine the Henry's Law constant for H_2O_2 as a function of salinity. Unfortunately the results indicate more experimentation is needed to fully characterize the salinity dependence. The results were presented during the Oceanography Department research seminar in December of 2001.

Synthesis and Mechanical Characterization of Model Polydimethylsiloxane Networks

Researcher: Midshipman 1/C Kelly M. Gray, USN
Adviser: Associate Professor Maria J. Schroeder
Sponsor: Naval Research Laboratory (NRL)

Many theoretical models have been developed to describe the elastic behavior of polymer networks. However, a single unifying theory that supports all of these models does not exist. In order to evaluate theories of polymer behavior, networks of well-known structure must be utilized. However the uncertainty inherent in many synthesis methods that rely on the random joining of different segments of two polymer molecules prevents clear structure-property relationships to be established.

Procedures for creating networks of well-defined structure were developed. Model trifunctional polydimethylsiloxane (PDMS) networks were synthesized by end-linking vinyl-terminated PDMS chains with a trifunctional silane crosslinker using a platinum catalyst. Mechanical properties of the trifunctional networks were measured and compared to previously synthesized model tetrafunctional networks. The Young's modulus, swelling ratios, and fracture behavior were studied for the various crosslink density networks. PDMS networks with tetrafunctional crosslinks exhibited larger Young's modulus values than their trifunctional counterparts yet fracture behavior was similar for both materials. For the tetrafunctional networks, significant differences in the mechanical behavior were observed for PDMS precursor molecular weights between 770 and 6000 g/mol indicating possible network changes at these crosslink densities.

Characterization of New High-Performance Polycarbonates for Transparent Armor Applications

Researcher: Midshipman 2/C Colin Browning, USN
Advisers: Associate Professor Maria J. Schroeder
and Associate Professor John T. Bendler (USNA Physics Department)
Sponsor: U.S. Army Research Office (USARO)

The United States Army is currently investigating the development of new synthetic polymers for use in transparent armor applications. Several new aromatic polycarbonate polymers have been synthesized for possible application as transparent armor materials. The synthesis procedures involve readily available starting materials and through the use of molecular modeling have been designed to provide greater impact resistance, processability, and chemical stability over the current polycarbonate materials. The goal of such work is to increase the dynamic weight of the polymer. Dynamic weight is the relationship between increased strength and toughness with decreased size and weight of the transparent system. The objective of this project is to characterize these new polycarbonate materials in hopes of determining the origin of their enhanced properties.

Three newly synthesized polycarbonate materials were characterized by molecular weight and thermal stability using the techniques of gel permeation chromatography and differential scanning calorimetry. These polymers did not show significant improvements over current transparent polycarbonates used in armor applications. The molecular weights of the materials suggest a low degree of polymerization and the lack of a strong glass transition temperature indicate poor thermal properties. However, information from the analyses can provide insight into new synthesis methodologies. As new materials continue to be synthesized, the role of characterization becomes important to evaluating the potential of these materials in transparent armor applications.

Synthesis and Evaluation of Molecular Electronic Materials

Researcher: Midshipman 2/C Ricky Buria, USN
Adviser: Assistant Professor Craig M. Whitaker
Sponsors: Naval Research Laboratory (NRL)
and Office of Naval Research (ONR)

The main goal of this research project was to synthesize and characterize a novel phenylacetylene molecular wire that was terminated with a pyridine molecule at one end and a terminal acetylene group at the other end. The molecule is a key component in the construction of the first functional, organometallic molecular electronic device generated via a self-assembly process.

Synthesis and Evaluation of Molecular Electronic Diodes

Researcher: Midshipman 2/C Ricky Buria, USN
Adviser: Assistant Professor Craig M.Whitaker
Sponsors: Naval Research Laboratory (NRL)
and Office of Naval Research (ONR)

The main goal of this research project was to synthesize and characterize a novel molecular diode structure. The basic component of the diode structure is a 1,1'-binaphthyl group which is substituted with terminal sulfur groups for attachment to a metal surface. One of the key circuit elements for the construction of a molecular scale electronic device is a molecule that can function as a diode.

Synthesis of Molecular Wires

Researchers: Midshipman 1/C David Russell, USN and Midshipman 1/C Michael Rea, USN
Adviser: Assistant Professor Craig M. Whitaker
Sponsors: Office of Naval Research (ONR), Naval Research Laboratory (NRL)
and Defense Advanced Research Projects Agency (DARPA)

The main goal of this project was to demonstrate the feasibility of functional molecular electronic devices by using different types of self-assembly approaches. Our first task involved the optimization of the functionality of different classes of

molecules that constitute the circuit elements of a molecular electronic device – switches, rectifying diodes, conductors and resistors. The studies initially looked at the synthesis and development of a molecular switch that posses a connection point (alligator clip) at both ends of the molecule for gold and palladium surfaces.

Synthesis and Evaluation of Molecular Electronic Materials

Researcher: Midshipman 2/C Michael Souza, USN
Adviser: Assistant Professor Craig M. Whitaker
Sponsors: Naval Research Laboratory (NRL)
and Office of Naval Research (ONR)

This independent research project was an extension of a synthesis performed during the Fall 2001 semester. The main goal of this research project was to synthesize and characterize a novel phenylacetylene molecular wire that was terminated with a pyridine molecule at one end and a terminal acetylene group at the other end. The molecule is a key component in the construction of the first functional, organometallic molecular electronic device generated via a self-assembly process. The addition of an ethyl group off of the molecular backbone greatly enhanced the solubility of the compound.

Trident Scholar Projects

Towards Improved Optical Limiters

Researcher: Midshipman 1/C Peter D. Huffman, USN
Adviser: Professor Jeffrey P. Fitzgerald
Sponsor: Office of Naval Research (ONR)

Optical limiters are materials that are transparent to low-intensity, ambient light but become opaque to high-intensity light. Such materials are of particular interest to the Navy for protecting optical sensors and human eyes from battlefield lasers. The most successful optical limiters known are soluble phthalocyanines, in particular those metallated with lead and indium. Yet further improvements are needed. This research project used a two-pronged approach to create improved optical limiters. The first approach was to synthesize and study soluble thallium phthalocyanines. Thallium, due to its proximity to lead and indium on the periodic table, should exhibit favorable optical limiting properties. Yet soluble thallium phthalocyanines had never been synthesized. A substituted thallium(III) phthalocyanine complex which is readily soluble in organic solvents has been prepared. The second approach to improved optical limiters was to prepare covalently-linked phthalocyanine complexes which allow control of aggregation, an important parameter affecting optical limiting properties. Towards this end, a “clamshell” phthalocyanine dimer has been prepared and metallated with lead. Both of these new materials, the soluble thallium phthalocyanine and the lead phthalocyanine dimer, have been characterized using UV-vis and NMR spectroscopy and mass spectrometry. Their optical properties have been examined using Z-scan and degenerate four wave mixing (DFWM) techniques. Preliminary results indicate that both the thallium phthalocyanine complex and the lead “clamshell” dimer are nonlinear optical materials comparable to the best lead and indium based limiters. The lead complex is particularly effective under high incident intensities. One potential drawback to the thallium complex is its strong ambient absorbance in the red region of the visible spectrum.

Biophysical Characterization of a Bifunctional Iron Regulating Enzyme

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Adviser: Assistant Professor Virginia F. Smith
Sponsor: Office of Naval Research (ONR)

In recent years, proteins have been discovered that can interchange forms and conduct two distinct functions. One such polypeptide with two specific functions is the mammalian iron responsive element (IRE) binding protein IRP-1. When iron levels within the cell are normal, this protein contains an iron-sulfur cluster and is known as cytoplasmic aconitase, an enzyme that catalyzes a specific chemical reaction. When iron levels fall below normal, however, the iron-sulfur cluster is lost, the protein loses its enzymatic activity and it becomes IRP-1, which binds to certain regions of ribonucleic acid (RNA). This binding action helps restore iron levels to normal, and in the process returns the protein to its cytoplasmic aconitase form.

In order to understand the structural features that stabilize this large bifunctional protein, folding studies were performed in the presence and absence of iron on a recombinant version of the human protein. Equilibrium unfolding experiments in urea revealed that human cytoplasmic aconitase undergoes a multi-state transition from the native to denatured form. Comparison of unfolding in the presence and absence of the [4Fe-4S] cluster indicate that the cluster does not have a significant effect on the equilibrium unfolding properties as monitored by fluorescence. Monitoring enzymatic activity as a function of urea concentration indicates that activity is lost at ~2M urea, presumably due to disruption of the enzyme active site, which is at the major interdomain cleft. The effect of thermal denaturation on the stability and activity of the IRP-1 was also studied. A preliminary model for the unfolding of aconitase based on its enzyme activity, equilibrium thermal properties, and chemical denaturation data is presented.

Publications

Journal (Refereed) Manuscripts

Bitterwolf, Thomas E., Saygh, Abdul, Haener, Jay L., Fierro, Ricardo, SHADE, Joyce E., Professor, Rheingold, Arnold L., Liable-Sands, Louise and Alt, Helmut G., "Synthesis and Photolysis of $[M(CO)_3H]_2((\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, where M = Mo and W. Photochemical 'twist' rearrangement of $M_2(CO)_6(\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ to give $[M(CO)_3][M(CO)_3H]$ $(\eta^5, \eta^5\text{: }\eta^1\text{-}C_5H_4CH_2C_5H_3)$, where M = Mo and W. The molecular structure of $[Mo(CO)_3][Mo(CO)_3Cl]($ $(\eta^5, \eta^5\text{: }\eta^1\text{-}C_5H_4CH_2C_5H_3)$," *Inorganica Chimica Acta*, Vol. 334, pp. 54-58 (2001).

> $M_2(CO)_6(\eta^5, \eta^5\text{-}C_5H_4CR_2C_5H_4)$, where R = H, M = Mo, **1**, or W, **2**, undergo protonation by HCF_3SO_3 at the M—M bond to give $[M_2(CO)_6(\mu\text{-}H)((\eta^5, \eta^5\text{-}C_5H_4CH_2C_5H_4)]+$ which have been characterized by ^1H NMR. Reduction of **1** and **2** with sodium potassium alloy followed by reaction with acid gives the bis(metal-hydride) compounds $[M(CO)_3H]_2((\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$. These bis(metal-hydride) species are stable in solution in the dark but undergo hydrogen loss to reform **1** and **2** when exposed to room light. **1** and **2** undergo photochemical rearrangement to the 'twist' products $[M(CO)_3][M(CO)_3H]($ $(\eta^5, \eta^5\text{: }\eta^1\text{-}C_5H_4CH_2C_5H_3)$. The tungsten product is thermally stable for several hours, but the molybdenum products rapidly return to **1**. The molybdenum 'twist' products of **1** and **3**, R=CH_3, M=Mo, may be efficiently trapped as their chlorides by carrying out the photolysis in 20% $CHCl_3$ in benzene. Photochemical studies of the efficiency of this reaction as a function of wavelength indicate that the 'twist' reaction requires photolysis into the higher energy band at 380 nm and does not proceed upon photolysis into the lower energy transition at 529 nm. The molecular structure of $[Mo(CO)_3][Mo(CO)_3Cl]($ $(\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ has been determined: monoclinic, $P2_1/c$, a = 9.257(3), b = 15.211 (5), c = 13.263(4) Å, β =107.76(2)°, V =1778.7(10) $Å^3$, Z = 4, T = 218 K, R(F) = 3.24%.

COTTEN, Gregory B., Lieutenant (USN), and Eldredge, H. B., "Nanolevel Magnetic Separation Model Considering Flow Limitations," *Separation Science and Technology*, Vol. 37, No.16, pp. 3759-3779 (2002).

> This work proposes an enhanced nanolevel magnetic separation model considering flow limitations using simplifying assumptions. The theoretical model builds on magnetic heteroflocculation models described in the literature and couples the magnetic and hydrodynamic forces between two spherical particles with different sizes and different magnetic properties under bulk fluid flow conditions. Separator performance figures are presented showing the relationship between input parameters such as applied magnetic field strength, flow rate, and matrix material size and composition, and output parameters such as Peclet number and capture propensity for various contaminant particle sizes. This purely predictive model work may be useful in estimating actual magnetic separator performance and serve as a starting point for experimental work or more accurate mathematical models.
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> This work provides a simplified mathematical model to predict magnetic separator performance based on single magnetic matrix particle and single magnetic contaminant particle interactions. Local maxima, or transition points, between matrix and contaminant particle size and separator performance indicate magnetic separator performance can be optimized by the selection of appropriate magnetic matrix particle size. Evaluation of points of maximum particle capture force using the Peclet number provides limiting conditions for retention of particles under Stokes flow conditions.

Davis, Cher H., Mathias, Lon J., Gilman, Jeffrey W., Schiraldi, David A., Trulove, Paul C., Sutto, Thomas E., and DELONG, Hugh, C., Major (USAF) and Assistant Professor, "Effects of Melt-Processing Conditions on the Quality of Poly(ethylene terephthalate) Montmorillonite Clay Nanocomposites," *J. Polym. Sci., Poly. Phys.*, Vol 40, pp. 2661-2666 (2002).

Organically modified montmorillonite was synthesized with a novel 1,2-dimethyl-3-*N*-alkyl imidazolium salt or a typical quaternary ammonium salt as a control. Poly(ethylene terephthalate) montmorillonite clay nanocomposites were compounded via melt-blending in a corotating mini twin-screw extruder operating at 285°C. The nanocomposites were characterized with thermal analysis, X-ray diffraction, and transmission electron microscopy to determine the extent of intercalation and/or exfoliation present in the system. Nanocomposites produced with *N*,*N*-dimethyl-*N*,*N*-dioctadecylammonium treated montmorillonite (DMDODA-MMT), which has a decomposition temperature of 250 °C, were black, brittle, and tarlike resulting from DMDODA degradation under the processing conditions. Nanocomposites compounded with 1,2-dimethyl-3-*N*-hexadecyl imidazolium treated MMT, which has a decomposition temperature of 350°C, showed high levels of dispersion and delamination.

Fang, Jiyu, WHITAKER, Craig M., Assistant Professor, Naciri, Jawad and Shashidhar, Rangnathan, "Synthesis and Properties of a Novel Coumarin Derivative," *J. Mater. Chem.*, Vol. 11, pp. 2992-2995 (2001).

We report the synthesis and self assembly of 7-(8-trimethoxysilane)octenyloxy coumarin into optically active monolayers on substrates. Atomic force microscopy and UV-vis spectroscopy have been used to characterize the self-assembly processes and photochemical reaction of coumarin silane on subtrates. We also show that when irradicated with linearly polarized UV light, the self-assembled coumarin monolayer can induce a homogeneous alignment of nematic liquid crystals.

Gilman, Jeffrey W., Awad, Walid H., Davis, Rick D., Shields, John, Kashiwagi, Takashi, VanderHart, David L., Harris, Richard H. Jr., Davis, Cher, Morgan, Alexander B., Sutto, Thomas E., Callahan, John, Trulove, Paul C., and DELONG, Hugh C., Major (USAF) and Assistant Professor, "Polymer Layered-silicate Nanocomposites from Thermally Stable Trialkyl-Imidazolium Treated Montmorillonite," *Chemistry of Materials*, Vol. 14(9), pp. 3776-3785 (2002).

The limited thermal stability of alkylammonium cations intercalated into smectite minerals (e.g., montmorillonite, MMT) and the processing instability of some polymers [polyamide-6 (PA-6) and polystyrene (PS)] in the presence of nanodispersed MMT have motivated the development of improved organophillic treatments for layered silicates. Success in this regard should enable the preparation of polymer/layered silicate nanocomposites from thermoplastic polymers that require high melt-processing temperatures or long residence times under high shear and from thermoset resins with high cure temperatures. Our efforts to address some of these issues focus on the use of new thermally stable imidazolium-treated layered silicates for the preparation of nanocomposites. Several trialkylimidazolium salt derivatives were prepared with propyl, butyl, decyl, and hexadecyl alkyl chains attached to the imidazolium through one of the nitrogens. These imidazolium salts were used to prepare the corresponding treated layered silicates. We report here that the use of 1-alkyl-2,3-dimethylimidazolium salts to replace the sodium in natural MMT gives organophillic MMT with a 100°C improvement in thermal stability (in N2) as compared to the alkylammonium-treated MMT. The use of 1-alkyl-2,3-dimethylimidazolium salt in fluorinated synthetic mica (FSM) also gives a 100°C improvement in thermal stability. The use of 1,2-dimethyl-3-hexadecylimidazolium-treated MMT gives an exfoliated PA-6 nanocomposite and, depending on processing conditions, either a partially exfoliated or an intercalated polystyrene nanocomposite.

HARRISON, Judith A., Associate Professor, (co-author), "Compression of Carbon Nanotubes Filled with C_{60}, CH_4, or Ne: Predictions from Molecular Dynamics Simulations," *Phys. Rev.* Lett., Vol. 88, 205505-1 through 205505-4 (2002).

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

HARRISON, Judith A., Associate Professor, "Packing-Density Effects on the Friction of n-Alkane Monolayers," *J. Am. Chem. Soc.*, Vol. 123, pp. 6873-6881 (2001).

The classical molecular dynamics simulations were used to examine the tribology associated with the sliding of a hydrogen-terminated diamond counterface across a monolayer of n-alkane chains that are covalently bound to a diamond substrate. Two systems using chains of fixed length (18 carbon atoms per chain) on diamond (111) were examined: a tightly packed (2 x 2) arrangement and a loosely packed system with approximately 30% fewer chains. Both systems give a similar average friction at low loads. Under high loads, the tightly packed monolayer exhibits significantly lower friction than the loosely packed monolayer. While the movement of chains is greatly restricted in both systems, the tightly packed monolayer under high loads is clearly more uniform in geometry and more constrained with respect to the movement of individual chains than the loosely packed monolayer. This suggests that efficient packing of the chains is responsible for the lower friction for tight packing under high load. This is supported by the fact that sliding initiates larger bond-length fluctuations in the loosely packed systems, which ultimately lead to more energy dissipation via vibration.

HARRISON, Judith A., Associate Professor, "A Second-Generation Reactive Empirical Bond Order (REBO) Potential Energy Expression for Hydrocarbons," *J. Phys. Condes. Matter*, Vol. 14, pp. 783-802 (2002).

A second-generation potential energy function for solid carbon and hydrocarbon molecules that is based on an empirical bond-order formalism is presented. This potential allows for covalent bond breaking and forming with associated changes in atomic hybridization within a classical potential, producing a powerful method for modeling complex chemistry in large many-atom systems. This revised potential contains improved analytic functions and an extended database relative to an earlier version (D.W. Brenner, *Phys. Rev. B* **42**, 9458 (1990)). These leads to a significantly better description of bond energies, lengths and force constants for hydrocarbon molecules, as well as elastic properties, interstitial defect energies, and surface energies for diamond.

HARRISON, Judith. A., Associate Professor, "Understanding Collision Cascades in Molecular Solids," *Nuclear Instruments and Methods in Physics Research B*, Vol. 180, pp. 159-163 (2001).

This paper describes simulations of the sputtering of a molecular solid that uses a reactive potential with both covalent bonding and van der Waals interactions. Recently, the adaptive intermolecular REBO (AIREBO)potential has been developed, which incorporates intermolecular interactions in a manner that maintains the reactivity of the original potential REBO potential. Preliminary simulations of the keV bombardment of a molecular solid have been performed using the AIREBO potential. Molecules that are initially struck by the bombarding particle break into fragments. The fragments initiate molecular collision cascades leading to the ejection of intact molecules and molecular fragments. The fragments initiate molecular collision cascades leading to the ejection of intact molecules and molecular fragments from the surface.

HEUER, William B., Associate Professor, (co-author), "Novel Two-Photon Absorbing Conjugated Oligomers/Polymers: Property Modulation by π-Center," *Polym. Prepr*. Vol. 43, p. 666 (2002).

Two-photon absorption (TPA) has been observed with various conjugated molecules bearing a pair of electron-donor (D) and/or acceptor (A) moieties. We have focused on the role of the p-conjugated linker (π-center) of the chromophores (D- π -D, D- π -A, and A- π -A) in the TPA activity. Previously synthesized oligomeric TPA chromophores based on dithienothiophene (DTT) as π -center and different D and/or A moieties displayed exceptionally large TPA cross sections, notably with D/D pair compared to D/A counterpart. This situation is reversed when the π-center is replaced with 9,9-spirobifluorene, exhibiting extraordinarily large enhancement of cross-section with A/A relative to D/D pair, contrasting to that of 9,9-diethylhexylfluorene-based counterpart. This suggests that molecular TPA is determined not only by the π-center but even more strongly by electronic interactions between π-center and residual D and/or A pair.

HEUER, William B., Associate Professor, (co-author), "Oligothiophene as Photonic/Electronic Property Modulator," *Optical Materials*, Vol. 21, p. 559 (2002).

Several different series of conjugated oligomers bearing various p-centers such as dithienothiophene (DTT), fluorene and terthiophene moieties, attaching electron donor (D) and/or acceptor (A) units through conjugation were synthesized and assessed for their nonlinear optical (NLO), two photo absorption (TPA) and redox properties. Discussion is made on the property modulation role of the p-centers, particularly by DTT oligothiophene which displays a unique and efficient electronic mediation.

MORSE, Daniel P., Assistant Professor, (co-author), "RNA Hairpins in Noncoding Regions of Human Brain and *Caenorhabditis elegans* mRNA are Edited by Adenosine Deaminases that Act on RNA," *Proc. Natl. Acad. Sci., USA*, Vol. 99, pp. 7906-7911 (2002).

Adenosine deaminases that act on RNA (ADARs) comprise a family of RNA editing enzymes that convert adenosine to inosine within double-stranded regions of RNA. We previously developed a method to identify inosine-containing RNAs and used it to identify five ADAR substrates in *Caenorhabditis elegans*. Here we use the same method to identify five additional *C. elegans* substrates, including three mRNAs that encode proteins known to effect neuronal functions. All ten of the *C. elegans* substrates are edited in long stem-loop structures located in non-coding regions, and thus contrast with previously identified substrates of other organisms, in which ADARs target codons. To determine if editing in non-coding regions was a conserved ADAR function, we applied our method to poly$(A)^+$ RNA of human brain and identified 19 previously unknown ADAR substrates. The substrates were strikingly similar to those observed in *C. elegans* since editing was confined to 3' UTRs, introns, and a non-coding RNA. Also similar to what was found in *C. elegans*, 15 of the 19 new substrates were edited in repetitive elements. The identities of the new ADAR substrates suggest that RNA editing may influence many biologically important processes, and that for many metazoa, A to I conversion in coding regions may be the exception rather than the rule.

O'SULLIVAN, Daniel W., Assistant Professor, (co-author), "Formaldehyde Over the Central Pacific during PEM-Tropics B," *Journal of Geophysical Research*, 106(D23), pp. 32, 717-32,731 (2001).

Formaldehyde, CH_2O, mixing ratios are reported for the central Pacific troposphere from a series of 41 flights, which took place in March-April 1999 as part of the NASA Pacific Exploratory Mission (PEM)-Tropics B mission. Ambient CH_2O was collected in aqueous media and quantified using an enzyme-derivatization fluorescence technique. Primary calibration was performed using aqueous standards and known flow rates. Occasionally, CH_2O gas standard additions to ambient air were performed as a secondary calibration. Analytical blanks were determined by replacing ambient air with pure air. The estimated precision was ±30 pptv and the estimated accuracy was the sum of ±30 parts per trillion by volume (pptv) ±15% of the measured value. Approximately 25% of the observations were less than the instrumental detection limit of 50 pptv, and 85% of these occurred above 6 km. CH_2O mixing ratios decreased with altitude; for example, near the equator the median value in the lowest 2 km was 275 pptv, decreased to 150 pptv by 6 km and was below 100 pptv above 8 km. Between 130 and 170 W and below 1 km, a small variation of CH_2O mixing ratio with latitude was noted as near-surface median mixing ratios decreased near the equator (275 pptv) and were greater on either side (375 pptv). A marked decrease in near-surface (200 pptv) was noted south of 23°S on two flights. Between 3°and 23°S, median CH_2O mixing ratios were lower in the eastern tropical Pacific than in the western or central Pacific; nominal differences were > 100 pptv near the surface to » 100 pptv at midlatitude to »50 pptv at high altitude. Off the coast of Central America and Mexico, mixing ratios as high as 1200 pptv were observed in plumes that originated to the east over land. CH_2O observations were consistently higher than the results from a point model constrained by other photochemical species and meteorological parameters. Regardless of latitude or longitude, agreement was best at altitudes above 4 km where the difference between measured and modeled CH_2O medians was less than 50 pptv. Below 2 km the model median was approximately 150 pptv less than the measured median.

SCHROEDER, Maria J., Associate Professor, (co-author), "Segmental Relaxation of End-Linked Polydimethylsiloxane Networks," *Macromolecule*s, Vol. 35, pp. 2676-2681 (2002).

End-linked polydimethylsiloxane (PDMS) networks, spanning a broad range of crosslink densities, were prepared by the reaction of vinyl-terminated linear PDMS with a tetrafunctional silane crosslinking agent and a platinum catalyst. Dielectric a-relaxation spectra, thermal expansivities, and the (rubbery) elastic modulus were measured for these networks. From the crosslink density at which marked changes occur in the segmental relaxation times and the T_a-scaled temperature dependence (fragility), a characteristic length for the a-relaxation was determined. The result, 14 Å at T_a, is quite close to the length scale associated with constraint of crystallization in similar PDMS networks. Crosslinking also affects the thermal expansion and elastic modulus, although these properties exhibit a more modest variation with crosslink density.

Sutto, Thomas E., DELONG, Hugh C., Major (USAF) and Assistant Professor, and Trulove, Paul C., "Physical Properties of Substituted Imidazolium Based Ionic Liquids Gel Electrolytes," *Z. Naturforsch,* Vol. 57a, pp. 829-846 (2002).

The physical properties of solid gel electrolytes of either polyvinylidene diflurohexafluoropropylene or a combination of polyvinylidene hexafluoropropylene and a polyacrylic acid, and the molten salts 1-ethyl-3-methylimidazolium tetrafluoroborate, 1,2-dimethyl-3-n-propylimidazolium tetrafluoroborate, and the new molten salts 1,2-dimethyl-3-n-butylimidazolium tetrafluoroborate, and 1,2-dimethyl-3-n-butylimidazolium hexafluorophosphate were characterized by temperature dependent ionic conductivity measurements for both the pure molten salt and of the molten salt with 0.5 M Li^+ present. Ionic conductivity data indicate that for each of the molten salts, the highest concentration of molten salt allowable in a single component polymer gel was 85%, while gels composed of 90% molten salt were possible when using both polyvinylidene hexafluorophosphate and polyacrylic acid. For polymer gel composites prepared using lithium containing ionic liquids, the optimum polymer gel composite consisted of 85% of the 0.5 M Li^+/ionic liquid, 12.75% polyvinylidene hexafluoropropylene, and 2.25% poly (1-carboxyethylene). The highest ionic conductivity observed was for the gel containing 90% 1-ethyl-3-methyl-imidazolium tetrafluoroborate, 9.08 mS/cm. For the lithium containing ionic liquid gels, their ionic conductivity ranged from 1.45 to 0.05 mS/cm, which is comparable to the value of 0.91 mS/cm, observed for polymer composite gels containing 0.5 M $LiBF_4$ in propylene carbonate.

TEICHERT, Melonie A., Captain (USAF) and Assistant Professor, and Stacy, A.M., "Promoting Understanding of Chemical Bonding and Spontaneity through Student Explanation and Integration of Ideas," *Journal of Research in Science Teaching*, Vol. 39, pp. 1-33 (2002).

This article explores the effectiveness of intervention discussion sections for a college general chemistry course designed to apply research on student preconceptions, knowledge integration, and student explanation. Two interventions, on bond energy and spontaneity, were tested and intervention student performance was compared with that of a control group that did not use the experimental pedagogy. Results indicate that this instruction, which identifies students' initial conceptions and integrates those ideas into class discussion, leads to enhanced conceptual understanding. The intervention group outperformed the control group on a written course midterm, the thermodynamics portion of a standardized American Chemical Society examination, and an in-depth interview. In interviews, the intervention group students explained the energetics of bond breaking and formation at a more sophisticated level than did the control students. In contrast, control students were more tenuous in their thinking, tended to contradict themselves more when discussing bond energy, and harbored more misconceptions about spontaneity.

Wertsching, A., COTTEN, Gregory B., Lieutenant (USN), and Harrup, M.K., "Examination of the Physical Properties of Polyphosphazene-Silicate Nanocomposites Using Novel Synthetic Strategies," *Composite Interfaces*, Vol. 9, No. 1, pp. 77-87 (2002).

Phosphazene-silicate nancomposites were synthesized and their mechanical properties analyzed. Three distinct types of catalysts were employed to drive the ceremaic condensation – acid, base and ionic salt species – resulting in a wide variety of mechanical properities. To validate the correlations between the physical properties observed

and the ceramic morphologies formed, a survey of the extent of parent polymer degradation under these catalytic conditions was undertaken. Further, the effects of carious ionic strengths of casting solutions resulting from relative dissociation constants, hence active catalyst availability, on salt-catalzyed silicate interpenetrating network (IPN) matrices were also investigated. The resulting information provides the appropriate synthetic control, needed to produce nanocomposites with specifically tailored properties for a variety of applications.

Conference Proceedings

Awad, W. H., Gilman, J. W., Nyden, M., Davis, R. D., Harris, R. H., Jr., Sutto, T. E., Callahan, J., Trulove, P. C., and DELONG, H. C., Major (USAF) and Assistant Professor, "Thermal Degradation Studies of Trialkyl-Imidazolium Salts and their Application in Nanocomposites," in *Proceedings of the 13th International Symposium on Molten Salts*, Trulove, DeLong, Stafford, and Deki, (eds.), The Electrochemical Society: Pennington, NJ, Vol. 19, pp. 200-212, 2002.

Increasing the thermal stability of organically modified layered silicates is one of the key points in the successful application of polymer layered-silicate nanocomposites on the industrial scale. To circumvent the detrimental effect of the lower thermal stability of alkyl ammonium treated montmorillonite, a series of alkyl imidazolium molten salts were prepared and their thermal properties characterized by thermal gravimetric analysis (TGA) and thermal desorption mass spectroscopic (TDMS). The effect of different parameters such as: counter ion, alkyl chain length and structural isomerism on the thermal stability of the imidazolium salts was also examined. Alkyl imidazolium treated montmorillonite clays were prepared by ion exchange of the imidazolium salts with Na-montmorillonite. These organically modified clays were then characterized by XRD and TDMS, and compared to the conventional quaternary alkyl ammonium montmorillonite. Results indicate that the counter ion has an effect on the thermal stability of the imidazolium salts, and that imidazolium salts with PF_6^-, $N(SO_2CF_3)_2^-$ and BF_4^- anions are thermally more stable than the halide salts. A relationship was observed between the chain length of the alkyl group and the thermo-oxidative stability; as the chain length increased from propyl, butyl, decyl, hexadecyl, octadecyl to eicosyl, the stability decreased. The results also show that the imidazolium treated montmorillonite has excellent compatibility with polystyrene (PS) and poly(ethylene terephthalate) (PET) thus enabling preparation of polymer layered silicate nanocomposites.

CHEEK, Graham T., Professor, "Electrochemical Deposition of Aluminum at Vitreous Carbon in a Room-Temperature Molten Salt," Trulove, De Long, and Mantz, (eds.), *Electrochemical Society Proceedings*, Volume PV 2002-19, pp. 873-880 (2002).

The electrochemical deposition of aluminum at vitreous carbon has been studied in the $AlCl_3$: 1-ethyl-3-methylimidazolium chloride molten salt system. In a 1.2:1.0 acidic melt, multiple Al stripping peaks are observed at low coverage, which implies that there are several types of nucleation sites on the carbon surface. In neutral buffered (NaCl) melts, a symmetrical oxidation peak at –0.4 V (vs Al/1.5:1.0 melt) suggests aluminum stripping after initial deposition at –1.40 V. This oxidation process becomes two peaks, at –0.2 V and 0.0V, if the potential is held for 180s at –1.40 V before scan reversal. This behavior is believed to be due to the loss by diffusion of NaCl, formed during $Al_2Cl_7^-$ reduction, from the electrode surface during potential hold. As a result, aluminum stripping soon exhausts the supply of NaCl at the surface, and the remainder of the aluminum is stripping into an essentially acidic melt at 0.0 V. Scanning electron microscopy of long-term (3600 s) deposits on vitreous carbon show considerable amounts of chlorine and sodium, in addition to aluminum, suggesting that inclusion of melt has occurred during deposition.

CHEEK, Graham T., Professor, "Electrochemical Studies of the Fries Rearrangement in a Room-Temperature Molten Salt," Trulove, DeLong, and Mantz, (eds.), *Electrochemical Society Proceedings*, Volume PV 2002-19, pp. 923-930 (2002).

The importance of Lewis acids in promoting the Fries rearrangement has been studied by observing the rearrangement of phenyl benzoate in the aluminum chloride: 1-ethyl-3-methylimidazolium chloride (EMIC) molten salt system. Additions of the Lewis acidic species $Al_2Cl_7^-$ to phenyl benzoate in a neutral melt gave an estimate of the K value (140) for the interaction. The rearrangement did not occur at 20°C in the basic melt; however, the reaction

went to completion in 12 hours at 77°C in a weakly acid melt. The rearrangement products were 4-hydroxybenzophenone and 2-hydroxybenzophenone, formed in a 3 to 1 mole ratio, as is typical of this reaction in other solvent systems. Further studies were carried out in the neutral buffered melt, under which conditions the reaction required 3 days for completion at 77°C, with the same product distribution. In crossover experiments, addition of benzene to the neutral buffered melt produced only the usual hydroxybenzophenone products; however, addition of m-cresol gave mostly methylhydroxybenzophenone products, strongly suggesting that the Fries rearrangement is intermolecular in the neutral buffered melt.

Mantz, R. A., Sutto, T. E., DELONG, H. C., Major (USAF) and Assistant Professor, and Trulove, P. C., "Ion Transport in Ionic-Liquid/Polymer Gel Electrolytes," *Proceedings of the 13th International Symposium on Molten Salts*, Trulove, DeLong, Stafford, and Deki, (eds.), The Electrochemical Society: Pennington, NJ, Vol. 19, pp. 94-101, 2002.

Pulsed-field-gradient spin-echo nuclear magnetic resonance (NMR) has been used to determine the diffusion coefficients of the cation and anion species in 1,2-Dimethy-3-n-butyl imidazolium bis(trifyl)imide ($DMBI^+$ $N(SO_3CF_3)_2^-$) ionic liquids and poly-vinylidene-difluoro hexfluorophosphate (PVdF/HFP) polymer gels. The transference number of the ionic liquid and the polymer gel has been calculated. The conductivities of both the ionic liquid and polymer gel have been measured as a function of temperature and the activation energies calculated.

SMITH, Virginia F., Assistant Professor, DELONG, H. C., Major (USAF) and Assistant Professor, Trulove, P. C., and Sutto, T. E., "Non-enzymatic Synthesis of Peptides in an Ionic Liquid," *Proceedings of the 13th International Symposium on Molten Salts*, Trulove, DeLong, Stafford, and Deki, (eds.), The Electrochemical Society: Pennington, NJ, Vol. 19, pp. 268-275, 2002.

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

Sutto, T. E., Trulove, P. C., and DELONG, H. C., Major (USAF) and Assistant Professor, "Investigations of the Influence of Polymer Type on the Electrochemical Behavior of Ionic Liquid/Polymer Gel Electrolytes," *Proceedings of the 13th International Symposium on Molten Salts*, Trulove, DeLong, Stafford, and Deki, (eds.), The Electrochemical Society: Pennington, NJ, Vol. 19, pp. 54-62, 2002.

The electrochemical properties of polymer gel electrolytes, prepared using either polyethylene oxide (PEO) or Polyvinylidenedifluoro-hexafluoropropene (PVdF-HFP) and the ionic liquid 1,2-dimethyl-3-n-propylimidazolium tetrafluoroborate, were evaluated. The composition of all polymer gels studied was 20% polymer and 80% ionic liquid. A solvent dissolution method was used for preparation of both polymer gel types. The PEO gels were white, waxy, and somewhat fragile, while the PVdF-HFP gels were translucent and rubbery. The room-temperature ionic conductivities for both types of polymer gels were in the range of 1 to 5 mS/cm. Cyclic voltammetry was performed using graphitic paper, and good cationic intercalative behavior was observed. However, the anionic intercalative behavior was poor. The PVdF-HFP gels exhibited 80% cation charge/discharge efficiencies, with a discharge potential of –1.1 V, while the PEO gels exhibited only 50% charge-discharge efficiencies at –0.45 V. For both gel systems, the anionic charge-discharge efficiencies were below 50%.

Sutto, T. E., Trulove, P. C., and DELONG, H. C., Major (USAF) and Assistant Professor, "Investigations of the Electrochemical Behavior of Trialkylimidazolium Bis(trifluoromethylsulfonimide) Ionic Liquids and Their Polymer Gel Electrodes," *Proceedings of the 13th International Symposium on Molten Salts*, Trulove, DeLong, Stafford, and Deki, (eds.), The Electrochemical Society: Pennington, NJ, Vol. 19, pp. 134-144, 2002.

The physical and electrochemical properties of 1,2-dimethyl-3-n-*R*-imidazolium bis(trifluoromethylsulfonimide) ionic liquids (*R* = propyl and butyl) were investigated. In addition, the physical and electrochemical properties of polymer gel electrolytes prepared from these ionic liquids were studied. In the case of *R* = propyl, the room-temperature ionic conductivity of the ionic liquid was 5.32 mS/cm and for its polymer gel (20% polymer and 80% ionic liquid) was 3.89 mS/cm. For *R* = butyl, the pure ionic liquid exhibited a room-temperature ionic conductivity of 4.42 mS/cm, and its 20%/80% polymer gel had a room-temperature ionic conductivity of 3.17 mS/cm. Cyclic voltammograms for both the ionic liquids gave almost identical electrochemical windows of approximately 4.9 V, with the *R* = butyl based ionic liquid having a slightly larger window. The charge-discharge behavior for the ionic liquids and polymer gels, in a Dual Intercalating Molten Electrolyte cell, showed over 80% efficiency for the cation, while the anion exhibited less than 60% efficiency.

Trulove, P. C., DE LONG, H. C. Major (USAF) and Assistant Professor, and Sutto, T. E., "Direct X-ray Evidence of the Electrochemical Induced Intercalation of Substituted Alkylimidazolium and Lithium Cations into Graphite from Ambient-Temperature Ionic Liquids," *Proceedings of the 13th International Symposium on Molten Salts*, Trulove, De Long, Stafford, and Deki, (eds.), The Electrochemical Society: Pennington, NJ, Vol. 19, pp. 87-93, 2002.

1,2-dimethyl-3-n-butylimidazolium tetrafluoroborate was electrochemically characterized at a graphitic paper, working electrode. Cyclic voltammetry indicated reversible cationic intercalation of the graphitic paper. X-ray powder/thin film diffraction measurements of intercalated graphitic paper gave one primary diffraction peak at 3.44671 Å. In addition, detailed diffraction studies revealed several additional reflections at **00l** positions. The x-ray diffraction results are consistent with a $DMBI^{+}_{x}C$ intercalate that has a c-axis of 10.33 ± 0.0051 Å and a resulting c-axis expansion of 6.98 Å. This result appears to suggest that the plane of the five membered imidazolium ring is lying nearly parallel to the graphite sheets above and below the ring.

Patents

PITZER, Kevin K., Major (USA), U.S. Patent # 6284772.

This invention relates to new and existing indolo[2,1-b]quinazoline-6,12-dione derivatives which are useful in killing malaria parasites, to antimalarial compositions containing the compounds, and to the use of the compounds and compositions, alone or in combination with other antimalarial agents, in the treatment of malaria.

Technical Reports

KINTER, Christopher M., Associate Professor, (co-author), "New Synthetic Approaches to Geminal Difluoramino Compounds," Office of Naval Research (ONR) Report, 30 July 2001.

This report details progress made on establishing efficient synthetic methods for the production of high energy density compounds with mixed nitramine-gem difluoramine functionality. The specifics target compounds for this research include HNFX, RNFX, and TNZX which are all difluoramino analogs of the known explosive materials HMX, RDX, and TNAZ, respectively.

Lyons, K.S., COTTEN, Gregory B., Lieutenant (USN), Stanley, J.A., Dmowski, W., and Egami, T., "Low-Platinum and Platinum-Free Catalysts for Oxygen Reduction at PEMFC Cathodes," 2001 Annual Report of the Transportation Fuel Cell Power Systems Program of the Department of Energy (DOE) Office of Advanced Automotive Technologies.

State-of-the-art proton-exchange membrane fuel cells (PEMFCs) contain high loadings of platinum (Pt), making the fuel cells costly and subject to fluctuations in the market availability of the noble metal. By using little or no Pt in fuel cell cathodes, the cost of the fuel cells and imports of noble metals can be drastically reduced.

The catalytic activity of the oxygen reduction reaction (ORR) at the fuel cell cathode is known to be relatively slow, presumably because it is a 4-electron mechanism: $O_2 + 4H^+ + 4e^- \rightarrow 2\ H_2O$.

For this reaction to proceed unencumbered, the catalyst site must also have a supply of oxygen, protons, and electrons, and must be able to transport away water. The reaction above becomes limited when the transport of any of these four species is slow.

Hydrous ruthenium oxide (RuO_xH_y) is an example of a material that has both high proton and electron transport. Pair-density function analysis of the x-ray diffraction pattern (PDF-XRD) of "amorphous" RuO_xH_y indicates that the most catalytically active material is comprised of ordered regions from 0.5 to 1.5 nm which are intertwined with unordered regions. Using this PDF-XRD data, plus magnetic measurements, we have surmised that the high electrochemical and catalytic activity of RuO_xH_y is due to its inherent nanocomposite structure of ordered regions for electron transport and hydrous regions for proton transport. The naturally forming structure of RuO_xH_y is used in this program as an inspiration for designing new catalytically active materials.

Laboratory Experiments

SCHROEDER, Maria J., Associate Professor, (co-author), "Physical Testing of Polymer Samples – Tensile Properties Lab," in *Materials Science and Engineering Laboratory Manual*, A. L. Moran (ed.), Kendall/Hunt Publishing, pp. 43-47 (2001).

In this experiment, physical testing is used to determine the properties of various polymeric materials so that the relationships between the measured properties and the intended applications of these materials can be investigated. Tensile strength, elastic modulus, breaking strength, and % elongation are measured on samples of Teflon, Mylar, paper, inkjet paper, and Parafilm. Students apply ASTM methods and learn how to interpret stress-strain curves.

Presentations

Awad, W. H., Gilman, J. W., Nyden, M., Davis, R., Harris R.H., Jr., Sutto, T. E., Callahan, J., Trulove, P. C., and DELONG, H. C., Major (USAF) and Assistant Professor, "Thermal Degradation Studies of Trialkyl-Imidazolium Salts and their Application in Nanocomposites," 13th International Symposium on Molten Salts, The Electrochemical Society, Philadelphia, PA, 12-17 May 2002.

CHEEK, Graham T., Professor, "Electrochemical Deposition of Aluminum at Vitreous Carbon in a Room-Temperature Molten Salt," 201st Electrochemical Society Meeting, Philadelphia, PA, 14 May 2002.

CHEEK, Graham T., Professor, "Electrochemical Studies of the Fries Rearrangement in a Room-Temperature Molten Salt," 201st Electrochemical Society Meeting, Philadelphia, PA, 17 May 2002.

CHEEK, Graham T., Professor, "Studies of the Fries Rearrangement in a Room-Temperature Molten Salt," 35th Middle Atlantic Regional Meeting, Fairfax, VA, 29 May 2002.

ELERT, Mark L., Professor, "Molecular Dynamics Modeling of Impact-Induced Shock Waves in Hydrocarbons," American Physical Society Conference on Shock Compression of Condensed Matter, Atlanta, GA, 24-29 June 2001.

ELERT, Mark L., Professor, "Atomistic Modeling of Orientation Dependence of Shock Wave Properties in Diamond," American Physical Society Conference on Shock Compression of Condensed Matter, Atlanta, GA, 24-29 2001.

ELERT, Mark L., Professor, "Molecular Dynamics Modeling of Non-Reacting Shock Waves in Hydrocarbon Molecular Crystals," American Physical Society National Meeting, Indianapolis, IN, 18-22 March 2002.

ELERT, Mark L., Professor, "Molecular Dynamics Simulation of Shock-Induced Polymerization of Hydrocarbons," American Physical Society National Meeting, Indianapolis, IN, 18-22 March 2002.

FERRANTE, Robert F., Professor, (co-author), "IR Studies of Irradiated N_2 Ices Containing CH_4 and CO: Implications for Triton and Pluto," 33rd Annual Meeting, Division of Planetary Sciences, American Astronomical Society, New Orleans, LA, November 2001.

FERRANTE, Robert F., Professor, HEUER, William B., Associate Professor, and SCHROEDER, Maria J., Associate Professor, "An Integrated Laboratory Curriculum," 223rd National Meeting, American Chemical Society, Orlando, FL, April 2002.

FERRANTE, Robert F., Professor, (co-author), "Synthesis of HCN and HNC in Ion-Irradiated N_2-Rich Ices," NASA Laboratory Astrophysics Workshop, Moffett Field, CA, May 2002.

FERRANTE, Robert F., Professor, (co-author), "N_2-Rich Ices," Space Telescope Science Institute Astrophysics of Life Symposium, Baltimore, MD, May 2002.

FITZGERALD, Jeffrey P., Professor, (co-author), "Towards Improved Optical Limiters," 223rd National Meeting, American Chemical Society, Orlando, FL, 8 April 2002.

Gilman, J. W., Davis, R. D., Awad, W. H., Morgan, A. B., Trulove, P. C., DELONG, H. C., Major (USAF) and Assistant Professor, Sutto, T. E., Mathias, L., Davis, C., and Schiraldi, D., "Improved Thermal Stability of Imidazolium Treatments for Polymer Layered-Silicate Nanocomposites," 13th International Symposium on Molten Salts, The Electrochemical Society, Philadelphia, PA, 12-17 May 2002.

HARRISON, Judith A., Associate Professor, "The Molecular-Scale Tribology of Amorphous Carbon Films," Air Force Office of Sponsored Research (AFOSR) Tribology Program Review, Annapolis, MD, 4-5 June 2002.

HARRISON, Judith A., Associate Professor, "The Atomic-Scale Investigation of Friction at Hydrocarbon Interfaces," Society of Tribologists and Lubrication Engineers 57th Annual Meeting, Houston, TX, 20-23 May 2002. (Keynote address)

HARRISON, Judith A., Associate Professor, "Theoretical Investigation of Atomic-Scale Friction and Wear in Hydrocarbon-Containing Systems," Emory University, Atlanta, GA, 29 April 2002.

HARRISON, Judith A., Associate Professor, "The Atomic-Scale Investigation of Friction at Hydrocarbon Interfaces," Northwestern University, Evanston, IL, 8 February 2002.

HARRISON, Judith A., Associate Professor, "Effects of Packing Density on the Friction of Alkane Monolayers," American Vacuum Society 48th International Symposium, San Francisco, CA, 29 October – 2 November 2001.

HARRISON, Judith A., Associate Professor, "Molecular Dynamics Simulations of the Friction of Self-Assembled Monolayer Systems," George Mason University, Fairfax, VA, 15 October 2001.

HARRISON, Judith A., Associate Professor, "Modeling of Real Tribological Systems," Office of Naval Research (ONR) Computational Chemical Dynamics Review, Arlington, VA, 4-5 October 2001.

HARRISON, Judith A., Associate Professor, "Molecular Dynamics Simulations of the Friction of n-Alkane Monolayers: Tip and Sliding Direction Effects," Scanning Tunneling Microscopy/Spectroscopy and Related Techniques (STM01), Vancouver, British Columbia, Canada, 15-20 July 2001.

HARRISON, Judith A., Associate Professor, (co-author), "Molecular Dynamics Simulations of the Friction of n-Alkane Monolayers: Tip and Sliding Direction Effects," World Tribology Congress, Vienna, Austria, 3-7 September 2001.

HARRISON, Judith A., Associate Professor, (co-author), "Modification of Carbon Nanotubes by Functionalization and Filling: Predictions from Molecular Dynamics Simulations," The 2nd Dartmouth Molecular Materials Symposium, Dartmouth College, Hanover, NH, 13 October 2001.

HARRISON, Judith A., Associate Professor, (co-author), "Modification of Carbon Nanotubes by Chemical Functionalization and Filling: Predictions from Molecular Dynamics Simulations," Department of Material Science and Engineering, The Pennsylvania State University, College Park, PA, 26 February 2002.

HARRISON, Judith A., Associate Professor, (co-author), "Compressibility of Carbon Nanotubes Filled with Gases and Fullerenes," Carbon 2001 Conference, Lexington, KY, 14-19 July 2001.

HARRISON, Judith A., Associate Professor, (co-author), "Compression of Filled Carbon Nanotubes: Predictions from Molecular Dynamics Simulations," 9th Foresight Conference on Molecular Nanotechnology, Santa Clara, CA, 9-11 November 2001.

HEUER, William B., Associate Professor, (co-author), "Oligothiophene as Photonic/Electronic Property Modulator," International Conference on Photo-Responsive Organics and Polymers 2001, Cheju Island, Korea, 19-25 August 2001.

HEUER, William B., Associate Professor, (co-author), "Novel Two-Photon Absorbing Conjugated Oligomers/Polymers: Property Modulation by π-Center," 223rd National Meeting, American Chemical Society, Orlando, FL, 7-11 April 2002.

LOMAX, Joseph F., Associate Professor, DILLNER, Debra K., Associate Professor, and TEICHERT, Melonie A., Captain (USAF) and Assistant Professor, "Online General Chemistry Laboratory Submissions: Assessment and Advances", 222nd National Meeting, American Chemical Society, Chicago, IL, 26 August 2001.

LOMAX, Joseph F., Associate Professor, and SCHROEDER, Matthew J., USNA Chemist, "Intercalation Laboratory," 222nd National Meeting, American Chemical Society, Chicago, IL, 28 August 2001.

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

Lyons, K.S., Stanley, J.A., Ugarte, N., COTTEN, Gregory B., Lieutenant (USN), Dmowski, W., and Egami, T., "Low-Platinum and Platinum-Free Catalysts for Oxygen Reduction at Fuel Cell Cathodes," Department of Energy Fuel Cell Review, National Renewable Energy Laboratory, Golden, CO, 9-10 May 2002.

Lyons, K.S., COTTEN, Gregory B., Lieutenant (USN), Dmowski, W., and Egami, T., "Low-Platinum and Platinum-Free Catalysts for Oxygen Reduction at Fuel Cell Cathodes," Department of Energy Laboratory Fuel Cell Review, Oak Ridge National Laboratory, June 2001. (Invited presentation)

Mantz, R. A., Sutto, T. E., DELONG, H. C., Major (USAF) and Assistant Professor, and Trulove, P. C., "Ion Transport in Ionic-Liquid/Polymer Gel Electrolytes," 13th International Symposium on Molten Salts, The Electrochemical Society, Philadelphia, PA, 12-17 May 2002.

McCLEAN, Roy E., Associate Professor, "Association Reaction Kinetics of Iron and Cobalt Atoms with Sulfur Dioxide: Experimental, RRKM, and DFT Studies," 5th International Conference on Chemical Kinetics, Gaithersburg, MD, 16 July 2001.

McDIVITT, Jonathon D., Midshipman 1/C (USN) and DILLNER, Debra K., Associate Professor, "Synthesis of Substituted Cyclopentanes from a Bicyclic Precursor," 223rd National Meeting, American Chemical Society, Orlando, FL, 9 April 2002.

Rickey, D., TEICHERT, Melonie A., Captain (USAF) and Assistant Professor, and Tien, L.T., "Designing Chemistry Education Research Studies, Part I," 223rd National Meeting, American Chemical Society, Orlando, FL, 7-11 April 2002.

SCHROEDER, Maria J., Associate Professor, "Segmental Relaxation in End-Linked Polydimethylsiloxane Networks," Gordon Research Conference on Elastomers, New London, NH, 7 August 2001.

SCHROEDER, Maria J., Associate Professor, (co-author), "Synthesis and Characterization of Polydimethylsiloxane Networks," 223rd National Meeting, American Chemical Society, Orlando, FL, 8 April 2002.

SMITH, Virginia F., Assistant Professor, DELONG, Hugh C., Major (USAF) and Assistant Professor, Trulove, P. C., and Sutto, T. E., "Non-enzymatic Synthesis of Peptides in an Ionic Liquid," 13th International Symposium on Molten Salts, The Electrochemical Society, Philadelphia, PA, 14 May 2002.

SMITH, Virginia F., Assistant Professor, "Protein Folding Studies of Recombinant Human IRP-1/cytoplasmic Aconitase," 46th Annual Meeting of the Biophysical Society, San Francisco, CA, 25 February 2002.

Sutto, T. E., DELONG, Hugh C., Major (USAF) and Assistant Professor, and Trulove, P. C. "Comparative Electrochemical Behavior of 1,2-Dimethyl-3-n-Propylimidazolium Tetrafluoromethanesulfonyl-imide, 1,2-Dimethyl-3-n-Butylimidazolium Tetraflurometh anesulfonyl-imade, and 1,2-Dimethyl-3-n-Butylimidazolium Nitrate," 13th International Symposium on Molten Salts, The Electrochemical Society, Philadelphia, PA, 12-17 May 2002.

Sutto, T. E., Trulove, P. C. and DELONG, H. C., Major (USAF) and Assistant Professor, "Investigations of the Effects of Lithium Ion and Polymer Type on the Electrochemical Behavior of Ionic Liquid/Polymer Gel Electrolytes," 13th International Symposium on Molten Salts, The Electrochemical Society, Philadelphia, PA, 12-17 May 2002.

TEICHERT, Melonie A., Captain (USAF) and Assistant Professor, Rickey, D., and Tien, L.T. "Designing Chemistry Education Research Studies, Part II," 223rd National Meeting, American Chemical Society, Orlando, FL, April 2002.

Trulove, P. C., DELONG, H. C., Major (USAF) and Assistant Professor, and Sutto, T. E., "Direct X-ray Evidence of the Electrochemical Induced Intercalation of Substituted Alkylimidazolium and Lithium Cations into Graphite from Ambient-Temperature Ionic Liquids," 13th International Symposium on Molten Salts, The Electrochemical Society, Philadelphia, PA, 12-17 May 2002.

WHITAKER, Craig M., Assistant Professor, "Synthesis and Evaluation of Laterally Substituted Mesogens," Office of Naval Research (ONR) Review for Optics and Electronics, Arlington, VA, June 2001.

WHITAKER, Craig M., Assistant Professor, "Design and Synthesis of Molecular Electronic Devices," Moletronics II Program, Phoenix, AZ, January 2002.