

2007 Frontiers in Chemical Physics Workshop University of Tennessee

Each spring, we host a workshop to highlight important areas in Chemical Physics. The two day event consists of presentations by internationally acclaimed speakers, a graduate student round table discussion, plenty of time for lab tours, and a reception. The Frontiers in Chemical Physics Workshop is an important part of the dynamic scientific environment for interdisciplinary research at the University of Tennessee.

Chemical Physics is an exciting and interdisciplinary area of science lying midway between the traditional fields of Chemistry and Physics. Although interdisciplinary in character, the field of Chemical Physics is quite broad, covering everything from elementary excitations in atoms, to the theory of weakly bond complexes, to nanoscience and technology involving novel materials. Chemical Physicists tend to focus on solving complex problems, using a variety of experimental and theoretical techniques from different areas of science to understand the fundamental properties of nature.

Useful phone numbers

Cumberland House Hotel	865-971-4663
Department of Chemistry	865-974-3141
Janice L. Musfeldt	865-974-3392
Robert Compton	865-974-9513

Wish you a pleasant and fruitful workshop.

**Janice L. Musfeldt
Robert Compton**

SCHEDULE
2007 Frontiers in Chemical Physics Workshop
University of Tennessee

All presentations are in second floor conference room, Cumberland House Hotel

Wednesday, February 21, 2007

6.30pm Arrival and Dinner

Thursday, February 22, 2007

8.00am Coffee & petit-déjeuner

8.30am Vincent Croquette Single DNA Molecule Micromanipulation: A Tool to
Ecole Normale Supérieure Investigate Enzymatic Reactions Cumberland House

9.30am Jairo Sinova Challenges and Chemical Trends in Achieving a
Texas A&M University Room Temperature Dilute Magnetic Semiconductor:
A Spintronics Tango Between Theory and
Experiment

10.30am Shaun Ard Probing the Coulomb Barrier for Multiply Charged
University of Tennessee Anions

11.00am Steve Overbury Experimental and Computational Studies of Reaction
Oak Ridge National Lab Pathways and Size Dependence in Au Catalysis

12.00pm Lunch

1.30pm Graduate Student Round Table Discussion

2.30pm Dong-Sheng Yang Infrared and Ultraviolet Laser Spectroscopy of
University of Kentucky Transient Metal-organic Complexes in the Gas
Phase

3.30pm Steve Leone Chemical Imaging and a Dynamical View of the
University of California, Nanoscale
Berkeley

4.30pm Lab Tours, Discussion

6.30pm Dinner and Reception @ Women's Basketball Hall of Fame

Friday, February 23, 2007

8.00am	Coffee & petit-déjeuner	
8.30am	Ward Plummer University of Tennessee, Oak Ridge National Lab	Materials for the 21 st Century: A Revolutionary, not an Evolutionary Approach
9.30am	Yucel Yildirim University of Tennessee	Large-Scale Monte Carlo Study of Realistic Lattice Model for $\text{Ga}_{1-x}\text{Mn}_x\text{As}$
10.00am	Mike McBride Yale University	Is There a Mechanism for Crystal Growth and Dissolution? Studying DL-Serine by AFM and Computer Simulation
11.00am	Geoffrey Greene University of Tennessee	The Neutron and the Cosmos
12.00pm	Lunch	
1.30pm	Brooks Harris University of Pennsylvania	Symmetry Properties of Multiferroics
2.30pm	Jay Jellison Oak Ridge National Lab	Generalized Ellipsometry: Going Beyond Isotropic Samples
3.30pm	David Singh Oak Ridge National Lab	A Microscopic View of Piezoelectric Oxides
4.30pm	Lab Tours, Discussion	
6.30pm	Dinner @ Regas	

2007
Frontiers in Chemical Physics
Workshop

Thursday, Feb. 22nd and Friday, Feb. 23rd, 2006
University of Tennessee, Knoxville

ABSTRACTS

Single DNA Molecule Micromanipulation: A Tool to Investigate Enzymatic Reactions

Vincent Croquette, Laboratoire de Physique Statistique, Ecole Normale Supérieure

In the last ten years, micro-manipulation techniques have emerged allowing to investigate enzymatic reactions at the single molecule level. Using magnetic tweezers, we pull and twist a micron size bead attached to one end of a DNA molecule by biotin/streptavidine while its second end is attached to the glass substrate by digoxigenin and its antibody. Monitoring the position of the bead with nanometer resolution allows us to record the minute changes done by a single enzyme interacting with the DNA molecule. In a first example, we shall show how this assay may be used to characterize the binding of the galactose repressor with DNA with which it forms a loop. In ensemble experiment one usually only has access to the constant of association which is the ratio of the on and off time of the interaction. In single molecule experiment, we measure directly the binding and unbinding times. Varying the force applied on the molecule we access to the binding energy of this simple reaction. In a second example, we study a molecular motor acting on DNA. We use a hairpin DNA molecule, which resembles the “replication fork” used to duplicate DNA in our cells. We observe that DNA replication enzymes indeed work on this hairpin. We shall show, in particular, how the gp41 helicase opens up the double helix like a zipper opener. This experimental assay reveals in real time how this molecular motor travels along DNA allowing accurate investigations of their chemical cycles. This motor is propelled through the hydrolysis of ATP. We observe that the rate of this molecular motor depends exponentially on the force applied to pull apart the DNA hairpin. By monitoring the rate of this reaction versus the force applied we access the energy landscape of this reaction. In particular we have measured at which distance is located the transition state of the reaction.

Challenges and Chemical Trends in Achieving a Room Temperature Dilute Magnetic Semiconductor: A Spintronics Tango Between Theory and Experiment

Jairo Sinova, Texas A&M University

In the world of spintronics the revolution of the strongly correlated systems dubbed as diluted magnetic semiconductors has seen a resurgence over the past five years in attempting to achieve ever higher Curie temperatures. This has been fueled in part from our clearer understanding of the paradigm of these materials, (Ga,Mn)As, which is at present one of the best understood ferromagnetic systems in its most metallic form. Through a diversity of theoretical tools and in constant comparison with experiments, the understanding of what it takes to achieve a room temperature DMS has gained a strong foothold and new attempts to find the ultimate combination which optimizes the diverse parameters which determines the Curie temperature is underway. I will review part of the current understanding of (Ga,Mn)As gained through phenomenological effective Hamiltonian models and other more microscopic calculations and what it makes us believe its understanding is quite good, and what new materials are being explored to reach a room temperature ferromagnetic semiconductor.

Probing the Coulomb Barrier For Multiply Charged Anions

Shaun Ard, University of Tennessee

The interaction of an electron or negative ion with another negative ion gives rise to the so-called Coulomb Barrier. This barrier is a result of the interaction of the long-range coulomb repulsion and the short-range polarizability attraction between the two charged species. Extensive studies of this barrier have been made possible due to the advent of the electrospray ionization source. This source has made many species of multiply charged ions available for study in the gas phase. Previous studies of autodetachment, photodetachment, and collisional dissociation of multiply charged anions will be summarized with regards to characterization of this barrier. Past work has primarily focused on the Coulomb Barrier with respect to electron detachment; however, attention is beginning to focus on ionic fragmentation. Several studies have shown that ionic fragmentation dominates over electron detachment in collisions with gas targets. In this regard we will describe our recent studies on collisional dissociation of sodium chloride dianions. Measurements of relative barrier heights for dissociation into various singly charged fragments will be discussed with reference to theoretical calculations and predictions. Finally we will describe our future experiments aimed at probing this important aspect of multiply charged anions.

Experimental and Computational Studies of Reaction Pathways and Size Dependence in Au Catalysis

Steven H. Overbury, Oak Ridge National Laboratory

Size or structure sensitivity is well known in catalysis for many metals and for certain “demanding reactions”. Au is unusual among noble metals for its strong size dependence for the CO oxidation reaction. Au catalysts are highly sensitive to many factors relating to their synthesis and support type and so the size sensitivity is difficult to extract from comparison of many different catalysts. We have performed experiments in which Au particle size was systematically increased by a sequence of thermal treatments which are monitored in situ by EXAFS. Simultaneous measurements of the activity for CO oxidation permitted direct correlation between particle size and activity for a single catalyst type. Various geometric models for size sensitivity based upon Au coordination have been assessed, based on comparison with the data, and it is concluded that the rate controlling sites must be low coordinate Au sites such as corner sites or periphery sites. Microscopic evidence indicates that a change in the Au morphology from raft-like to “round” 3D particles may occur at the lowest temperatures and smallest particles size, a transformation which is accompanied by a change in activation energy. Computational studies of the effect of low coordination has also been carried out and indicate that low coordinate Au permits a flexibility in the reaction coordinate which lowers the activation barrier and makes Au more active than Pt at low temperature reactions. To better understand mechanistic aspects in CO oxidation, we have utilized a reactor capable of dynamically monitoring adsorbate species and gaseous products by FTIR and sampling mass spectrometry under transient reaction conditions. Using this transient approach, the adsorption and desorption behavior of the reactants, the competition for sites, and the role of carbonates have been explored and the pathways for reaction have been mapped.

Infrared and Ultraviolet Laser Spectroscopy of Transient Metal-organic Complexes in the Gas Phase

Dong-Sheng Yang, University of Kentucky

Transient metal-organic complexes are coordinately unsaturated, in which one or more ligands have fallen off stable compounds, and are potential intermediate in catalysis and building blocks of coordination or supramolecular networks. Spectroscopy and structural determination of these species have challenged experimentalists for many years because of their low densities and short-lived nature. In our work, coordinately unsaturated metal-organic or organometallic complexes are synthesized by reactions of laser-vaporized metal atoms or clusters with the vapor of organic compounds and examined by single-photon pulsed field ionization-zero electron kinetic energy (PFI-ZEKE) and IR-UV two-photon photoionization and photoelectron spectroscopy. In this talk, we will discuss the applications of these spectroscopic techniques to determine the molecular structures and electronic states of metal-aromatic hydrocarbons and heterocycles.

Chemical Imaging and a Dynamical View of the Nanoscale

Steve Leone, University of California, Berkeley

Imaging with chemical specificity provides a new window onto nanoscale materials. Coherent anti-Stokes Raman microscopy with single broadband femtosecond laser pulses obtains images of polymer mixtures with molecular selectivity. Apertureless near field optical microscopy distinguishes semiconductor hetero materials and nanodots. Ultrafast pump-probe spectroscopies interrogate the dynamics of single nanowire lasers. Scanning transmission x-ray microscopy discriminates chemical species in polymer reaction zones. Optical physics and novel laser methods combine with chemistry to produce a variety of new molecular-specific imaging methods that address intriguing nanoscale problems. From biological systems to polymers and semiconductor nanoscale materials, chemical imaging offers breathtaking advances in the study of molecular-specific structures and dynamics.

Materials for the 21st Century: A Revolutionary, not an Evolutionary Approach

E.W. Plummer, University of Tennessee

I will begin this presentation by discussing the societal needs for new materials for the 21st century, driven by our need for energy, preserving our environment and responding to the President's American Competitiveness Initiative. The time frame needed requires a revolutionary, not evolutionary approach to the design and discovery of new materials. I will then compare and contrast the Einstein reductionary philosophy with Andersen's complexity and emergent phenomena philosophy. I will use magnetism in nanostructured materials to illustrate the Andersen viewpoint, stressing the need for Discovery-Based Research. This presentation will describe unexpected magnetic properties observed in artificially nano-structured materials[1]. Time permitting I will discuss five different examples. 1) Two-dimensional arrays of nano-dots of Fe can be fabricated with controlled density and size. They exhibit "superferromagnetic" behavior instead of the expected superparamagnetic ordering. 2) Stacked arrays of these dots show the transition from ferromagnetism to a pseudo spin-glass accompanying the 2-dimensional to 3-dimensional cross over. 3) The use of "subsurfactant" epitaxy growth to generate a dilute magnetic semiconductor with ~0.25% interstitial Mn in Ge. The ferromagnetic ordering temperature is $T_C > 440\text{K}$. All of these examples can't be explained with conventional pictures of magnetic coupling. 4) Magnetic nanoparticles in polymers to create an efficient, flexible photovoltaic device, 5) Size filtered Fe nanoparticles as a way of passively targeting brain tumors. I will conclude with a few sociological and philosophical observations.

Large-Scale Monte Carlo Study of Realistic Lattice Model for $\text{Ga}_{1-x}\text{Mn}_x\text{As}$

Yucel Yildirim, University of Tennessee

The properties of Mn-doped GaAs are studied at several doping levels and hole compensations using a real-space Hamiltonian on an fcc lattice that reproduces the valence bands of undoped GaAs. Large-scale Monte Carlo (MC) simulations on a Cray XT3 supercomputer, using up to a thousands nodes, were needed to make this effort possible. Our analysis includes both the spin-orbit interaction and the random distribution of the *Mn* ions. Hopping amplitudes are obtained as a function of GaAs Luttinger parameters. At the coupling $J \sim 1.2$ eV deduced from photoemission experiments, the MC Curie temperature is in excellent agreement with experimental results for annealed samples. Although there are sizable differences with mean-field predictions, the system is found to be qualitatively closer to a hole-fluid regime than to localized carriers. The methodology described here introduces a quantitative tool to analyze a variety of diluted magnetic semiconductors.

Is There a Mechanism for Crystal Growth and Dissolution? Studying DL-Serine by AFM and Computer Simulation

Mike McBride, Yale

For more than 300 years scientists have been fascinated by the intricate process of self-assembly involved in crystal growth and dissolution. Until quite recently they had to depend on phenomenological theories based on bulk observation. Now it is possible to observe the dynamics of monolayer patterns on growing and dissolving crystal surfaces using AFM and to use this information to work toward a detailed structural theory of these processes. Recent work with the amino acid DL-serine will be used to illustrate an approach to this problem.

The Neutron and the Cosmos

Geoffrey Greene, University of Tennessee and Oak Ridge National Laboratory

The Spallation Neutron Source (SNS), now in operation at Oak Ridge National Laboratory will provide an immensely powerful tool for the study of materials through the application of neutron scattering. It is less well known that the SNS will also be used to address several problems in fundamental nuclear and particle physics. Measurements of the free neutron lifetime and the search for a possible neutron electric dipole moment can shed light on important issues in cosmology including the origin of matter and the details of Big Bang Nucleosynthesis. I will give an introduction to the SNS and an overview of the proposed fundamental neutron physics program and will briefly discuss how this work addresses current issues in cosmology.

Symmetry Properties of Multiferroics

A. Brooks Harris, University of Pennsylvania

In this talk I will briefly describe the three elements that lead to the phenomenological description of the combined magnetic and ferroelectric phase transitions in systems such as TbMnO₃ (TMO), Ni₃V₂O₈ (NVO), which display incommensurate magnetic ordering. The first issue is to include the consequences of inversion symmetry in the interpretation of diffraction data. Although the role of symmetry on magnetic structure determinations is an ancient topic investigated by such authors as Bertaut and Rossat-Mignod, it is surprising that even they did not consider inversion symmetry and it is only for NVO and TMO that the analysis has been done correctly (by us). The second issue is to systematically describe the magnetic ordering by order parameters whose transformation properties under the symmetry operations of the paramagnetic crystal can be tabulated. Finally, one can construct the trilinear magnetoelectric interaction (proportional to the square of the magnetic order parameters and linear in the spontaneous polarization) to explain magnetically induced ferroelectricity. This formulation usually explains the observed direction of the spontaneous polarization and the experimental observation that the temperature dependence of the polarization follows the intensity of a magnetic Bragg reflection (which is proportional to the square of a magnetic order parameter).

Generalized Ellipsometry: Going Beyond Isotropic Samples

Gerald Jellison, Jr., Oak Ridge National Laboratory

Standard ellipsometry experiments are used to determine the optical functions (refractive index and extinction coefficient) and thicknesses of thin films, and optical functions of materials, where the assumption is made that film and substrate are isotropic. To proceed to anisotropic samples requires more sophisticated measurements, called generalized ellipsometry (GE). Moreover, GE measurements can also be performed in non-standard configurations and with imaging optics to dramatically improve the optical resolution. This talk will focus on several examples of the types of information available from GE measurements: 1) measurement of the optical functions (refractive index and extinction coefficient) of anisotropic materials, 2) Spatially resolved transmission GE, which can be used to examine internal stresses and penetrating electric fields in certain materials, 3) Spatially resolved normal-incidence reflection GE, where preferential orientation of graphite nanocrystals in nuclear fuel particles can be observed.

A Microscopic View of Piezoelectric Oxides

David J. Singh, Oak Ridge National Laboratory

This talk presents a case study on the application of computer simulations to find new materials for given applications, here transducers. Piezoelectric oxides, particularly certain Pb containing perovskites, are widely used for electro-mechanical transducers, that is, devices that convert sound into electrical energy and vice versa. Applications range from medical ultrasounds to SONAR. In this talk I will overview the physics of these materials and their piezoelectric properties. As will be seen their performance depends on a remarkable balance between different lattice instabilities of the perovskite structure. These in turn depend on the chemistry of Pb, which poses a challenge, because environmental regulations mandate the removal of Pb from electronics. We have been using density functional calculations to understand the details of the lattice instabilities in microscopic terms. This has yielded understanding of how to control them, which is summarized in four design rules as well as a new mechanism for strong ferroelectricity in perovskites.