Monitoring Excited State Charge Transfer of Transition Metal Mixed-Valence Complexes with Femtosecond X-ray Absorption and Emission Spectroscopy

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Abstract: Femtosecond X-ray absorption and emission spectroscopies are 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.

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1. Introduction

Developing an understanding of photochemical reactions at a molecular level requires experimental probes of coupled electronic and atomic motions of transient molecular species with femtosecond time resolution and atomic specificity. This information is key to both understanding and controlling energy flow during complex photochemical phenomena in chemistry, biology, and material science. The development of X-ray free electron lasers (XFELs) makes it possible to measure photochemical processes with high spatial and temporal resolution [1-3]. In this work, we use intense, sub-50 fs X-ray pulses at the Linac Coherent Light Source (LCLS) to monitor the changes in the electronic structure of transition metal mixed valence complexes at the Fe K-edge following metal-to-metal charge transfer excitation with an optical pump pulse.

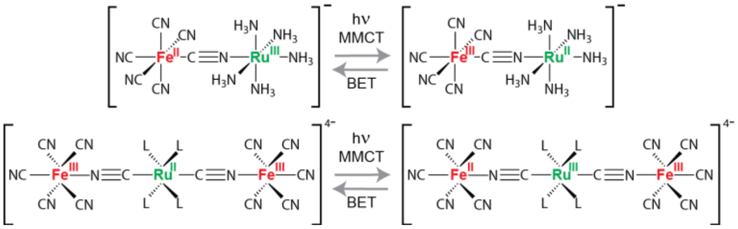

Fig. 1. Structures and photochemical reactions of mixed valence complexes studied in this work. L = pyridine

The solvated complexes in this work are shown in Fig. 1 and include $[(NH_3)_5Ru^{III}\text{-NC-}Fe^{II}(CN)_5]^-$ (FeRu), which undergoes an intramolecular MMCT of an electron from Fe^{II} to Ru^{III}, and *trans*-$[(NC)_5Fe^{III}\text{-CN-}Ru^{II}(L)_4\text{-NC-}Fe^{III}(CN)_5]^{4-}$ (FeRuFe), which undergoes an initial MMCT from Ru^{II} to Fe^{III}. Previous ultrafast transient optical and infrared absorption studies with FeRu have observed that the system returns to the ground electronic state via a back electron transfer (BET) within 200 fs following MMCT excitation [4, 5]. It has been difficult to directly measure the back electron transfer dynamics due to a lack of spatial sensitivity with optical and IR studies and the lack of adequate time resolution. Time-resolved X-ray absorption (XA) and emission (XE) spectroscopies are excellent tools to measure element-specific electronic structural changes in solution. X-ray absorption near edge structure (XANES) at the Fe K-edge is sensitive to the unfilled valence orbitals including quadrupole allowed 1s→3d transitions. As the metal and ligand orbitals are often strongly mixed in molecular systems, the XANES region reports on electronic delocalization in Fe complexes. The Kα and Kβ lines in the XE spectra result from the 2p →1s and 3p →1s transitions, respectively. The intensities, positions, and lineshapes of the transitions in the fluorescence spectra are extremely sensitive reporters of the electron-electron correlations, spin-orbit splitting, and the number of unpaired d electrons in the emitting atom. When the incident X-ray energy is tuned to the pre-edge region of transition metal K-edges, resonant inelastic X-ray scattering (RIXS) occurs. The higher frequency resolution in a RIXS measurement is achieved by spreading out the pre-edge features at the K-edge in two dimensions consisting of the incident energy and the transfer energy axes. In this work we use XA, XE and RIXS spectroscopies at the Fe K-edge to directly monitor the time-evolution of the charge transfer excited states of FeRu and FeRuFe dissolved in water following MMCT excitation.

2. Results and Discussion

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 [6]. All samples were flowed through a 50 μm free flowing circular jet in a He atmosphere providing fresh sample for each X-ray shot. XE experiments used a pink X-ray beam centered at 8 keV (45 fs, 120 Hz). The fluorescence emission lines were detected using spectrometers arranged in Von Hamos and Rowland circle geometries for the $K\beta_{1,2}$ and $K\alpha_1$ measurements, respectively. A channel-cut monochromator was placed in the X-ray path before the sample for the XA experiments. A constant emission energy (CEE) plane in the RIXS spectrum was measured by setting the Rowland spectrometer to detect at the peak of the $K\alpha_1$ energy (6.404 keV). The FeRu sample was a 30 mM aqueous solution and pumped with 4 μJ of 800 nm (40 fs) light, while the FeRuFe sample was a 40 mM aqueous solution and pumped with 10 μJ of 800 nm (40 fs) light. X-ray diffuse scattering (XDS) signals were also measured by placing a large area CSPAD detector directly behind the sample. Here, we will focus on the fs XA and XE experiments. Difference signals for XE and XA were constructed using X-ray pulses with and without laser excitation, *i.e.* [laser on (delay time) – laser off].

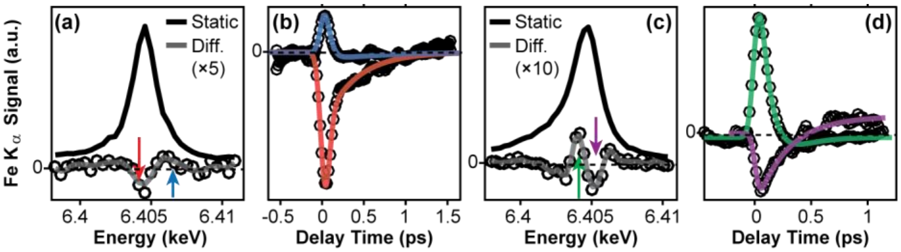

Fig. 2. Femtosecond Fe $K\alpha_1$ X-ray emission spectroscopy following 800 nm MMCT excitation of 30 mM FeRu (a-b) and 40 mM FeRuFe (c-d). The ground state XE spectra are shown as black solid lines and the black circles are the difference signals. The difference signals in figures (a) and (c) are obtained by integrating the data across the instrument response of 50 fs. The solid gray lines in (a) and (c) are obtained by applying a Sovitzky-Golay filter to the difference signal and are meant to guide the eye. The kinetic traces in (b)/(d) are plotted at energies indicated by the arrows in (a)/(c). The solid lines are fits to the data with an ~50 fs instrument response time.

Figure 2 displays the XE $K\alpha_1$ time-resolved spectral traces for FeRu (a-b) and FeRuFe (c-d) following 800 nm excitation. Static XE spectra for $[Fe^{x}(CN)_6]$ compounds (x = II and III) were used as a model to determine the expected shift upon MMCT in FeRu and FeRuFe. 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 (Fig. 2a). Transient XE spectra for FeRuFe (Fig. 2c) exhibits the opposite, a red peak shift with spectral narrowing consistent with an Fe^{III} to Fe^{II} transition. Preliminary fits of the kinetic trace data in Figs. 2 b and d reveal that the initial forward 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 BET occurs within 100 fs for each compound.

To explore the electron delocalization and metal-ligand interactions in the photoexcited charge transfer states of FeRu and FeRuFe, we used XA and RIXS spectroscopies following MMCT excitation. The results are shown in Fig. 3. The static ground state XA spectrum of FeRu in Fig 3(a) shows two transitions labelled B and C. We have performed TD-DFT calculations to assign transition B to quadrupolar contributions from Fe (1s) → Fe (3d, e_g) orbitals and also contributions to Fe (p) and C (p) orbitals. The peak labelled C includes contributions from Fe (1s) →Ru (4d, e_g) and Fe (1s) → Fe (3d, e_g) + Fe (p) + Ru (p). In the difference XA signal we see the growth of peak A which is a transition to Fe (1s) → Fe (3d, t_{2g}). The presence of this transient feature upon MMCT indicates that a hole is created in the t_{2g} orbital. Peaks B and C 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. The RIXS CEE spectrum of FeRu in Fig. 3(b) detected at an emission energy of 6.404 keV can be thought of as a high resolution XANES spectrum allowing us to clearly monitor changes along the metal-ligand-metal backbone during the MMCT and BET process. The XA and RIXS CEE spectra for FeRuFe in the ground state and following photoexcitation are plotted in Figs. 3(c-d). Here we see that the vacancy in the t_{2g} orbital of Fe as indicated by peak A is filled following MMCT from the Ru to the Fe atom. This change is accompanied by a reshaping and red-shifting of the peaks B and C in response to the new electronic configuration of the transient $Fe^{II}Ru^{III}Fe^{III}$ species.

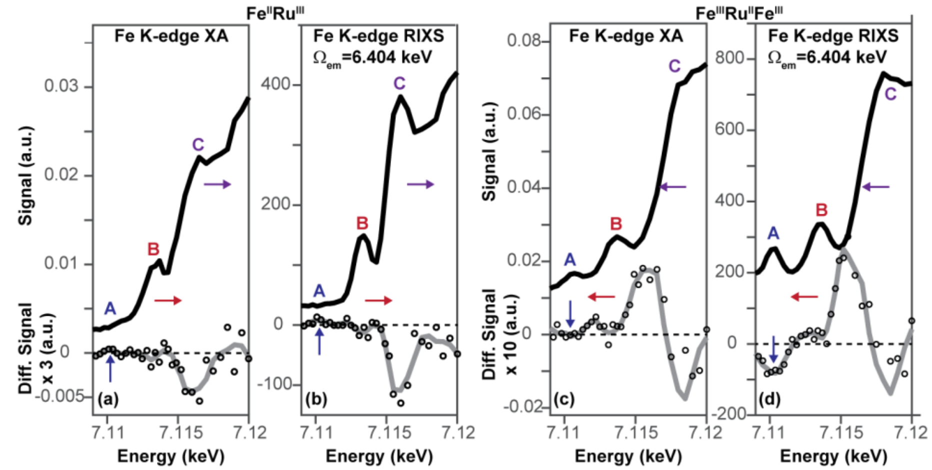

Fig. 3. Femtosecond Fe K-edge X-ray absorption and RIXS/CEE spectroscopy following 800 nm MMCT excitation of 30 mM FeRu (a-b) and 40 mM FeRuFe (c-d). The ground state XA and RIXS spectra are shown as black solid lines and the black circles are the difference signals. The difference signals in figures (a) and (c) are obtained by integrating the data across the instrument response of 50 fs. The solid gray lines in (a) and (c) are obtained by applying a Sovitzky-Golay filter to the difference signal and are meant to guide the eye. The peaks A, B and C are located at 7.110 (7.110) keV, 7.113 (7.114) keV and 7.116 (7.118) keV respectively for FeRu (FeRuFe) dissolved in water.

3. Summary

In summary, femtosecond XA and XE measurements are performed at the Fe K-edge on transition metal mixed valence compounds in solution at LCLS. The measurements provide a clear description of the time-evolving electronic structure at the atomic level during the MMCT and subsequent BET along the metal-ligand-metal backbone. While the initial MMCT is near instantaneous, the time resolution at LCLS allows the observation of the sub 100 fs BET process using complementary X-ray techniques.

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