

Ultrafast Charge Transfer and Electron Delocalization in a Cyanide-Bridged Ru-Ru Dimer Investigated with Femtosecond Transient X-Ray and IR Spectroscopies

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Abstract: Transient IR and X-Ray spectroscopies were used to investigate excited state delocalization of a mixed valence Ru based donor-bridge-acceptor complex on a femtosecond timescale revealing the role of the electron density on the Ru-CN-Ru fragment. © 2020 The Author(s)

Introduction: Characterizing the extent of electron delocalization on the excited states of donor-bridge-acceptor complexes remains an important target in the field of mixed-valence chemistry. Addressing this challenge, is a fundamental requirement for the targeted synthesis of the next generation of mixed-valence complexes designed for artificial light-harvesting and photocatalysis. In this work we use femtosecond transient IR (tIR) and advanced X-ray spectroscopies to study the photophysics of a Ru based donor-bridge-acceptor system, $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy})(\mu\text{-CN})\text{Ru}^{\text{II}}(\text{bpy})_2(\text{NCCH}_3)]^{3+}$ (Fig. 1a, ‘Ru dimer’). Recent studies have shown that there is Class III 4d electron delocalization in the photoexcited state of this complex (i.e. the Ru metal centers are strongly coupled according to the Robin-Day classification [1, 2]). However, the extent of electron delocalization and the resultant dynamics due to electronic coupling in the M-L-M bridge have not been studied and are the subject of this work.

Femtosecond X-ray spectroscopies are ideally suited to address the question of electron delocalization because they are sensitive to the local electronic and atomic structure in an element specific manner. Here, we utilize femtosecond X-ray absorption (XAS) and emission (XES) spectroscopy at the Ru L-edge to monitor the photoinduced delocalization of 4d electrons. X-ray pulses from the SwissFEL Alvrá Prime instrument were used to probe the ultrafast delocalization process in terms of the valence electron and hole motion following metal-to-ligand charge transfer (MLCT) excitation of the Ru dimer. We measure the Ru L₃-edge XAS which reports on the unoccupied valence orbitals ($2p_{3/2} \rightarrow 4d$). Simultaneously, the Lα XES was recorded, reporting on occupied orbitals ($3d \rightarrow 2p_{3/2}$) allowing for the collection of time-resolved 2p3d Ru resonant inelastic X-ray scattering (RIXS) maps. The energy difference between the incoming and outgoing photons corresponds to the energy splitting between the 3d and 4d levels (see Fig. 1c) and thus reports on the arrangements of the 3d and 4d electrons.

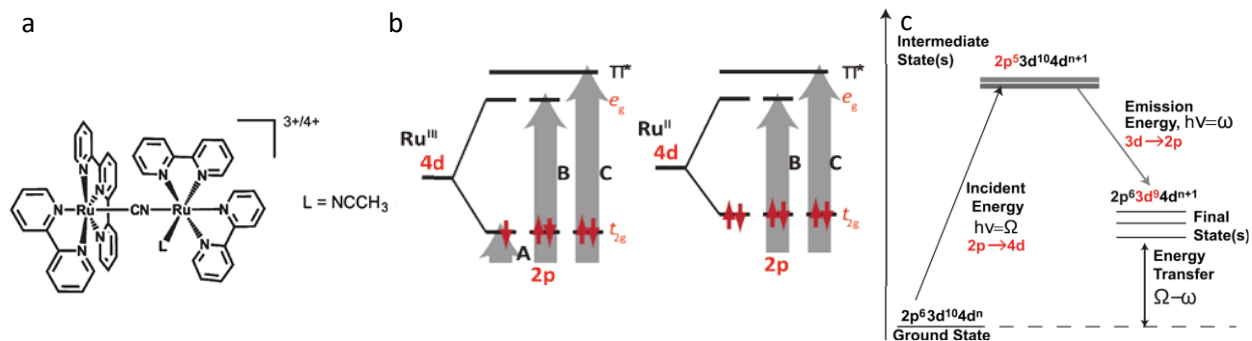


Figure 1: a. The Ru-Ru mixed valence complex (ground state charge = 3^+ , $\text{L} = \text{CH}_3\text{CN}$). b. Energy diagrams detailing the Ru^{II} and Ru^{III} L-edge absorption transitions. The A transition corresponds to $2p \rightarrow 4d$ (Ru , t_{2g}), B corresponds to $2p \rightarrow 4d$ (Ru , e_g), and C corresponds to $2p \rightarrow 4d$ ($\text{Ru} + \text{CN } \pi^*$). c. Diagram of the Ru 2p3d RIXS process including the electron configurations of the ground, intermediate, and final states.

Experimental Methods: The Ru dimer was synthesized using previously published procedures [1] and was dissolved in acetonitrile to prepare 20 mM solutions for the experiments. The tIR experiments were performed using an experimental set-up described previously [3]. The 20 mM sample was delivered by a 50 μm spaced flow cell to minimize sample damage. The pump pulse was centered at 400 nm (30 fs, 1.2 $\mu\text{J}/\text{pulse}$, 1 kHz) and the IR probe pulse was centered at $\sim 2100\text{ cm}^{-1}$ (80 fs, 1 $\mu\text{J}/\text{pulse}$, 1 kHz). The transient X-Ray experiments were performed at the Alva endstation of the SwissFEL facility at the Paul Scherrer Institute in Villigen, Switzerland [4]. The X-ray experiment was done in a helium atmosphere and the sample was delivered by a 50 μm cylindrical jet. The incident X-rays were scanned across the Ru L_3 -edge (2838-2850 eV) and the X-Ray emission from the sample was analyzed with a photodiode to capture total fluorescence yield XAS spectra. A von Hamos type spectrometer (0.3 eV resolution) was used in tandem to disperse the emitted X-Rays with a Si (111) crystal onto an array detector to monitor the $L\alpha$ emission lines ($\sim 2558\text{ eV}$). The sample was excited using a 400 nm pulses (50 fs, 1.2 $\mu\text{J}/\text{pulse}$, 25 Hz) and probed with X-ray pulses ($\sim 2.8\text{ keV}$, 24 fs, 200-500 $\mu\text{J}/\text{pulse}$, 50 Hz).

Results and Discussion:

Transient Infrared Spectroscopy: We utilized transient IR spectroscopy to probe the ultrafast dynamics that occur in the Ru dimer after photoexcitation through the response of the cyanide bridging ligand. Upon photoexcitation, a broad, asymmetric excited state absorption (ESA), $\sim 2050\text{ cm}^{-1}$, and a ground state bleach (GSB), $\sim 2100\text{ cm}^{-1}$, are observed (Fig. 2a). The observed excited state frequency is in good agreement with previous spectro-electrochemical studies [1] and the red-shift reflects increased electron delocalization in the excited state. Further analysis of the ESA reveals two ultrafast decay constants during the $\sim 50\text{ ns}$ excited state lifetime (Fig. 2b). The time constants of $0.70 \pm 0.10\text{ ps}$ and $6.40 \pm 0.17\text{ ps}$ were extracted by fitting the tIR difference signal at 2034 cm^{-1} and 2050 cm^{-1} , respectively.

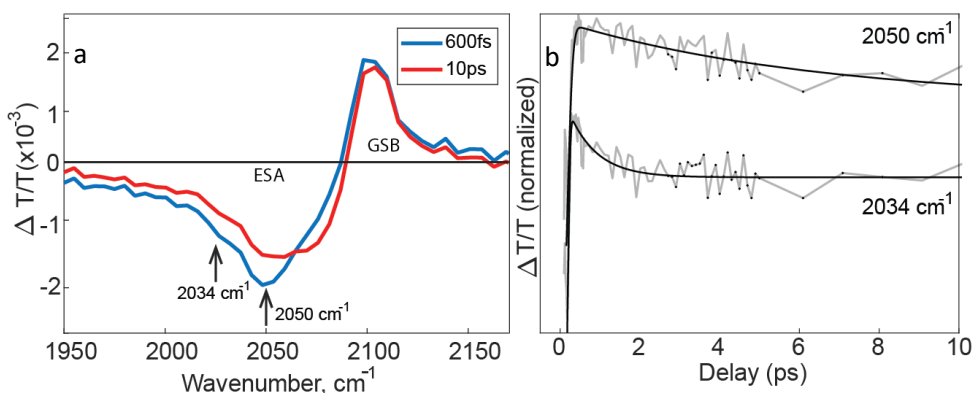


Figure 2: a: IR difference spectra in the cyanide stretching region of the Ru dimer at 600 fs and 10 ps. The GSB does not change significantly as a function of time, but the peak shape, intensity, and position of the ESA appears to have time dependence on the femtosecond-picosecond timescale. b: The tIR signal intensities at 2034 cm^{-1} and 2050 cm^{-1} were recorded as a function of time and subsequently fit with a single exponential decay (black) yielding time constants of $\sim 0.70\text{ ps}$ and $\sim 6.40\text{ ps}$ respectively.

It has been shown in similar systems [5], that upon MLCT photoexcitation there is an ultrafast intersystem crossing (within the instrument resolution) from a $^1\text{MLCT}$ state to a manifold of $^3\text{MLCT}$ states. The identity and nature of these $^3\text{MLCT}$ states have been shown to carry important information about the extent of charge delocalization in similar mixed-valence systems [6]. As the CN bridge is strongly sensitive to π backbonding interactions with both of the Ru centers, the interactions between the 4d electrons and the bridge likely play a strong role in the transient charge delocalization processes resulting in the time-evolution of the ESA feature in the tIR signal.

Transient X-Ray Spectroscopy: Transient Ru L-edge X-Ray spectroscopies directly probe the local Ru electron density. Transient XAS (t-XAS) of the Ru dimer at 600 fs and 10 ps (Fig. 3a,b) presents three main features: A, B and C (shown schematically in Fig. 1b) which indicate transient changes in the electron density around the metal and ligands [7]. The A peak grows in at 2838 eV, which corresponds to a hole in the t_{2g} orbitals appearing upon photoexcitation, and the B peak undergoes a frequency shift to 2841 eV, a change in the energies of the e_g orbitals. These both correspond to a transient oxidation state change from Ru^{II} to Ru^{III} [3]. The C feature reports on the 4d electron density present in the Ru-CN-Ru fragment. From Fig. 3b, we note that the signal-to-noise of the t-XAS is not high enough to observe any ultrafast changes in the difference spectrum. However, difference spectra created from the 2p3d RIXS map's constant incident energy (CIE) cut at the C peak (2842.5 eV, Fig. 3c/d) do show a clear transient change between 600 fs and 10 ps. This suggests that dynamic changes in the electron density in the Ru-CN-Ru fragment play a significant role in the delocalization dynamics that occur after photoexcitation. This study demonstrates the first use of femtosecond Ru 2p3d RIXS to monitor excited state electron density changes in a donor-bridge acceptor complex.

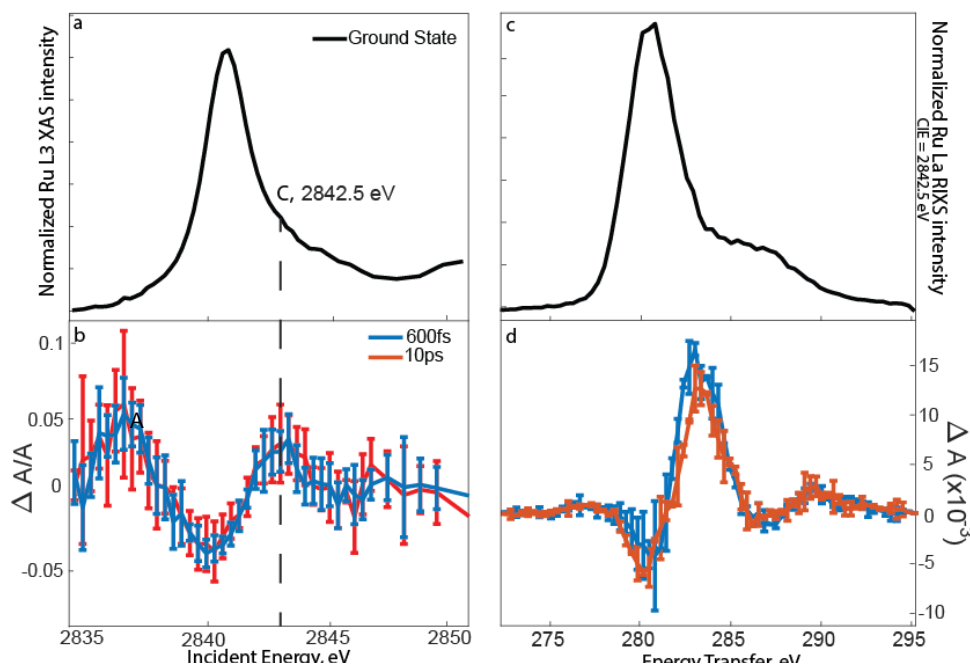


Figure 3: a: The ground state L_3 XAS spectrum of the Ru dimer. b: t-XAS difference spectra at 600 fs and 10 ps with error bars corresponding to the standard error of the measurement. The maxima/minima of the A, B, and C features in the difference spectra occur at 2838 eV, 2840 eV, and 2842.5 eV. c: The ground state CIE RIXS cut taken at 2842.5 eV (C feature). d: Difference spectra of the CIE cut taken at 600 fs and 10 ps. The highest degree of change between the two difference spectra can be seen at 280 eV and 284 eV in energy transfer.

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