

## Session D

### Understanding Metal-Ligand Covalency in DMSO Reductase Family Enzymes by X-ray Absorption Near Edge Structure (XANES)

Khadanand KC and Martin L. Kirk  
University of New Mexico

Dimethyl sulfoxide reductase (DMSOr) family enzymes play critical roles in C, S, and N biogeochemical cycles. These enzymes are coordinated by the ene-1,2-dithiolate side chains of two pyranopterin cofactors, typically an amino acid donor (e.g. SCys, SeSec, or OSer) and for oxidized enzyme forms a terminal oxo or sulfido ligand. The structures of fully oxidized and fully reduced enzyme forms have been probed by X-ray crystallography, EXAFS, and resonance Raman spectroscopy. Unfortunately gaining insight into their electronic structures via optical spectroscopy has proven to be quite difficult due to the presence of other chromophores strongly absorbing chromophores such as Fe-S clusters and hemes. Similarly, obtaining Mo-S covalency information using S K-edge XAS is effectively impossible due to the presence of other, non-coordinating Cys and Met amino acids in the protein. Paramagnetic Mo(V) enzyme intermediates have been extensively studied by electron paramagnetic resonance (EPR) spectroscopy, but these enzyme forms are typically not amenable to crystallographic studies. To address this problem, we have elected to synthesize new models for paramagnetic DMSOr enzyme intermediates. This allows us to correlate enzyme EPR spin-Hamiltonian and EXAFS structural parameters with model systems of known structure. Specifically, we will detail the results of S K-edge XAS, EXAFS, electronic absorption and EPR spectroscopies on  $[\text{Mo}(\text{dithiolene})_2(\text{E-E})]^{1-}$  complexes in order to understand the relationships between the geometric and electronic structure of Mo(V) enzyme species and understand how covalency effects control electron transfer reactivity in the enzymes.

*Keywords: XANES, Enzymes, DMSO*

## Session D

### **Radical Appended Donor-Acceptor Pt complexes: An Ideal Platform for Electron Transfer, Electron Transport, and Excited State Processes**

Ranjana Dangi, Jing Yang, David A. Shultz, and Martin L. Kirk  
University of New Mexico

Square planer Pt donor-acceptor complexes have garnered considerable interest due to their rich photochemical properties and their photoluminescence behavior. These complexes possess a low energy Donor  $\rightarrow$  Acceptor ligand-to-ligand charge transfer (LL'CT) transition that effectively creates charge separated singlet biradicals (semiquinone and bpy $\cdot^-$ ) in the LL'CT excited state. Herein, we describe a new molecular biradical framework to develop greater insight into excited state magnetic coupling and spin polarizations. Importantly, these new complexes will allow for detailed spectroscopic interrogation by magnetic circular dichroism (MCD) spectroscopy to understand their electronic structure, and by time-resolved spectroscopies to understand their excited state lifetimes and dynamics. Understanding these complex excited state interactions is crucial for the further development of quantum information science, molecular electronics, and molecular spintronics applications. We will discuss here our latest results in the context of how to create novel excited states where three spin  $\frac{1}{2}$  centers are localized on three different sites in the same molecule

*Keywords: Donor, Acceptor, Radical, Biradical, Spin*

## Session D

### **New Oligo-Phenylene-Based Materials in Probing Electron Delocalization for Organic Photovoltaics**

Juchao Yan  
Eastern New Mexico University

Phenylene-based conjugated oligomers and polymers (e.g., fluorenes) are promising candidates for organic electronics and solar cells. To control the energetics and dynamics of electrons, we have selected time-resolved infrared spectroscopy coupled with pulse radiolysis for a series of newly designed ladder-type oligo(*p*-phenylene)s. Such oligo(*p*-phenylene)s are rigidified, and bear a nitrile group as an infrared reporter group and hexyl side chains for increasing their solubility. Compared to the oligofluorene counterparts, they have conformational rigidity and planarity and are expected to exhibit sharper infrared peaks and faster electron transfer rates.

In this talk, I will illustrate our organic syntheses and characterizations of several title oligo(*p*-phenylene)s, and will discuss our time-resolved infrared spectroscopic results from the laser-electron accelerator facility at Brookhaven National Laboratory. The focus will be on their optical signatures of the charged and triplet states.

*Keywords: Oligo-(p-phenylene)s, Electron Delocalization, Organic Photovoltaics, Pulse Radiolysis*

## Session D

### **Predicting the Effects of Density Gradients on the Hydrodynamic Behavior of PBX9502 in Shaped Charges**

Irene Fang, John D. Yeager, W. Lee Perry, and Amanda L. Duque  
Los Alamos National Laboratory

High explosive materials may be exposed to a variety of thermal stimuli during their service lifetime. For TATB-based explosives, which are often anisotropic, the explosive component may undergo irreversible volume expansion or density reduction. For example, if asymmetric heating is applied, the initially uniform part will develop a density gradient. In a real-world scenario, this can be caused by something as simple as exposing part of an explosive to the sun. Here, we seek to investigate the hydrodynamic effects of these density gradients in the explosive PBX 9502 on the performance of a common military shaped charge by varying density regions around the shaped charge liner. Previous work with flyer impact simulations shows that density gradients affect wave shape. Wave shape affects performance in shaped charges, and therefore we expect to observe significant changes in the resulting jet due to the presence of low-density regions.

*Keywords: TATB, Hydrodynamic, PBX 9502*