

DEPARTMENT OF CHEMISTRY
College of Arts & Sciences

SUMMER RESEARCH OPPORTUNITIES
FOR UNDERGRADUATE WOMEN

APPLICATION DEADLINE: MARCH 3, 2003

The Chemistry Department is pleased to offer the following research projects for the summer of 2003. Interested students are urged to contact the faculty member(s) directing the project(s) that most interest them. By contacting the faculty member, you can discover more about the project, learn what your responsibilities will be, and if possible, develop a timetable for the twelve-week research period.

Matrix Isolation Studies of Reactive Intermediates

Professor Bruce S. Ault

401 Crosley (513) 556-9238 FAX: (513) 556-9239 E-Mail: Bruce.Ault@UC.Edu

Our research interests lie with the exploration of the mechanisms of important chemical reactions by isolating, identifying and characterizing reactive intermediates that are created and destroyed during the course the reaction. The matrix isolation technique, which involves trapping the intermediates of interest in an argon crystal at nearly absolute zero, is employed to permit the study of very reactive intermediate species. High resolution infrared spectroscopy is one of the primary techniques for characterization of the trapped species, along with theoretical calculations using modern computational chemistry software. The reactions of particular interest are those involving high valent transition metal oxo compounds, which are commonly used as oxidizing agents in organic synthesis, and as models for active sites of enzymes. The goal of this project will be the identification and characterization of reaction intermediates, from which we can obtain a better understanding of the mechanistic details of these oxidation reactions.

An Understanding of the Factors that Determine the Efficiency and Selectivity of Catalytic Oxygen Activation Catalysts

Professor Michael Baldwin

302 Crosley (513) 556-9225 FAX: (513) 556-9239

E-Mail: Michael.Baldwin@UC.Edu

Many biological oxidation reactions use metalloenzymes to activate O₂ as the oxidant. This strategy of using a transition metal catalyst to activate O₂ is desirable for industrial oxidation reactions as well, as O₂ is a cheap, waste-free, environmentally friendly oxidant. However, relatively few examples of effective oxygen activation catalysts have been put into commercial use. Our group is interested in further developing an understanding of the factors that determine the efficiency and selectivity of catalytic oxygen activation catalysts so that this "green" technology can be more widely applied. Our strategy is to study the O₂ reactivity and substrate oxidations by a transition metal in

an oxidation state that generally *does not* react with oxygen, since this will highlight the critical features required for O₂ activation and will likely result in unique reactions. Thus, we have developed a new ligand system that supports unusual O₂ reactivity by Ni(II). Our complexes are the *first Ni(II) complexes to react with O₂ without the requirement of ligand oxidation*. We have a number of ongoing projects to understand and optimize the Ni(II)-O₂ reactions, expand the substrate oxidation chemistry, discover other related reactions of the Ni(II) complexes with other environmentally or biologically relevant oxidants, and investigate complexes of these ligands with other metals. A variety of opportunities are available from which an undergraduate researcher may choose, depending on her interests. These would include projects that focus on inorganic synthesis of metal complexes of interest, organic synthesis of new ligands to expand our ligand library, physical methods such as various spectroscopic and electrochemical techniques to characterize the complexes, or analytical methods to evaluate the mechanisms of the O₂ reactions. Some exposure to each of these areas will accompany the chosen project, which will be guided by both Dr. Baldwin and a graduate student in the group.

Designing Two-Electron Photo-eagents

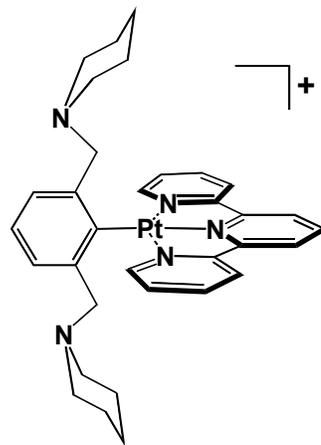
Professor Bill Connick

305 Crosley (513) 556-0148 FAX: (513) 556-9239

E-Mail: Bill.Connick@UC.Edu

Depletion of fossil fuel reserves, pollution, and national security are driving efforts to improve solar energy technologies. In this field, the most difficult challenge we face is the conversion of sunlight energy to useful chemical energy. The traditional approach to this problem relies on molecules that, when excited by light, undergo one-electron transfer reactions. The resulting reduction and oxidation reactions can produce useful chemical fuels. Unfortunately, these systems tend to be inefficient.

We are investigating a new approach to this problem that involves designing molecules that will transfer more than one-electron when excited by light. An example is illustrated in the adjacent figure. These molecules offer significant advantages over traditional solar catalysts. One of the side benefits is that they are expected to exhibit very slow rates of charge recombination. Therefore, these molecules may be useful in designing molecular-scale optical and electronic devices. More importantly, investigations of these systems will provide insight into the mechanisms of catalytic reactions that are important to industrial and biological chemistry. This project will provide students with experience in the design, synthesis and characterization organic molecules and inorganic transition metal complexes. No prior chemistry research experience is necessary.



Photorelease of Fragrances

Professor Anna D. Gudmundsdottir

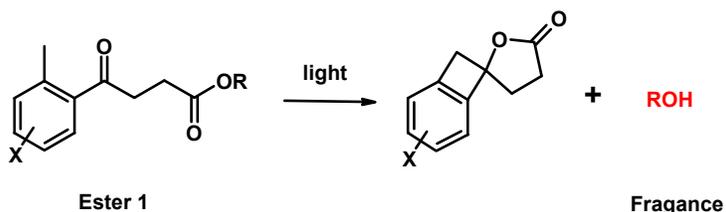
805 Crosley (513) 556-3380 FAX: (513) 556-9239

E-Mail: Anna.Gudmundsdottir@UC.Edu

We are interested in the release of alcohols since they are used as fragrances in applications such as body care and household cleaning goods. One of the drawbacks of using volatile alcohols in fragrances is that the desired aroma is detected for only a relatively short time in applications. Thus by forming a phenyl butyric ester (1) of a volatile alcohol it is possible to release the fragrance in a controlled manner over an extended time period by exposure to light.

A summer project would focus on preparing various derivatives of ester 1 and investigate if they release alcohol upon exposure to sunlight. After spending a

summer in my research laboratory the student will have gained experience in carrying out synthesis and will have contributed to the development of photoprotections groups.



An Environmentally Friendly Conversion of an Aziridine to an Oxazolidinone

Professor Allan Pinhas

604 Crosley (513) 556-9255 FAX: (513) 556-9239

E-Mail: Allan.Pinhas@UC.Edu

Our research deals with converting a three membered ring compound that contains nitrogen, called an aziridine, to biologically and medically active 1,2-diamines and oxazolidinone. Normally, these reactions are run in organic solvents. Recently however, we have discovered that the formation of the oxazolidinone can be done in water with carbon dioxide (CO₂) as the only stoichiometric reagent. This now becomes a very environmentally friendly reaction.

For this summer's WISE project, a student will extend this initial discovery to determine what substituents on the aziridine are compatible with the reaction conditions. The student will also determine the regiochemistry of the ring opening of the aziridine, and the relative stereochemistry between the starting aziridine and the final oxazolidinone for this novel conversion.

Research Topics in the Reineke Group

Professor Theresa M. Reineke

701 Crosley (513) 556-9250 FAX: (513) 556-9239

E-Mail: Theresa.Reineke@UC.Edu

Our research efforts are interdisciplinary in nature and encompass the areas of chemistry, materials science, and biology. The focus of my program is the design and study of self-assembling functional materials. By utilizing synthetic methods from both organic and inorganic chemistry, novel materials can be developed. Students in my lab will become familiar with materials characterization methods such as solution and solid-state NMR, powder and single crystal x-ray diffraction, FT-IR, mass spectrometry, as well as static and dynamic light scattering. No prior knowledge of these research areas is required. Currently, we are interested in the three projects described below:

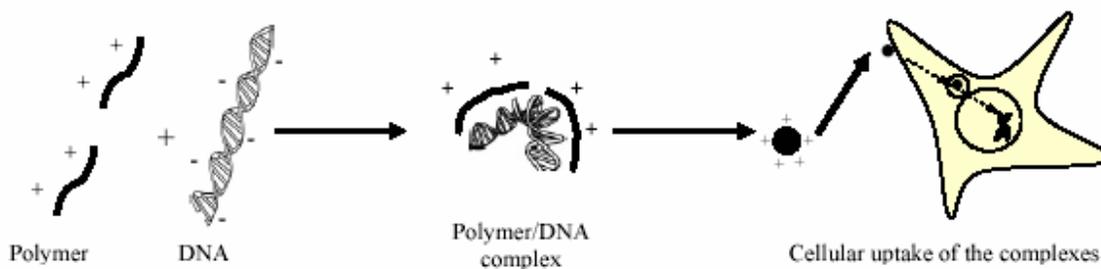
Carbohydrate-Containing Polymers for Gene Delivery

Professor Theresa M. Reineke

701 Crosley (513) 556-9250 FAX: (513) 556-9239

E-Mail: Theresa.Reineke@UC.Edu

With the completion of the human genome, gene-based therapies to treat diseases such as cancer, muscular dystrophy, and arthritis are becoming increasingly feasible, but gene therapy is still in a very young and experimental stage. Several factors have hindered the development of successful treatments with the first hurdle being the delivery method. In the past, viruses have been used for gene delivery but this delivery technique has presented several problems, for example, viruses can cause immune and inflammatory responses in the body. My interests in this area lie in the study of non-viral methods of delivering therapeutic genes and the elucidation of how structural differences in these materials can affect the properties of such systems. Currently, my group is focusing on developing polymers and dendrimers that self-assemble with DNA and can deliver genetic material through cell membranes in a nontoxic and effective manner. We are concerned with the design, synthesis, and characterization as well as with the examination of the mechanism of toxicity and gene delivery of the materials in cell culture.



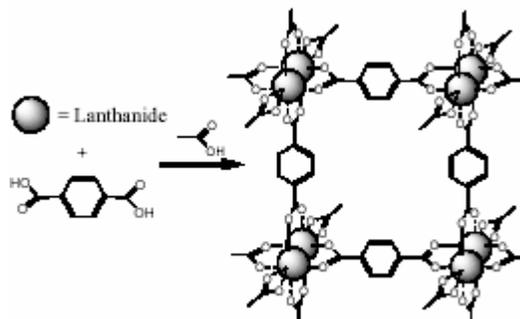
Lanthanide-Organic Molecular Sensors

Professor Theresa M. Reineke

701 Crosley (513) 556-9250 FAX: (513) 556-9239

E-Mail: Theresa.Reineke@UC.Edu

The aim of this project is to utilize the unique properties of the lanthanide metals, europium and terbium, to create molecular sensors. Through coordination chemistry, these metals can be linked to chromophoric ligands to create luminescent molecules with host-guest characteristics. By changing the length and geometry of the organic ligands, size and shape selective inclusion compounds may be formed. Additionally, specific analyte sensing may be realized through template-driven synthesis of these molecules. In collaboration with the chemical sensors group, I am also interested in casting thin films of these fluorescent porous molecules on surfaces.



Ionic Liquids as Electrophoretic and Chromatographic Media in the Separation of Biomolecules

Professor Apryll Stalcup

201 Crosley (513) 556-9216 FAX: (513) 556-9239

E-Mail: Apryll.Stalcup@UC.Edu

Separations are extremely important to a wide variety of health-related areas. Distinguishing key analytes within the complex matrices encountered in bioseparations remains a huge challenge. The proposed work addresses the critical need for novel and more universal separation strategies for the challenges of biomolecule/biopolymer separations. In addressing these challenges, the project focuses on two specific aims:

- Investigation of interactions between “ionic liquids” and selected biomolecules using capillary electrophoresis
- Synthesis and evaluation of high performance liquid chromatographic “fuzzy ion” stationary phases derived from ionic liquids

The proposed work encompasses capillary electrophoresis and high performance liquid chromatography. The goal of the capillary electrophoretic component of the project is to develop a rapid screening method for assessing relative affinities between ionic liquid ions and target analytes. The high performance liquid chromatographic component of the project will be to evaluate a new class of “fuzzy ion” stationary phases, which will enable the more universal separation of complex mixtures of structurally similar and dissimilar analytes. The student will work on a specific subset of analytes selected from the following classes of biomolecules: amino acids and peptides, proteins, nucleotides, oligonucleotides, or phenols and polyphenols.

GART Enzyme

Pearl Tsang

804 Crosley (513) 556-2301 FAX: (513) 556-9239 E-Mail: Pearl.Tsang@UC.Edu

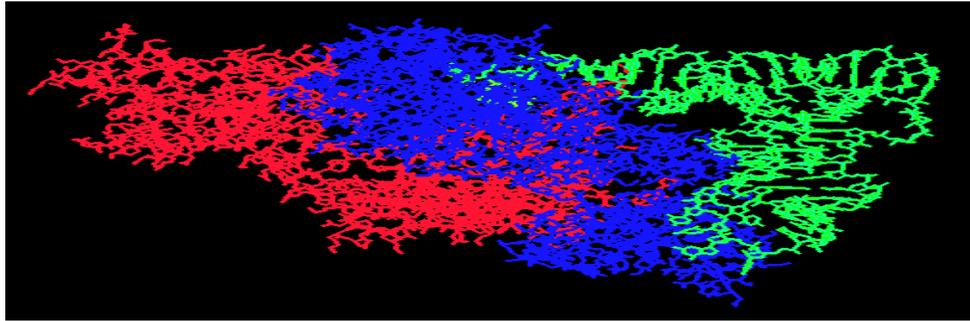
This research involves studies of the substrate and ligand binding properties of an enzyme involved in *de novo* purine biosynthesis. This enzyme is being studied in order to better understand its mechanism and function. GART represents an important target for chemotherapy since cancer cells engage employ *de novo* purine biosynthesis more than normal cells do. This research involves the use of techniques such as protein assays, protein expression, protein purification and spectroscopic techniques, including Circular Dichroism (CD), fluorescence and NMR. This work is done in collaboration with Prof. Caperelli, College of Pharmacy, U. of Cincinnati.

tRNA synthetase N-terminal domain

Pearl Tsang

804 Crosley (513) 556-2301 FAX: (513)556-9239 E-Mail: Pearl.Tsang@UC.Edu

This research involves the study of peptides derived from the N-terminal domain of human lysyl tRNA synthetase. This synthetase extension does not exist in prokaryotic systems and its precise function is still unknown but is critical for proper enzyme functions during protein translation. The exact role of this N-terminal domain will be investigated by studying the binding properties of this domain with tRNA and DNA. This work will also involve spectroscopic studies to characterize where and how this domain interacts with DNA and tRNA molecules.



The above is a graphics image of a tRNA synthetase multimer complexed with its cognate tRNA molecule (green).

Envelope proteins of HIV-1

Pearl Tsang

804 Crosley (513) 556-2301 FAX: (513)556-9239 E-Mail: Pearl.Tsang@UC.Edu



The role and function of different glycosylated proteins during the process of infection by HIV-1 virus represents an ongoing area of active research. A portion of one such HIV-1 protein is studied in our lab in order to investigate how its structural properties are pertinent to its function during infection. The research will entail use of spectroscopic and chromatographic methods aimed at characterizing the interaction of these viral proteins with antibodies and other proteins related to virus infection.

This cartoon of HIV-1 infection shows the viral glycoproteins interacting with specific proteins on the host cell membrane.

Photochemical Reagents for the Manipulation of DNA

Professor R. Marshall Wilson

404 Crosley (513)556-9261 FAX: (513)556-9239 E-Mail:

Marshall.Wilson@UC.Edu

Past work in this group has demonstrated the dihydrodioxins (DHDs) can be constructed to bind to specific sites in DNA. When these DHD-DNA complexes are irradiated with an argon ion laser, they cleave the DNA at the targeted site. Photochemical techniques such as this offer great promise for development of strategies for manipulation of DNA in the laboratory and for the development of drugs that provide significant alternatives to the traditional antibiotics strategies. Present research efforts are focused on determining how these DHD agents cause the cleavage of DNA. The pyrene DHD is one of the best cleaving reagents found to date, cleaving large strands of DNA in seconds, and displaying unusual spectroscopic properties that make their binding to DNA very easy to observe and study. Very recently, it has been observed that pyrene DHD forms unusually stable, very long live radical cations. Since species such as this have previously been invoked as DNA cleaving agents, one project that we shall be working on this summer is the study of effect of the laser generation of DHD radical cations in the presence of DNA.

In another project, we shall be working with a group at Ohio State on the mechanism of action of 8-azidoadenosine. This substance is a widely used reagent for the cross-linking of DNA. Some years ago, we worked out the photochemistry of this molecule and observed some very surprising results that provide some pointers as to how this molecule may react with DNA. We intend to explore this chemistry further this summer using mass spectrometry to analyze the reaction products in further detail. While the group at Ohio State will be using picosecond (10^{-12} second) infrared spectroscopy in an attempt to observe the course of this reaction when the 8-azidoadenosine is incorporated into the DNA molecule.

WISE students could be involved in either of these two projects in ways that would provide them with meaningful experiences in a very rapidly evolving area of modern research.