FINAL REPORT

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Probing Ultrafast Electron (De)localization Dynamics in Mixed Valence Complexes Using Femtosecond X-ray Spectroscopy

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The overall goal of this research program was to understand valence electron and vibrational motion following metal-to-metal charge transfer (MMCT) excitation in the following mixed valence complexes dissolved in aqueous solution: $[(NH_3)_5Ru^{III}NCFe^{II}(CN)_5]^-$ (FeRu), *trans*-$[(NC)_5Fe^{II}CNPt^{IV}(NH_3)_4NCFe^{II}(CN)_5]^{4-}$ (FePtFe) and *trans*-$[(NC)_5Fe^{III}CNRu^{II}(L)_4NCFe^{III}(CN)_5]^{4-}$ (FeRuFe, L=pyridine). The project objectives were (i) to observe the time-dependent re-arrangement of *d* electrons across two transition metal sites and the bridging ligand following photoinduced MMCT excitation on a sub-50 fs timescale using femtosecond X-ray pulses generated at LCLS (ii) to simulate femtosecond X-ray absorption and emission spectra of solvated, photo-excited, transition metal mixed valence complexes using a realistic treatment of multi-electron correlations/transitions, spin-orbit coupling and final state lifetime effects and to propose and study the feasibility of nonlinear X-ray experiments on solvated transition metal mixed valence systems using future X-FEL light sources and (iii) to determine the role of coupled electronic and vibrational motions during ultrafast photoinduced charge transfer. The scientific highlights of the DOE supported work are outlined below:

Development of Two-Dimensional Vibrational-Electronic (2D VE) Spectroscopy to Measure Coherently Coupled Vibrational and Electronic Motions.[1-3] We developed Fourier transform (FT) 2D vibrational-electronic (2D VE) spectroscopy employing a novel mid-IR and optical pulse sequence. This new femtosecond third-order nonlinear spectroscopy provides the high time and frequency resolutions of existing 2D FT techniques, but is sensitive to cross-peaks

containing IR and electronic dipole moment cross terms. We have used 2D VE spectroscopy to help understand the vibrational-electronic couplings in the cyanide-bridged transition metal mixed valence complex, FeRu dissolved in formamide. The amplitude of the cross-peaks in the 2D VE spectra revealed that three of the four intramolecular cyanide stretching vibrations are coherently coupled to the MMCT electronic transition. Analysis of the 2D VE lineshapes reveals positive and negative frequency correlations of the cyanide stretching modes with the charge transfer transition. We will use this spectroscopy to measure the vibrational-electronic couplings in other mixed valence complexes over the next two years. We believe that the 2D VE and 2D EV techniques will find wide applicability in fields of chemistry, biology, and material science, specifically in mode-selective chemistry, coupled vibrational and electron transfer, proton and electron transfer processes, and the study of materials with strong electronic correlations where vibrations have been shown to coherently drive electronic phase transitions.

The viability of femtosecond multidimensional spectroscopy as an analytical tool requires improvements in data collection and processing to enhance the signal-to-noise ratio and increase the amount of data collected in these experiments. We have developed a continuous fast scanning technique for the efficient collection of 2D VE spectroscopy is described. The resulting 2D VE spectroscopic method gains sensitivity by reducing the effect of laser drift, as well as decreasing the data collection time by a factor of 10 for acquiring spectra with a high signal-to-noise ratio within 3 dB of the more time intensive step scanning methods. This work opens the door to more comprehensive studies where 2D VE spectra can be collected as a function of external parameters such as temperature, pH, and polarization of the input electric fields.

Signatures of Vibronic Coupling in Two-Dimensional Vibrational-Electronic (2D VE) Spectroscopy.[4] We have developed a Fourier transform (FT) 2D vibrational-electronic (2D VE) spectroscopy employing a sequence of mid-IR and optical pulses to interrogate coupled vibrational and electronic motions in the condensed phase. We simulated 2D VE spectra using a model Hamiltonian consisting of one anharmonic vibration and two electronic states. Equilibrium displacement of the vibrational coordinate and vibrational frequency shifts upon excitation to the first electronic excited state were included in our Hamiltonian through linear and quadratic vibronic coupling terms and we explicitly considered the nuclear dependence of the electronic transition dipole moment and demonstrated that these spectroscopies are sensitive to non-Condon effects. Our simulations showed that one of the following conditions must be met to observe signal: (1) non-zero linear and/or quadratic vibronic coupling in the electronic excited state, (2) vibrational-coordinate dependence of the electronic transition dipole moment, or (3) electronic-state-dependent vibrational dephasing dynamics.

Development of Protocols to Perform Ab Initio Molecular Dynamics/Molecular Mechanics (AIMD/MM), XA, UV/Vis and IR Spectroscopies of Model Transition Metal and Mixed Valence Complexes in Water on the Ground and Electronic Excited States.[5-7] In order to study solvated model $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ complexes in water, we have performed extensive hybrid AIMD/MM based molecular dynamics simulations with NWChem. The FeRu dimer complex QM/MM model involved the solvation in a simulation box containing the dimer complex with 5000 water molecules to give a density close to 1 g/cm^3. The FeRuFe and FePtFe complexes contained 7919 and 5842 water molecules respectively to give a density close to 1 g/cm^3. The QM region in our approach comprises the transition metal complex, while the aqueous environment was treated using a MM representation. The QM region was treated with a hybrid exchange-

correlation functional (PBE0). Following the AIMD/MM runs, we extracted snapshots of the complex with an explicit solvation environment of water molecules from the trajectory to perform the XANES, UV/Vis, IR, EXAFS spectra calculations. The Fe K-edge XANES and UV/Vis spectra were calculated with our restricted excitation window (REW) TDDFT approach. We have extended our TDDFT code to capture the quadrupole transitions in the Fe K-edge XANES. For FePtFe, our extensive ground state calculations reveal that the closed-shell singlet configuration is the lowest energy state compared with the triplet configuration in agreement with experiment. This is in contrast to previously published theoretical work on this system that reported a lower triplet state. For the FeRu and FeRuFe complexes, we have developed a new theoretical approach to tackle the transient-XAS to probe the x-ray absorption response of the UV-Vis excited transition metal complex. Our calculations, so far, are in good agreement with experiment. We have also performed VtC-XES calculations on representative clusters of the FeRu and FeRuFe complexes. For these calculations, we treat the solvent environment explicitly, which results in systems of approx. 300-350 atoms. VtC-XES calculations using the ground and excited-state geometries for the FeRu and FeRuFe complexes have also been performed.

Simulations of Core-Resonant Circular Dichroism Signals.[8] Core-resonant circular dichroism (CD) signals are induced by molecular chirality and vanish for achiral molecules and racemic mixtures. The highly localized nature of core excitations makes them ideal probes of local chirality within molecules. Our simulations of the circular dichroism spectra of several molecular families illustrate how these signals vary with the electronic coupling to substitution groups, the distance between the X-ray chromophore and the chiral center, geometry, and chemical structure. Clear insight into the molecular structure is obtained through analysis of the X-ray CD spectra. Spin–orbit coupling (SOC) of the 2p electrons splits the XANES spectra and the electron–hole exchange interaction blurs the physical picture of the independent particle, thus the experimental intensity branching ratio of the transitions from the $2p_{3/2}$ and $2p_{1/2}$ orbitals may stray far from the ideal value of 2:1. Similarly, SOC should also play an important role in L-edge XCD. We neglected spin-orbit effects in our paper. However, there is every reason to expect that SOC should not affect the most important findings, *i.e.*, for molecules with a chiral center the amplitude of the XCD signals strongly decreases with the distance between the X-ray chromophore and the chiral center if the corresponding excitations are very localized to the excited atom, and that for globally chiral molecules the XCD signals also strongly depend on the chromophore position. A two-component TDDFT approach is under development for future XCD simulations including SOC of large molecules. This development potentially opens up new directions for our project.

Developing Protocols for Simulating Valence-to-Core X-ray Emission Spectroscopy.[9] Valence-to-Core X-ray Emission Spectroscopy (VtC-XES) is a sensitive tool to identify ligands and characterize ligand valence orbitals in transition metal complexes. In the past year we studied how linear-response time-dependent density functional theory (LR-TDDFT) can be extended to simulate K-edge VtC-XES reliably. LR-TDDFT allows one to go beyond the single-particle picture. Specifically, we developed a "black box" protocol in NWChem to simulate these spectra. A systematic study of the K-edge VtC-XES spectra of a series of low- and high-spin model Fe-, Mn- and Cr-complexes was performed and compared with experiment. Our results are in good agreement with experiment. The study also revealed that our method has advantages over the conventional single-particle DFT approach in describing VtC-XES features that have multi-configuration character.

Time-Resolved X-ray Spectroscopy of Hydrogen-Bonded Complexes.[10, 11] Our efforts to study intramolecular H-bonding dynamics by following changes in the local electronic structure around specific atoms have focused on the excited state proton transfer reaction of the conversion of 2-Thiopyridone (2TP) to the thiol (2-Mercaptopyridine, 2MP) following photoexcitation. We used picosecond XA spectroscopy at the sulfur K-edge to follow the excited state dynamics of 2-Thiopyridone (2TP) dissolved in acetonitrile following 400 nm excitation. Our work monitored the formation and decay of two transient species by following specific pre-edge absorption peaks at the sulfur K-edge. Time-dependent density functional theory was used to identify the two transient species as the lowest-lying triplet states of 2TP and 2MP, respectively. This study demonstrates transient sulfur K-edge XA spectroscopy as a sensitive and viable probe of time-evolving charge dynamics near sulfur sites in small molecules with future applications towards studying complex biological and material systems. Following the picosecond XA experiments, we initiated a collaboration with Prof. Alexander Föhlisch (Helmholtz-Zentrum Berlin) to develop resonant inelastic X-ray scattering spectroscopy (RIXS) at the N K-edge of H-bonded complexes to monitor charge density at the donor/acceptor site following proton transfer. Our work has revealed that the femtosecond excited-state dynamics following resonant photoexcitation enable the selective deformation of N-H and N-C chemical bonds in 2-thiopyridone in aqueous solution with optical and X-ray pulses, respectively. The orbital-specific electronic structure and its ultrafast dynamics is studied with RIXS at the N 1s level using synchrotron radiation and the soft X-ray free-electron laser at LCLS. The RIXS spectra provide direct evidence for the photoinduced molecular deformation on an ultrashort timescale.

Femtosecond X-ray Absorption and X-ray Emission Spectroscopy of Transition Metal Mixed Valence Complexes in Solution. We were awarded beam time at LCLS under proposal LJ67 for five shifts in October 2015 and four shifts in December 2016. During 2015, experiments were performed at the X-ray pump probe (XPP) instrument at LCLS using 800 nm laser light to photo excite the sample preceding X-ray measurements. Femtosecond XA and XE spectroscopies were used at the Fe K-edge to directly monitor transient oxidation states and orbital occupancy during charge transfer in a series of solvated mixed-valence complexes. A transition from Fe^{II} to Fe^{III} (as in FeRu) would result in a blue peak shift of ~0.2 eV and broadening of the $K\alpha_1$ peak consistent with the experimental transient XE result for FeRu. Transient XE spectra for FeRuFe exhibit the opposite, a red peak shift with spectral narrowing consistent with a Fe^{III} to Fe^{II} transition. Fits of the kinetic traces reveal that the initial MMCT from $Fe^{II}Ru^{III}$ to $Fe^{III}Ru^{II}$ and $Fe^{III}Ru^{II}Fe^{III}$ to $Fe^{II}Ru^{III}Fe^{III}$ occurs within the response of the instrument (50 fs) and the back electron transfer (BET) occurs within 100 fs for each compound. In the difference XA signal for FeRu, we see the growth of a transient feature upon MMCT which indicates that a hole is created in the t_{2g} orbital. The other XANES peaks undergo shifts to the blue upon photoexcitation and a change in the linewidth indicating the adjustments of the metal *d* orbitals following the initial MMCT. Simulations of the transient XANES features reveal the extent of electron delocalization during the MMCT process. We are currently preparing a manuscript outlining these results.

Femtosecond X-ray scattering of excited-state structural dynamics of solvated mixed-valence complexes. Ultrafast X-ray diffuse scattering (XDS) experiments at LCLS provide important insight to the early structural dynamics of photoexcited FeRu in water, and the coupling of solute-solvent interactions with the MMCT/BET dynamics. Analysis of the XDS data is well advanced, supported with equilibrium and non-equilibrium MD simulations of the solvent response is underway. Preliminary indications are that the change in oxidation state of the FeRu molecule couples to: (1) the bulk dielectric response of the solvent via solvent dipole interactions, and (2)

local solvation effects with specific changes in hydrogen bonding between solute ligands and solvent molecules. This is consistent with an interpretation that MMCT/BET dynamics are mediated in part by solute coupling to the solvation shell. We are currently writing a manuscript describing our results.

Besides the highlights given above, there were several publications outlining our efforts at developing ultrafast X-ray spectroscopy in the water window,[12] understanding vibrational relaxation in mixed valence complexes, [13] and benchmarking X-ray simulation protocols.[14]

DOE Supported Research in Peer-Reviewed Publications (2014- 2018):

[1] T. L. Courtney, Z. W. Fox, L. Estergreen, and M. Khalil,"Measuring coherently coupled intramolecular vibrational and charge-transfer dynamics with two-dimensional vibrational–electronic spectroscopy", The Journal of Physical Chemistry Letters **6** (2015) 1286-1292.

[2] T. L. Courtney, Z. W. Fox, K. M. Slenkamp, and M. Khalil,"Two-dimensional vibrational-electronic spectroscopy", The Journal of chemical physics **143** (2015) 154201.

[3] Z. W. Fox, T. J. Blair, R. B. Weakly, T. L. Courtney, and M. Khalil,"Implementation of continuous fast scanning detection in femtosecond fourier-transform two-dimensional vibrational-electronic spectroscopy to decrease data acquisition time", Review of Scientific Instruments **89** (2018) 113104.

[4] J. D. Gaynor, and M. Khalil,"Signatures of vibronic coupling in two-dimensional electronic-vibrational and vibrational-electronic spectroscopies", The Journal of chemical physics **147** (2017) 094202.

[5] M. Ross, A. Andersen, Z. W. Fox, Y. Zhang, K. Hong, J. H. Lee, A. Cordones, A. M. March, G. Doumy, S. H. Southworth, M. A. Marcus, R. W. Schoenlein, S. Mukamel, N. Govind, and M. Khalil,"Comprehensive experimental and computational spectroscopic study of hexacyanoferrate complexes in water: From infrared to x-ray wavelengths", The journal of physical chemistry. B **122** (2018) 5075-5086.

[6] M. Galib, M. D. Baer, L. B. Skinner, C. J. Mundy, T. Huthwelker, G. K. Schenter, C. J. Benmore, N. Govind, and J. L. Fulton,"Revisiting the hydration structure of aqueous na+", The Journal of chemical physics **146** (2017) 084504.

[7] K. Henzler, E. O. Fetisov, M. Galib, M. D. Baer, B. A. Legg, C. Borca, J. M. Xto, S. Pin, J. L. Fulton, G. K. Schenter, N. Govind, J. I. Siepmann, C. J. Mundy, T. Huthwelker, and J. J. De Yoreo,"Supersaturated calcium carbonate solutions are classical", Science Advances **4** (2018) eaao6283.

[8] Y. Zhang, J. R. Rouxel, J. Autschbach, N. Govind, and S. Mukamel,"X-ray circular dichroism signals: A unique probe of local molecular chirality", Chemical Science **8** (2017) 5969-5978.

[9] Y. Zhang, S. Mukamel, M. Khalil, and N. Govind,"Simulating valence-to-core x-ray emission spectroscopy of transition metal complexes with time-dependent density functional theory", Journal of Chemical Theory and Computation **11** (2015) 5804-5809.

[10] S. Eckert, J. Norell, P. S. Miedema, M. Beye, M. Fondell, W. Quevedo, B. Kennedy, M. Hantschmann, A. Pietzsch, B. E. Van Kuiken, M. Ross, M. P. Minitti, S. P. Moeller, W. F. Schlotter, M. Khalil, M. Odelius, and A. Fohlisch,"Ultrafast independent n-h and n-c bond deformation investigated with resonant inelastic x-ray scattering", Angew Chem Int Ed Engl **56** (2017) 6088-6092.

[11] B. E. V. Kuiken, M. R. Ross, M. L. Strader, A. A. Cordones, H. Cho, J. H. Lee, R. W. Schoenlein, and M. Khalil,"Picosecond sulfur k-edge x-ray absorption spectroscopy with applications to excited state proton transfer", Structural Dynamics **4** (2017) 044021.
[12] B. E. Van Kuiken, H. Cho, K. Hong, M. Khalil, R. W. Schoenlein, T. K. Kim, and N. Huse,"Time-resolved x-ray spectroscopy in the water window: Elucidating transient valence charge distributions in an aqueous fe(ii) complex", The Journal of Physical Chemistry Letters **7** (2016) 465-470.
[13] K. M. Slenkamp, M. S. Lynch, J. F. Brookes, C. C. Bannan, S. L. Daifuku, and M. Khalil,"Investigating vibrational relaxation in cyanide-bridged transition metal mixed-valence complexes using two-dimensional infrared and infrared pump-probe spectroscopies", Structural Dynamics **3** (2016) 023609.
[14] D. R. Mortensen, G. T. Seidler, J. J. Kas, N. Govind, C. P. Schwartz, S. Pemmaraju, and D. G. Prendergast,"Benchmark results and theoretical treatments for valence-to-core x-ray emission spectroscopy in transition metal compounds", Physical Review B **96** (2017) 125136.

DOE Supported Research in Ph.D. Theses (2014-2018):

1. Van Kuiken, Benjamin E. "Interrogating the Electronic Structure and Photochemistry of Molecules with Transient X-ray Absorption Spectroscopy." Ph.D., University of Washington, 2014.
2. Slenkamp, Karla M. "Examining the vibrational couplings and dynamics in cyanide-bridged transition metal mixed valence complexes using ultrafast nonlinear infrared spectroscopy" Ph.D., University of Washington, 2015.
3. Fox, Zachary W. "Two-Dimensional Vibrational-Electronic Spectroscopy: The Design and Development of a Novel Multidimensional Spectroscopic Technique to Directly Measure Coherent Coupling Between Vibrational and Electronic Degrees of Freedom." Ph.D., University of Washington, 2018.