FINAL REPORT

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CORRELATING ELECTRONIC AND VIBRATIONAL MOTIONS IN CHARGE TRANSFER SYSTEMS

The goal of this research program was to measure coupled electronic and nuclear motions during photoinduced charge transfer processes in transition metal complexes by developing and using novel femtosecond spectroscopies. The scientific highlights of the DOE supported work are outlined below:

Probing photoinduced metal–nitrosyl linkage isomerism of sodium nitroprusside in solution using transient infrared spectroscopy.[1] We investigated photoinduced metal–nitrosyl linkage isomerism in sodium nitroprusside ($Na_2[Fe^{II}(CN)_5NO]\cdot 2H_2O$, SNP) dissolved in methanol to understand the interplay between inter-molecular and intra-molecular structural relaxation pathways following metal-to-ligand charge transfer (MLCT) excitation. This photoinduced process has been widely studied for fundamental understanding on iron-nitrosyl photochemistry, applications in medicine as a nitric oxide delivery agent and for the development of high capacity optical storage devices. Despite previous work, a detailed understanding of the photochemistry of SNP in solution was lacking. We performed transient infrared (IR) spectroscopy following 400 nm excitation of the sample to exploit the structural sensitivity of the nitrosyl stretching vibration. The high sensitivity and specificity of this technique allowed the simultaneous observation of two known bound metastable (MS) iron–nitrosyl linkage isomers of SNP, $[Fe^{II}(CN)_5(\eta^1\text{–ON})]^{2-}$ (MS1) and $[Fe^{II}(CN)_5(\eta^2\text{–NO})]^{2-}$ (MS2), at room temperature. Unbound nitrosyl in the form of free nitrosyl radicals (NO·) were also measured in the sample solution. The simultaneous detection and characterization of photoinduced linkage isomerism (MS1 and MS2) and photodissociation of the metal-NO bond in SNP highlights the importance of understanding the role played by metastable metal-nitrosyl linkage isomers in the photochemistry of metal-nitrosyl compounds in chemistry and biology.

Development of transient heterodyne-detected dispersed vibrational echo (t-HDVE) spectroscopy to study non-equilibrium vibrational relaxation during photoinduced processes in solution.[2] We have developed doubly resonant fifth-order nonlinear visible−infrared spectroscopies to probe non-equilibrium vibrational dynamics among coupled high-frequency vibrations during an ultrafast charge transfer process using a heterodyne detection scheme. The method enables the simultaneous collection of third- and fifth-order signals, which respectively measure vibrational dynamics occurring on electronic ground and excited states on a femtosecond time scale. The fifth-order signals contain information on (i) time-dependent anharmonic vibrational couplings, (ii) nonequilibrium frequency−frequency correlation functions, (iii) incoherent and coherent vibrational relaxation and transfer dynamics, and (iv) coherent vibrational and electronic (vibronic) coupling as a function of a photochemical reaction. We have successfully developed the experimental and data analysis methodology and used it to measure non-equilibrium vibrational relaxation dynamics in a transition metal mixed valence system. We believe that these experiments will find ready applications in studies of ultrafast photochemical transformations.

Understanding anharmonic vibrational couplings and vibrational relaxation in the ground electronic state of cyanide-bound transition metal mixed valence complexes.[3-5] Cyanide-bridged mixed valence complexes serve as model systems for understanding the role of coupled electronic and nuclear motions during ultrafast charge transfer processes. Using polarization-selective two-dimensional infrared (2D IR) spectroscopy, we measured anharmonic couplings and angles between the transition dipole moments of the four cyanide stretching (ν_{CN}) vibrations found in $[(NH_3)_5Ru^{III}NCFe^{II}(CN)_5]^-$ (FeRu) and $[(NC)_5Fe^{II}CNPt^{IV}(NH_3)_4NCFe^{II}(CN)_5]^{4-}$ (FePtFe). For this study, FeRu was dissolved in both formamide and D_2O, and FePtFe was dissolved in D_2O. The experimental 2D IR spectra of FeRu and FePtFe and their fits reveal a set of weakly coupled anharmonic ν_{CN} modes with the vibrational mode anharmonicities ranging from 14 to 28 cm^{-1} and the mixed-mode anharmonicities ranging from 2 to 14 cm^{-1}. Measurement of the relative transition dipole moments of the four ν_{CN} modes reveal that FeRu is almost linear in solution when dissolved in formamide, but bent when dissolved in D_2O. IR pump-probe experiments reveal that the vibrational lifetime of the radial, axial, and trans ν_{CN} modes are ~2 times faster when FeRu is dissolved in D_2O versus formamide. Our experiments demonstrate how vibrational relaxation and anharmonic couplings of the high frequency CN stretches and the molecular geometry of these complexes are dictated by the solvent environment. Combining the results from the $Fe^{II}Pt^{IV}Fe^{II}$ trimer and the FeRu dimer will allow more general conclusions regarding the role a coupled network of ν_{CN} modes plays in solution-phase electron transfer chemistry, which is important since cyanide bridges are a common building block in several bimetallic complexes and polymers.

The role of high-frequency intramolecular CN vibrations in charge transfer reactions measured in a trinuclear mixed-valence complex in solution.[6,7] The trinuclear mixed-valence complex $Fe^{II}Pt^{IV}Fe^{II}$ dissolved in D_2O has a high-energy metal-to-metal charge transfer band arising from charge transfer from Fe^{II} to Pt^{IV} over the cyanide bridging ligand. We used the four cyanide stretching (ν_{CN}) vibrations as a multidimensional probe of vibrational excitation, redistribution, and relaxation dynamics as ultrafast back-electron transfer (BET) from the Pt atom occurs. We determined that BET to the electronic ground state occurs in 110 ± 10 fs, during which greater than 6 quanta (n) of vibrational energy are directed into the ν_{bridge} mode

(n_{bridge} > 6). Intramolecular vibrational energy redistribution from the ν_{bridge} mode excites the solvent-accessible ν_{trans} mode on a 630 ± 50 fs time scale. Vibrational cooling to n = 1 and vibrational relaxation ensue on time scales of 1.3 ± 0.1 and 15–20 ps, respectively. These results clearly highlight the important role played by a coupled network of high-frequency vibrations in ultrafast charge transfer processes in solution. We applied t-HDVE spectroscopy to $Fe^{II}Pt^{IV}Fe^{II}$ dissolved in D_2O to probe coherent and incoherent vibrational relaxation energy dynamics among the highly excited CN stretching modes indirectly populated by BET, as observed in the transient IR experiments mentioned above. Our results provide experimental evidence that the nuclear motions of the molecule are both coherently and incoherently coupled to the electronic charge transfer process. We observe that intramolecular vibrational relaxation dynamics among the highly excited ν_{CN} modes change significantly en route to equilibrium. The ability to measure non-equilibrium vibrational relaxation pathways in a mode-specific manner during a photochemical reaction opens up the possibility of manipulating the time-evolving spectral density in a rational way and holds implications for molecular engineering and optical control.

Ab initio simulations of transient X-ray absorption spectroscopy of Fe^{II} spin crossover complexes.[8,9] The success of the nascent field of time-resolved X-ray absorption (XA) spectroscopy will rely on simultaneously developing computational tools to predict and simulate experimental spectra. My group has been using DFT methods to simulate transient X-ray absorption (XA) spectroscopy to develop a detailed understanding of the local electronic structure. First we considered the use of *ab initio* quantum chemical methods for interpreting the Fe K-edge (core level excitations from the 1s orbital) XA spectrum of the Fe^{II} complex, $[Fe(tren(py)_3)]^{2+}$. This octahedral complex undergoes a photoinduced spin crossover (SCO) reaction from a low-spin (LS) $^1A_1$ ground state to a high-spin (HS) $^5T_2$ excited state following MLCT excitation. The SCO phenomena on related Fe(II) complexes has been widely studied by the transient X-ray community. We applied transition potential and time dependent density functional theories (TP-DFT and TD-DFT) to simulate the Fe K-edge XA spectroscopy of low-spin (LS) and high-spin (HS) states of $[Fe(tren(py)_3)]^{2+}$. We showed that TP-DFT has the ability to simulate a large region (~40 eV) of the XA spectra of this SCO complex. The TP-DFT simulations agreed well with experiment demonstrating the ability of an *ab initio* tool to reproduce the entire near-edge spectrum of transition metal K-edges. In addition, we extended the previous experimental work by providing a molecular-level understanding of the pre-edge region of the XA spectrum. The pre-edge region of Fe K-edge spectra has recently received a great deal of attention because it contains electric quadrupole 1s → 3d transitions that report directly on the metal—ligand interactions. Analysis of experimental data reveals that the LS ground state spectrum contains a single spectral feature while the transient HS state contains two features. The TD-DFT simulation of the pre-edge region of this complex show a single feature arising from two transitions for the LS complex and two features arising from four transitions for the HS complex. The appearance of a second spectral feature in the HS state arises from the rearrangement of the Fe 3d electrons as the molecule converts from its $^1A_1$ ground state to its $^5T_2$ excited state. Consequently, our simulations identified the spectral signature of this process providing a spectroscopic handle for studying complex electronic rearrangements in Fe^{II} complexes. In a related study we investigated the SCO process in $[Fe^{II}(bpy)_3]^{2+}$ by TD-DFT simulations of equilibrium and transient nitrogen K-edge XA spectroscopy. The most prominent feature in N K-edge spectra is a 1s → π* transition which shifts to lower energies following the SCO process. We have performed TD-DFT calculations and our results are in good agreement

with experiment predicting a –0.3 eV shift in the 1s → π* transition energy. Analysis of the electron density maps show that there is a greater charge density on the N atoms in the $^5T_2$ state, which destabilizes the N 1s orbitals leading to a smaller transition energy. The SCO process involves populating anti-bonding Fe 3d orbitals that are delocalized over the coordinating N atoms. Consequently, the N K-edge spectra of ligating nitrogen atoms can be used to track changes in metal-ligand bonding following photochemical events.

Understanding the local electronic structure of a photoexcited solar cell dye with ultrafast Ru L_3-edge X-ray absorption spectroscopy.[10] Our next XA study focused on understanding the ground and excited state electronic structure of $Ru(dcbpy)_2(NCS)_2$ (termed N3), a widely used dye molecule in dye sensitized solar cells (DSSCs). Many studies focusing on the design of DSSCs have shown that the electronic structure of the dye molecule is important for efficient charge-carrier creation and dye regeneration. We applied transient Ru L-edge XA spectroscopy to study the rearrangement of electron density following photoexcitation of $N3^{4-}$. The $^1A_1$ spectrum exhibits two features labeled B and C and the ^{3}MLCT spectrum contains three features labeled A', B', and C'. The appearance of the A' feature in the ^{3}MLCT spectrum arises from a hole in the Ru 4d orbitals created by the MLCT excitation. We also observe energetic shifts of +1.0 eV from B to B' and +0.9 eV from C to C' are observed. TD-DFT simulations of the Ru L_3-edge allow us to assign the features observed in the XA spectra of $N3^{4-}$. Our simulated spectra are able to reproduce all the experimentally observed spectral features and energy shifts. The TD-DFT simulation enables us to plot the difference densities. These maps show the spatial distribution of the core-excited electron for a particular transition. We find that the A' feature arises from a transition from a Ru $2p_{3/2}$ orbital to an orbital of mixed Ru 4d and NCS π character. The spectral features B and B' arise from transitions to states that are mostly Ru 4d orbitals of e_g character, and features C and C' are probes of the NCS π* orbitals. The MLCT transition in $N3^{4-}$ moves an electron from an orbital of mixed Ru 4d and NCS π * character to one of the dcbpy ligands. This results in a decrease in electron density at the Ru center and on the NCS ligands. We can identify shifts in the B and C features as markers of a decrease in electron density at the Ru atom and on the NCS ligands, respectively. Our combined experimental and computational study provides a microscopic understanding of how the initial MLCT transition modifies the electronic structure on the NCS ligands providing a driving force for the regeneration process.

Developing a quantitative understanding of the Ru L_3-edge with experiment and theory.[11,12] The photoexcited MLCT states of Ruthenium(II) complexes are widely used in solar harvesting. Ru L-edge XA spectroscopy is an excellent probe of the 4d electrons which are crucial players in photochemical energy conversion processes. We have benchmarked the use of TD-DFT as a general tool to simulate Ru L_3-edge XA spectroscopy. TD-DFT was used to simulate the Ru L_3-edge spectra of a series of Ru^{II} and Ru^{III} model complexes including: $[Ru(NH_3)_6]^{2+/3+}$, $[Ru(CN)_6]^{4-/5-}$, $[RuCl_6]^{4-/3-}$, and the $^1A_1/^3$MLCT states of $[Ru(bpy)_3]^{2+}$. We have assessed a range of density functionals and conclude that B3LYP most accurately predicts the location of spectral features with an RMSD of 0.2 eV for the various peak positions. The advantage of using TD-DFT to assign complicated Ru L-edge spectroscopy is illustrated by its ability to identify ligand specific charge transfer features in complex molecules. We have been studying mixed valence transition metal complexes of the form $[(NC)_5M^{II}—CN—Ru^{III}(NH_3)_5]^-$ where M = Fe, Ru (denoted FeRu and RuRu). Since Ru L-edge XA spectroscopy is sensitive to the oxidation state and electron configuration, it provides an ideal tool for probing electron

distributions in Ru based mixed valence complexes. The Ru L_3-edge spectrum of FeRu in water. shows two clear features and resembles the XA spectrum of the prototypical Ru^{III} complex $[Ru(NH_3)_6]^{3+}$ confirming the +3 oxidation state of the Ru atom in FeRu. To perform the TD-DFT simulation of the Ru L_3-edge XA spectroscopy, FeRu and the nearest water molecules are treated quantum mechanically, but longer range solvent interactions are treated by an implicit model. The simulated Ru L_3-edge spectrum using the explicit solvent model is in good agreement with the experimental measurement. This study underscores the important role that the solvent plays in determining electronic configurations of molecules in solution.

DOE Supported Research in Peer-Reviewed Publications (2009- present):

(1) Lynch, M. S.; Cheng, M.; Van Kuiken, B. E.; Khalil, M. Probing the Photoinduced Metal-Nitrosyl Linkage Isomerism of Sodium Nitroprusside in Solution Using Transient Infrared Spectroscopy. *J. Am. Chem. Soc.* **2011**, *133*, 5255.

(2) Lynch, M. S.; Slenkamp, K. M.; Cheng, M.; Khalil, M. Coherent Fifth-Order Visible–Infrared Spectroscopies: Ultrafast Nonequilibrium Vibrational Dynamics in Solution. *J. Phys. Chem. A* **2012**, *116*, 7023.

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(5) Slenkamp, K. M.; Brookes, J. F.; Lynch, M. S.; Bannan, C. C.; Daifuku, S. L.; Khalil, M. Solvent-Dependent Vibrational Relaxation and Dephasing of Cyanide Stretching Vibrations in Mixed Valence Complexes. *Journal of Chemical Physics* **2014**, to be submitted.

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(11) Van Kuiken, B. E.; Valiev, M.; Daifuku, S. L.; Bannan, C.; Strader, M. L.; Cho, H.; Huse, N.; Schoenlein, R. W.; Govind, N.; Khalil, M. Simulating Ru L_3-Edge X-Ray Absorption

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DOE Supported Research in Ph.D. Theses (2009- present):

1. Lynch, Michael S. "Correlating Electronic and Nuclear Motions in Ultrafast Photoinduced Charge Transfer Reactions with Femtosecond Multidimensional Spectroscopies." Ph.D., University of Washington, 2013.
2. Van Kuiken, Benjamin E. "Interrogating the Electronic Structure and Photochemistry of Molecules with Transient X-ray Absorption Spectroscopy." Ph.D., University of Washington, 2014.