Chemistry Seminar Abstracts for the Year 2016

Tomorrow's Innovators and Instigators: Mars Rover Design Team

Alyssa McCarthy: Chief Executive Officer, Katelyn Brinker: Chief Technology Officer, Caroline Dziak: Science Team Leader, MS&T

Abstract: The Mars Rover Design Team designs and builds next generation rovers that will one day work alongside astronauts in the field. The team operates under the vision statement "Today. Tomorrow. Forever" and the technical branch of the team is divided into four sub-teams: Mechanical, Power, Telemetry and Controls, and Science. The science team focuses on developing systems and experiments to identify habitability. They are currently working on refining their custom Raman spectrometer and are developing a sample bay that will allow for collection of up to six samples. Furthermore, they are creating experiments to test for nitrates, salts, carbonates, and barium sulfate. Details about the rover, the team, the competition, and the science will be discussed.

The Microwave Spectrum and Large-Amplitude Motions of Pinacolone

Jon T. Hougen, Sensor Science Division, National Institute of Standards and Technology, Gaithersburg, MD

Abstract: The research for this talk consists entirely of microwave spectroscopic measurements and quantum mechanical calculations that are quite similar to the work in one group at the Department of Chemistry of Missouri University of Science and Technology. Nevertheless, because the audience will presumably consist of many different kinds of chemists, I hope to spend about half of the talk mentioning various chemical considerations associated with pinacolone (even though that will take me far outside my area of expertise).Peripheral topics for the first 20 minutes of the talk at the "Wikipedia level" are:

1) Volatile esters, aldehydes, and ketones as odorant molecules in the perfume and food industries.
2) The high sensitivity and specificity of the mammalian nose as a sensor of odors.
3) Volatile compounds as pheromones for plants and animals.

Is there any hope that the precise molecular structures obtained from microwave spectroscopy will be of use in elucidating the mechanism(s) of smell at the molecular biology level? In the second 20 minutes of the talk pinacolone (methyl tert-butyl ketone, CH3-C(=O)-C-(CH3)3) will be used as the basis for a (hopefully) pedagogical discussion of some basic ideas concerning:

1) The microwave instrumentation and supersonic cooling.
2) Chemically interesting intramolecular motions where the atoms move by more than one bond length = large-amplitude motions.

3) Electronic, vibrational, and rotational degrees of freedom in molecular spectra.
4) The main quantum mechanical ideas used in this research (time-independent stationary states = boundary value problems), which are different from the main quantum mechanical ideas used to study chemical reactions (reactants change with time into products = initial value problems).

In addition, I will try to give a (light-hearted) overview of present-day scientific competition in the various laboratories around the world in this field.

In Coherent Control of Wave Transport in Scattering Media: Looking Through Walls and Around Corners

Alexey Yamilov, Dept. of Physics., MS&T

Abstract: The concept of diffusion is widely used to study the propagation of light through multiple scattering media such as clouds, interstellar gas, colloidal solutions, paint, and biological tissues. Diffusion, however, is an approximation as it neglects wave interference effects. Most of the scattered waves follow independent paths and have uncorrelated phases, so their interference is averaged out. Notwithstanding, a wave may return to a position it has previously visited after multiple scattering events, and there always exists the time-reversed path, which yields identical phase delay. Contributions due to constructive interference between these pairs of paths to transport coefficients, in particular second order quantities such as fluctuations and correlations, do not average out to zero.

In this talk, I will review recent progress in coherent control waves in turbid media and describe a novel scheme of changing spatial structure of eigenchannels in the medium. It allows one to control the crossing probability of scattering paths as a function of position. I will illustrate this approach with several experiments demonstrating how the spatial dependence of the average intensity as well as the long-range correlations can be deterministically modified.

In addition to fundamental importance, understanding and manipulating the spatial correlations of light inside the random system is useful for imaging and focusing of light in multiply scattering media using wave-front shaping techniques. The number and the spatial structure of the eigenchannels limit the degree of coherent control. Our results suggest that the sample geometry can provide an additional degree of freedom, which can be used alongside with wavefront shaping to control not only the transmitted and reflected light, but also the depth profile of energy density inside the scattering system.

Laser-induced Scalable Synthesis of Nanomaterials for Energy Storage and Conversion

Jian Lin, Dept. of Mechanical and Aerospace Engineering, MS&T

Abstract: Nanomaterials offer new opportunities for delivering efficient energy storage and conversion devices in people's life due to their unique physical and chemical properties. Production of these nanomaterials in a scalable and cost-effective manner is essential for achieving this goal. In this talk, I will discuss how to produce and engineer carbon-based nanomaterials by a recently developed laser-induced method to manipulate electrons and ions at the nanoscale, which enables us to create efficient energy storage and conversion devices. This talk is composed of two parts: 1) laser induced synthesis of porous graphene-like nanomaterials by experimental and molecular dynamic simulation. Discuss their applications in in-plane microscale energy storage devices for microelectronics; 2) experimentally demonstrate laser synthesis and patterning of nanocatalysts for the application in hydrogen evolution reactions.

Unlocking the Mysteries of a Medieval Chant Book with Multispectral Imaging

Nathan A. Oyler: Dept. of Chem., Virginia Boston: Dept. of English, UMKC

Abstract: CODICES is a collaborative working group of faculty, students, and librarians who are focused on the analysis of manuscripts, texts, and early printed books with optical and computational techniques. We draw collaborators from many disciplines including English, Computer Science, Chemistry, Art History, and History. We conduct our research in working groups that coalesce around specific research questions and analytical techniques. We hope to be an incubator for faculty research, a training ground for graduate students, and a venue for undergraduate research. Our investigations to date have focused in the following areas:

Visible Imaging: We capture visible-light images of manuscripts and early printed books and present them online in order to bring them to a broad public audience.

Multispectral Imaging: We image selected pages from these manuscripts and early printed books at various frequencies in the ultraviolet-visible-near-infrared spectrum to answer questions about the books' production and reception history.

Book Histories: We have extensive book histories of the objects that we are investigating, describing the physical characteristics and provenance of these works.

Our long-range goal is to develop tutorials that teach others how to build and use their own version of our home-built multispectral scanning system. We aim to offer humanities centers,

libraries, and archives the ability to conduct their own investigations with these techniques using readily available and affordable equipment. The result of our project will be an expansion of the number of scholars and librarians who are able to use multispectral visualization techniques to study books in their own collections.

In our presentation for MS&T, we will focus on the multispectral optical techniques we are using to study the palimpsests in a handwritten codex known as the Adair Chant Book, which is a fifteenth-century book of chants that have been scraped and rewritten, and the watermarks found in an early printed book, Antoninus' Summa theologica, which was printed by Anton Koberger in 1486/87. Our investigations of these books illustrates how optical techniques can be used to recover lost material, as well as to identify and categorize watermarks in the Koberger volume.

Applying Quantum Monte Carlo Methods to the Electronic Structure Problem

Andrew D. Powell, Dept. of Chem., MS&T

Abstract: This presentation will be an overview of our progress in using Quantum Monte Carlo methods to describe the electronic structure of small molecular systems. Quantum Monte Carlo (QMC) is a computational technique that can be applied to the electronic Schrödinger equation for molecules. QMC methods such as Variational Monte Carlo (VMC) and Diffusion Monte Carlo (DMC) have demonstrated the capability of capturing large fractions of the correlation energy, thus suggesting their possible use for high-accuracy quantum chemistry calculations. QMC methods scale particularly well (near linearly) with respect to parallelization, making them an attractive consideration in anticipation of next-generation computing architectures which will involve massive parallelization with millions of cores. Due to the statistical nature of the approach, in contrast to standard quantum chemistry methods, uncertainties (error-bars) are associated with each calculated energy. Cost, feasibility, and accuracy in the context of practical applications will be assessed.

Using Reaction Kinetics to Assess Chemistry of Prospective Importance to the Origin of Life

Paul Brancher, Dept. of Chem., St. Louis University

Abstract: The question of how the first living system developed on early Earth is history's greatest unsolved mystery, and its answer all but certainly hinges on chemistry. Determining how the mixture of abiotic chemicals present four billion years ago could have naturally assembled into an autoamplifying network of reactions is a challenge of extraordinary complexity, and it can be difficult to decide where to begin. When evaluating chemical reactions proposed as relevant to the origin of life on Earth, the universal importance of water to life necessitates the consideration of hydrolysis as a deleterious side reaction. This presentation summarizes measurements of the rates of thiol-thioester exchange and thioester hydrolysis to assess the feasibility of a Thioester World-a period in early evolution where thioesters may have filled an important role as a kinetically stable, high-energy species like ATP does today. We will also discuss our latest data measuring the influence of simple salts on the rates of coupling and hydrolysis of peptides.

Rapid Quantification of Trypsin Inhibitors in Food and Feed Formulation with Electrospray Mass Spectrometry

Radheshyam Panta, Dept. of Chem., MS&T

Abstract: Trypsin is a serine peptidase involved in breakdown of larger poly-peptides and proteins into smaller peptides which can be readily absorbed and thus plays an essential role in nutrition. Proteins in seeds of certain species such as legumes are known to inactivate trypsin and hinder digestion of protein and adversely affect nutrition. Such proteins are called trypsin inhibitors (TIs) and minimize or inhibit trypsin catalyzed degradation of the substrate thereby limiting the availability of amino acids to the animal. As a result, determination of TI content of feed and food is important to assess nutritive value of foods and feeds.

At present TI content is determined with the American Association of Cereal Chemists method 22-40.01. The method relies on measurement of p-nitroaniline through absorption of radiation at 410 nm. The absorption based method suffers issues of non-linearity unless carried out within specified limits. A rapid, accurate, and precise method for the quantification of trypsin inhibitor activity was evaluated. The method utilizes electrospray mass spectrometry (ESI-MS) monitoring of alpha hydroxyl acid capped di-lysines as the substrate. Hydrolysis yields unique residues that were readily quantified with ESI-MS. Accuracy and precision of the approach compares favorably with that of the standard test method.

Liposomal Drug Delivery to Erythrocystics

Elizabeth Bowles, Dept. of Chem., MS&T

Abstract: Previous studies have shown that the controlled release of adenosine triphosphate (ATP) from human erythrocytes is an important mechanism for the regulation of vascular caliber. However, erythrocytes from patients with pulmonary arterial hypertension (PAH) fail to release ATP in response to the physiological stimuli of exposure to low oxygen tension or mechanical deformation of a magnitude these cells would encounter in the pulmonary circulation. This defect could be a significant contributor to the increased pulmonary vascular resistance (PVR) that is the cause of the pathological increase in vascular pressures in humans with PAH.

One important approach to the treatment of PAH is the administration of drugs to reduce PVR. These drugs include prostacyclin or its analogs and phosphodiesterase 5 (PDE5) inhibitors that can be used alone or in combination. Each medication may have serious unwanted side effects that are additive when the drugs are used in combination.

In this presentation, an alternative drug delivery technique using drug-loaded liposomes will be investigated that may allow for increased drug efficacy and, possibly, reduced unwanted side effects. Liposomes can encapsulate drugs and deliver them directly to specific cells. The research presented will describe the successful incorporation and delivery of a clinically-used PDE5 inhibitor, tadalafil, via liposomes, to human erythrocytes. This approach is shown to increase ATP release when the erythrocytes are exposed to the prostacyclin analog, UT-15C. These findings demonstrate the effectiveness of this technique and form the basis for future in vivo trials to improve drug delivery and patient quality of life. Liposomal delivery, currently underutilized clinically, could represent a new treatment paradigm for patients with circulation issues.