CHEMISTRY 49900
UNDERGRADUATE RESEARCH

Chemistry 49900 provides a mechanism whereby undergraduate chemistry majors may participate in the research of the faculty and receive academic credit for that participation. While CHM 49900 is usually taken by students in their senior year, it may be taken by sophomores or juniors if the sponsoring professor feels that the student has had sufficient course work or previous work experience to be able to handle the specific project in mind.

Students interested in CHM 49900 should begin by reviewing the following list of projects. They should, then, talk to the sponsoring professors about those projects which interest them to obtain further information about the projects and eventually reach a decision.

After the student and sponsoring professor agree on a project and the number of hours of credit, it is only necessary then to register for the course in the usual manner. In this context, it should be kept in mind that three hours of laboratory work per week constitutes 1 hour of credit. Hence, a student who elects 3 credit hours of CHM 49900 should anticipate working 9 hours a week in the laboratory on his/her project. Students may repeat CHM 49900 for credit with the same or different instructor.

At the end of the semester, two copies of a research report should be prepared, one for the instructor, and one to be kept on file in the Chemistry Office (specified by the American Chemical Society for accreditation purposes). The title page of the research report must include the project title, the student's and advisor's names, and the semester and year enrolled in CHM 49900. The sponsoring professor has sole responsibility for determining the course grade. Please indicate the course grade on the Chemistry Office copy of the report. Should the work be published, the sponsoring professor will determine the extent of the student's contribution and, if appropriate, acknowledge the student's contribution in a footnote or else list the student as a co-author.

Students must also give an oral presentation of their work.

A final note:

A number of our chemistry graduates who took CHM 49900 reported that they found it indispensable in obtaining a job or in getting started on research in graduate school. Hence, it is highly recommended by the department as an elective.

Robert M. Berger

My research interests lie in the area of inorganic chemistry, particularly in the application of spectroscopy and electrochemistry to the characterization of transition metal complexes. Specifically, I am interested in the synthesis and characterization of transition metal complexes made up of an oxidizable metal center (such as Ru(II), Cu(I), Re(I), etc.) and ligands having low-lying π^* orbitals. These complexes typically have reasonably long-lived metal-to-ligand charge transfer excited states and may have applications in donor-photosensitizer-acceptor schemes.

I. DESIGN AND SYNTHESIS OF PHOTOACTIVE COMPLEXES

Another area of interest is the design and synthesis of both mononuclear and polynuclear Ru(II) coordination complexes having long-lived MLCT excited states. Complexes containing from one to four metal centers may be prepared using bridging ligands such as 2,2-bipyrimidine(bpym); 2,3-bis-(2-pyridyl)pyrazine (dpp); and 1,3,5-tris-(2-pyridyl)triazine (tpt). The tpt ligand, shown to the right, is unusual in the sense that it may, depending on the orientation of the pyridyl rings, coordinate, up to three metal centers in a symmetric bidentate fashion or two metals unsymmetrically, one in a tridentate fashion and the other in a bidentate fashion.

Mononuclear and polynuclear ruthenium(II) complexes of tpt in which the tpt functions as a tridentate ligand (see figure) will be prepared. 2,2':6',2"-terpyridine (trpy) or a combination of a bidentate and monodentate ligand will be used to complete the coordination sphere of the metal center. Purification of the complexes will be carried out by ion exchange chromatography.

The spectroscopic and electrochemical properties of the complexes will be investigated by the methods of electronic absorption spectroscopy, emission spectroscopy, cyclic voltammetry and bulk electrolysis.

II. PREPARATION AND CHARACTERIZATION OF DONOR-PHOTOSENSITIZER-ACCEPTOR COMPLEXES

Recently I have become interested in the study of so-called donor-photosensitizer- acceptor complexes in which a photosensitizer (P) is covalently bonded to both an electron donor (D) and an electron acceptor (A). Absorption of light (hv) promotes an electron from a lower energy orbital on the photosensitizer to a higher energy orbital (1) where it can begin an electron cascade (2,3) that ultimately results in a long range transfer from the donor to the acceptor. The photosensitizers are complexes of Ru(II) and Cu(I) with phenanthroline or bipyridine type ligands. The donors and acceptors are organic molecules with LUMOs and HOMOs of appropriate energies.

Michael R. Columbia

My current research interests focus on the chemistry of artists' materials:

EXTRACTION OF DYES AND THEIR DECOMPOSITION PRODUCTS FROM LAKE PIGMENTS:

Lake pigments are produced when dye molecules are deposited on solid substrates (typically alumina). Historically, lake pigments from natural dye sources were used in oil paintings from the Renaissance through the 19th century; many of these pigments have limited lightfastness and the paintings produced with them can suffer substantial degradation over time. This project seeks to develop reproducible methods for extracting the natural dye component or its decomposition products from lake pigments produced from historical recipes. Such methods could be used to generate a database of decomposition products to help identify the original lake pigment used in a painting.

IDENTIFYING COLORANTS IN EGYPTIAN PASTE:

Egyptian faience is a material used to produce jewelry and funerary objects in ancient Egypt. In general, the material is a glassrich clay body that was self-glazing. Modern attempts to reproduce this material are referred to as Egyptian paste and have been successful at generating the colors in Egyptian faience with the exception of red. This project studies the colors produced by varying the amounts of potential red-generating colorants (lead and iron salts) added to the base Egyptian paste recipe; this color analysis is based on the HSL color scale. Attribution of the color to a chemical species will be made using either vibrational analysis (Raman spectrometry) or elemental speciation (XPS analysis).

MONOCHROME PRODUCTION IN SIDEROTYPE PHOTOGRAPHY:

Siderotypy is an alternative photographic methodology based on the photosensitivity of certain organic salts of iron; the chemistry behind this process relies on the simultaneous reduction of iron (+3 to +2) and oxidation of the organic anion (usually citrate or oxalate) following exposure to light. The development of a permanent image is accomplished by a second redox reaction in which iron is reoxidized by noble metal ions (Ag, Au or Pt) and the resulting noble metal atoms are deposited on the photographic support medium. The composition of the developing solution can greatly influence the color of the final image with monochromes varying from slate blue through black/gray to a brownish-red; this variation is attributed to the deposition kinetics of the metal atoms and the size of the nanoparticles they form. This project uses atomic force microscopy to measure the size of nanoparticles produced during development as a way of verifying this connection.

Ronald S. Friedman

THEORETICAL PHYSICAL CHEMISTRY

The study of resonance phenomena is an extremely important area of research in the field of atomic and molecular scattering. From the simple elastic and inelastic atom-atom collisions to the more complex reactive scattering of chemical reactions, resonances play an influential role. We usually visualize resonances as quasibound or metastable molecular entities, for example, the intermediates of chemical reactions and even transition states of reactions. The existence of resonances is often the cause of marked variations in scattering cross sections or reactive transition probabilities; thus, resonances warrant careful examination. To study theoretically and rigorously resonance phenomena and scattering processes in general, we must use quantum mechanics and solve the Schrödinger equation, a second order differential equation. The research undertaken here is the analysis of quantum mechanical scattering processes via numerical (computational) studies of chemical reactivity.

Students engaged in such research will acquire a more detailed understanding of the mechanisms of chemical reactions (and scattering processes in general) as well as gaining valuable experience in computer use and numerical analysis. No previous programming experience is required.

REACTIVE SCATTERING AND TRANSITION STATES

The availability of high-powered supercomputers and the development of very efficient numerical algorithms have made possible full three-dimensional quantum mechanical studies of simple chemical reactions such as $H + H_2$ and Cl + HCl. Although these studies do not assume the existence of transition states (transient species composed of reactant atoms in a specific geometric arrangement which can then form the final products of a reaction), the studies can provide evidence of quantized transition states in the exact quantum dynamics. In fact, such quantized transition states are indeed seen and are dynamical bottlenecks which control chemical reactivity. The fundamental question posed in the study undertaken here of reactive scattering addresses the nature of quantized transition states: are quantized transition states reactive scattering resonances? An affirmative answer would imply that chemical reactivity can be described--at the ultimate quantum level of resolution--as a resonance phenomenon. This research involves solving the Schrödinger equation for one-dimensional models of chemical reactions using the computational resources available in the IPFW Chemistry Department. In particular, we are interested in looking at the simple hydrogen exchange reaction Cl + HCl to analyze the role of transition states in chemical reactivity. This work will also involve numerical fitting of potential energy curves for the chemical reaction.

MULTIPLE POTENTIALS AND NONADIABATIC EFFECTS

A commonly-made assumption in chemical reaction dynamics is that, for a given chemical reaction, a single potential energy surface governs the chemical reactivity. Although this assumption is often valid, there are numerous systems of importance for which the interaction between two or more coupled potential energy surfaces must be considered. For examples, multiple coupled surfaces are necessary to describe photochemical reactions, electron-transfer

reactions and Woodward-Hoffmann rearrangements. The effects of coupled potential energy surfaces on chemical reactivity, referred to as nonadiabatic effects, are often unknown. Studies of coupled potential energy surfaces in reduced dimensions, for example coupled two-dimensional potential energy curves, can provide insight into this important area of research in chemical dynamics. In addition, whereas in one dimension, potential energy curves cannot touch one another, in two-dimensions (and more) the potential energy surfaces can intersect in, what are called, conical intersections. These conical intersections have dramatic effects on chemical dynamics and are found in many chemical systems. The research undertaken here is to study in detail resonances arising from conical intersections of electronic potential energy surfaces.

COMPUTATIONAL ALGORITHMS

There are a number of computational issues to consider when solving coupled differential equations arising from the Schrödinger equation. These include issues of numerical stability and linear independence. It is also instructive to compare different numerical integration schemes (e.g. Hartree, Numerov, and Gear) in terms of their computational efficiencies and error analyses. In collaboration with Michael Jamieson of the University of Glasgow, Scotland, we have been looking at a number of issues important in the area of numerical analysis.

Peng Jing

In nature there exist a tremendous number of channel proteins that can form pores in the cell membrane and allow specific molecules/ions to pass through the pores. Such a process subsequently initiates a series of events important to biological activities. One feature that the proteins share is they can be embedded into a stand-alone phospholipid bilayer and the ionic current through one channel of some of the proteins can be detected at a single molecule scale by the patch-clamp technique. The feature indicates possible use of such channel proteins for biosensing motifs. Analytes such as ions, drugs, DNA/RNA, peptides, proteins and etc may be detected when they pass through the channels or interact with the channel proteins at the channel entrance. Such biosensing technology is called a nanopore sensor because all detection is achieved within a channel with a size of several nanometers.

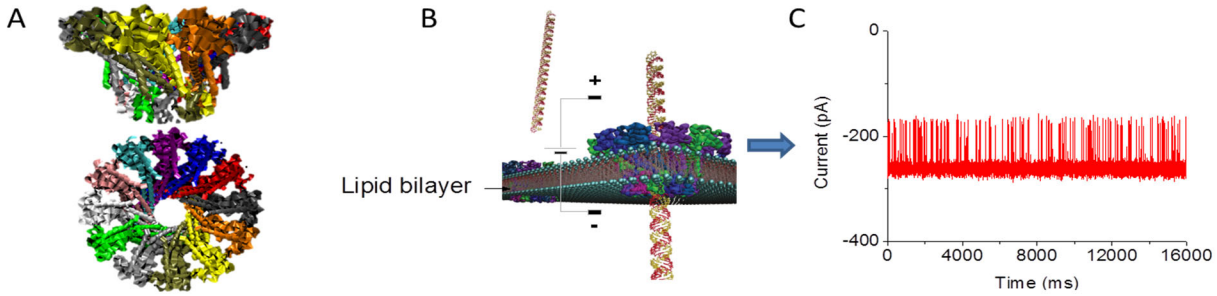

Figure: A) A side view and a top view of the structure of Phi29 channel protein; B) A schematic showing a stranded DNA passing through the channel of a phi29 channel protein embedded into a stand-alone phospholipid bilayer membrane; C) Patch-clamp measurement of ionic current through a phi29 connector channel; each of the current blockade events indicates translocation of a strand of DNA through the channel.

My primary research interest is to develop a nanopore sensor based upon channel proteins. In my recent work, a channel protein from a bacteriophage, phi29, has been successfully embedded into a bilayer membrane. Using the patch-clamp technique, translocation of double stranded DNA through the channel can be detected (Figure A-C). As a continuum of the research, we will address the following issues with the protein nanopore sensor:

1. Design and engineering of the channel protein. An ideal channel protein that can be used for bionsensing must have good pore-forming capability in the phospholipid bilayer membrane, stable channel properties, and transport ability for specific analytes. To meet the above requirements, design and engineering of the protein to customize it into a biosensor motif is an important task. In the research, students will learn how to use experimental techniques from molecular biology to prepare mutant channel proteins.
2. The structure and the function of the phi29 channel protein. Transport mechanisms of analytes through nanometer-sized channels are complicated because the intermolecular interactions between the molecules of interest and the channel wall will dominate when

analytes pass through the channels with a nanometer size. The transport properties are mainly determined by the surface charge of the channel. Some specifically designed mutant channel proteins may be the key to understanding the transport mechanisms. In the research, students will learn to use the patch-clamp technique to measure transport properties of the mutant channel proteins and compare their differences on the basis of experimental data.

3. Design and synthesis of a molecular recognition motif that can be tethered into the protein channel. A protein channel tethered with an organic molecule with molecular recognition capability may show specific transport properties for some analytes. In the research, students will learn to use the synthesis technique to prepare specifically designed organic molecules and attach them as a ligand inside of the protein channels by means of biochemical methods.

LIST OF RELEVANT PUBLICATIONS:

1. Peng Jing, Farzin Haque, Dan Shu, and Peixuan Guo, One-way Traffic of a Viral Motor Channel for DsDNA Translocation, Nano Letters, 2010, 2010, 10, 3620-3627.
2. Peng Jing, Farzin Haque, Anne P. Vonderheide, Carlo Montemagno, Peixuan Guo. Robust Properties of Membrane-Embedded Connector Channel of Bacterial Virus Phi29 DNA Packaging Motor. Molecular Biosystems, 2010, 2010, 6, 1844-1852.
3. David Wendell, Peng Jing, (Co-First Author), Jia Geng, Tae Jin Lee, Carlo Montemagno, Peixuan Guo, Double Stranded DNA Translocation through a Novel Phi29 Motor-Based Pore. Nature Nanotechnology, 2009, 4, 765-772.

Vincent M. Maloney

ZEOLITES AS ACTIVE SUPPORTS FOR HAZARDOUS GAS SENSORS

Although many methods for the detection of hazardous or biologically important gases (eg. CO, CO_2, O_2, NH_3, SO_2, and alkenes) have been developed for a wide range of applications, few have been commercially viable. One strategy for the detection of gases on the ppm level employes optochemical devices. These are based on an analyte causing changes in the absorption or emission characteristics of sensor molecules on a surface or embedded in a transparent solid. For example, the quenching of triplet excited states by oxygen is commonly used to determine oxygen concentrations in vitro.

ALKENE SENSORS

Alkene monomers used for the production of plastics such as acrylonitrile and methyl acrylate are often toxic, carcinogenic, and/or highly flammable. Threshold limits below 100 ppm have been set for various monomers. The decrease in the emission intensity of anthracene derivatives upon Lewis Acid catalyzed Diels Alder reactions with olefins could be used to detect these hazardous materials. Zeolites which are aluminosilicates with extensive networks of pores and channels can be prepared with Lewis and Bronsted Acid sites distributed throughout the interior In this way, the zeolite would not only support the sensing molecules but catalyze the reactions for the detection of the analyte.

CARBON MONOXIDE SENSORS

In the Gatterman Koch reaction, CO reacts with aromatic compounds in the presence of Lewis Acids to produce aromatic aldehydes. The absorption and emission characteristics of the product aldehydes differ significantly from the reactants. Pyrene embedded in acidic zeolites may react with CO to produce pyrenealdehyde whose formation can be detected by its emission. In each case, it may be possible to regenerate the original sensing molecules.

THE CHARACTERIZATION OF PHOSPHORYL- AND SULFONYLNITRENES AND THEIR APPLICATION TO POLYMER SURFACE MODIFICATION

Nitrenes are highly reactive chemical species which have found applications in polymer crosslinking, surface modification, and photoaffinity labeling (used for mapping enzyme active sites). Sulfonylnitrenes and to a lesser extent phosphorylnitrenes have been used for these purposes due to their ease of preparation and high selectivity. To design effective agents for surface modification, further characterization of the photochemistry and reactivity of sulfonyl- and phosphorylnitrenes and their precursors is required. In particular, the reactivity of the singlet states and the conditions under which the sulfonylnitrene rearranges must be understood. Standard physical organic techniques such as product studies, matrix spectroscopy, and laser flash photolysis will be employed. Ultimately, compounds will be designed and synthesized for modification of polymer surfaces.

Mohammad A Qasim

Serine proteases are a class of protein degrading enzymes. They are involved in a number of important functions such as blood clotting, fighting against invading microorganisms, processing of viral proteins, digestion of food etc. However, the action of serine proteases needs to be precisely controlled. Uncontrolled action of serine proteases will have catastrophic consequences for the cell. One of the mechanisms used by the cell to regulate the activity of serine proteases is by inhibition by serine protease inhibitors. My research work is focused on understanding the structure and function of serine protease inhibitors. The research projects going on in my laboratory are as follows:

DESIGN OF STRONG AND SPECIFIC SERINE PROTEASE INHIBITORS:
We have performed extensive research work on the preparation of bacterially expressed inhibitor variants and on the measurement of their interaction with several different serine proteases. These studies have enabled us to formulate simple rules which can be used for designing strong and specific inhibitors against the serine proteases we have studied. Designing specific inhibitors is important since many pathological conditions are associated with increased levels of serine proteases. The research work involves measuring inhibitor-protease association with selected serine proteases against a series of inhibitor variants. The inhibitor-protease association is measured using spectrophotometric or flurometric method and the data are used to calculate association equilibrium constant and related thermodynamic parameters. Association equilibrium constants measured against inhibitor variants provide us necessary information to design and test strong and specific inhibitors against the target serine protease.

INHIBITOR-PROTEASE INTERACTION AS MODEL OF NON-COVALENT INTERACTIONS THAT STABILIZE NATIVE PROTEIN STRUCTURE:
A fundamental problem in proteins is: How proteins which are made up of linear sequence of amino acids fold into a complicated and specific native three-dimensional structure. Protein chemists usually study this problem by performing chemical denaturations with the aim to understand the role of non-covalent interactions involved in the formation of native folded state of a protein. A number of approaches have been used to study this problem in the last few decades. We have started a research project in which we use chemical denaturants to disrupt inhibitor-protease interaction and use the data to understand the role of non-covalent interactions in the stability of inhibitor-protease complex. During fall 2009 semester an undergraduate student participated in this research and obtained highly encouraging results.

LIST OF IMPORTANT PUBLICATIONS:

1. "Structural insights into non-additivity effects in the sequence-to-reactivity algorithm for serine peptidases and their inhibitors" Lee, T-W, Qasim, M. A. Laskowski, M. Jr. amd James, M. N. G. (2007) Journal of Molecular Biology 367, 527-546.
2. "Despite having a common P1 Leu, eglin C inhibits alphalytic protease a million-fold more strongly than does turkey ovomucoid third domain" Qasim, M. A., Van Etten, R. L., Yeh, T., Saunders P. et al. (2006) Biochemistry 45, 11342-11348.
3. "The role of scaffolding in standard mechanism serine proteinase inhibitors" Kelly, Clyde A.; Laskowski, Michael, Jr.; Qasim, M. A (2005) Protein and Peptide Letters 12,, 465-

471.
4. "Testing of the additivity-based protein sequence to reactivity algorithm" Qasim, M. A., Lu, W., Lu, S. M., Ranjbar, M. et al. (2003) Biochemistry 42, 6460-6466.
5. "Additivity-based prediction of equilibrium constant for some protein-protein associations" laskowski, M. Jr., Qasim, M. A. and Yi, Z-P (2003) Current Opinion in Structural Biology 13, 1-10.
6. "Predicting the reactivity of proteins from their sequence alone: Kazal family of protein inhibitors of serine proteases" Lu, S. M., Lu, W., Qasim, M. A., Anderson, S. et al. (2001) Proceedings of National Academy of Science 98, 1410-1415.

Steven A. Stevenson

RESEARCH INTERESTS;

1. Reactor R&D: New Molecule Discovery
2. Separation R&D: New Purification Methods
3. Applications via Collaborative Research

RESEARCH SUMMARY:

AREA 1: REACTOR R&D GROUP

This subgroup of students pursues the science of synthesizing fullerene structures. Formed in the electric-arc plasma reactor, fullerenes can entrap molecular clusters. Students currently investigate the following areas: (a) entrapping new clusters (b) using new chemistries for yield improvements (c) investigating the effect of additives to the plasma, yield, and type of fullerene produced.

AREA 2: SEPARATION R&D GROUP

This subgroup of students focuses on separation science. With the rich array of fullerene structures produced by the Reactor R&D group, there is a strong need to develop novel ways to separate, isolate, and purify each type of fullerene. Specific areas of research for these students include the following: (a) using HPLC to isolate new molecules (b) synthesizing and using novel, functionalized solid supports that are selective for fullerene types (c) developing new HPLC stationary phases.

AREA 3: COLLABORATIVE RESEARCH

Sample dissemination and collaborative research is routine and key to advancing science with our endohedral fullerenes. Collaborators expand the genre of experiments. Samples are sent worldwide and used for research not being done in our labs.

Daryoush Tahmassebi

I- COMPUTATIONAL ORGANIC CHEMISTRY

I am interested in calculating different properties of organic molecules using quantum mechanical programs at different levels of theory such as ab initio and density functional theory methods. My main area of interest is studying the mechanism of organic reactions with theoretical approaches and finding the transition states and different pathways for reactions. Computational chemistry is a powerful tool which can be used to predict different properties of organic molecules such as energy, geometry and conformation, molecular orbitals, and IR, NMR, and UV spectra. The theoretical results can be useful for synthetic organic and other chemists to explain their data obtained in the laboratory.

II- GREEN CHEMISTRY

As an organic chemist, I am interested in applying green chemistry to organic reactions. My main interest and activity in the past few years was synthesizing some ionic liquids and using them in organic reactions as the solvent. Ionic liquids are nonvolatile compounds consisting of a large organic cation (such as 1-butyl-3-methylimidazolium) and an inert anion (such as PF6- or BF4-). These compounds are normally liquid at room temperature and therefore they can be used as the solvent in organic reactions. Ionic liquids have excellent capability to dissolve a wide range of substances from organic compounds to inorganic and transition metal catalysts. They have also shown some catalytic activities in some reactions. In the past decade ionic liquids and their applications were a big area of research in all disciplines of chemistry.

My other area of interest is using the green chemistry approach to redesign organic reactions by utilizing new catalysts or new set of conditions. I am looking for new methodologies for organic reactions which have the advantages of operational simplicity, neutral and mild reaction conditions, high yields of the products, lower toxicity and of course lower cost.p