

Following Metal-to-Ligand Charge-Transfer Dynamics with Ligand and Spin Specificity using Femtosecond Resonant Inelastic X-ray Scattering at the Nitrogen K-Edge

Raphael M. Jay,^{1,†} Sebastian Eckert,^{1,2} Benjamin E. Van Kuiken,^{3,} Miguel Ochmann,⁴ Markus Hantschmann,^{1,2} Amy A. Cordones,⁵ Hana Cho,^{5,6,\$} Kiryong Hong,^{6,\$} Rory Ma,^{4,6,&} Jae Hyuk Lee,^{5,&} Joshua Turner,^{7,8} Michael P. Minitti,⁷ Wilson Quevedo,² Annette Pietzsch,² Martin Beye,^{2,||} Tae Kyu Kim,⁹ Robert. W. Schoenlein,⁵ Philippe Wernet,¹⁰ Alexander Föhlisch^{1,2} and Nils Huse^{4,*}*

¹Institut für Physik und Astronomie, Universität Potsdam, 14476 Potsdam, Germany

²Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin für Materialien und Energie, 12489 Berlin, Germany

³European XFEL, 22869 Schenefeld, Germany

⁴Department of Physics, University of Hamburg and Center for Free-Electron Laser Science, 22761 Hamburg, Germany

⁵Ultrafast X-ray Science Lab, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

⁶Department of Chemistry and Chemistry Institute of Functional Materials, Pusan National University, Busan 46241, South Korea

⁷Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA

⁸Stanford Institute for Materials and Energy Sciences, Stanford University, Stanford, CA 94305, USA

⁹Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea

¹⁰Department of Physics and Astronomy, Uppsala University, 75121 Uppsala, Sweden

AUTHOR INFORMATION

Corresponding Author

*Email: benjamin.van.kuiken@xfel.eu, nils.huse@uni-hamburg.de

Present address

[†]Department of Physics and Astronomy, Uppsala University, 75121 Uppsala, Sweden

[§]Center for Analytical Chemistry, Division of Chemical and Medical Metrology, Korea Research Institute of Standards and Science, Daejeon 34113, Republic of Korea

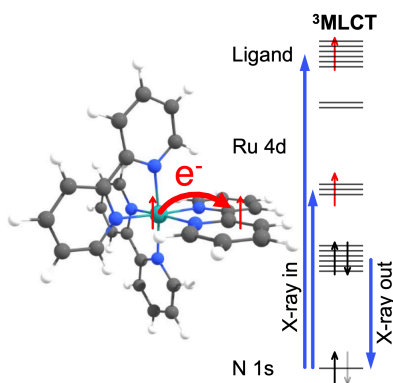
[§]Center for Gas Analysis, Division of Chemical and Medical Metrology, Korea Research Institute of Standards and Science, Daejeon 34113, Republic of Korea

[&]Pohang Accelerator Laboratory, Pohang, Gyeongbuk 37673, Republic of Korea

^{||}DESY Photon Science, 22607 Hamburg, Germany

Abstract: We demonstrate for the case of photo-excited $[\text{Ru}(\text{2,2' -bipyridine})_3]^{2+}$ how femtosecond resonant inelastic X-ray scattering (RIXS) at the ligand K-edge allows to uniquely probe changes in the valence electronic structure following a metal-to-ligand charge-transfer (MLCT) excitation. Metal-ligand hybridization is probed by Nitrogen-1s resonances providing information on both, the electron-accepting ligand in the MLCT state and the hole density of the metal center. By comparing to spectrum calculations based on density functional theory, we are able to distinguish the electronic structure of the electron-accepting ligand and the other ligands and determine a temporal upper limit of (250 ± 40) fs for electron localization following the charge-transfer excitation. The spin of the localized electron is deduced from the selection rules of the RIXS process establishing new experimental capabilities for probing transient charge and spin densities.

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Charge-transfer excitations are the initiating step of many photochemical reactions involving transition metal complexes. Owing to its wide applicability in fields like light-harvesting^{1,2} and

photocatalysis³, the metal-to-ligand charge-transfer (MLCT) excitation in $[\text{Ru}(\text{bpy})_3]^{2+}$ (where bpy = 2,2'-bipyridine) constitutes the prototypical example of such a process. Specifically, the system and its derivatives are investigated as photo-induced electron donors in potential inflammatory sensors⁴, water splitting⁵ and enzyme triggering reactions⁶, and as dye sensitizers models^{7–10} as well as active moieties in phototherapy^{11,12} and molecular switches^{13,14}. On an intra-molecular level, the charge-transfer process is initiated by an optical excitation, which elevates a Ru-4d electron into an unoccupied bpy π^* orbital. This effectively oxidizes the metal center, while reducing one bpy ligand and thereby breaking the symmetry of the electronic ground state. Ultrafast transient absorption and emission studies have established that the lowest charge-transfer excitation of many polypyridyl Iron(II) and Ruthenium(II) complexes from their singlet ground-state results in the initial population of a $^1\text{MLCT}$ state, which has a substantial spin admixture of the lower-lying $^3\text{MLCT}$ manifold, resulting in very fast intersystem crossing into a $^3\text{MLCT}$ state within tens of femtoseconds^{15–17}. In $[\text{Ru}(\text{bpy})_3]^{2+}$, the possibly delocalized initial charge distribution of the MLCT state triggers a solvent response that stabilizes the charge distribution of the MLCT state. From optical spectroscopy it has been concluded that the transferred electron is localized on one of the three bpy ligands^{18–20}. The localized electron will still hop between ligands but is stabilized by solute-solvent interactions analogous to a polaron in a crystalline solid (an excited electron localized in the center of a lattice distortion that forms in response to the sudden creation of a mobile charge carrier). While optical spectroscopy provides robust measures of the involved timescales, the broad and overlapping spectral features are often difficult to relate to the electronic structure and spin configuration of the excited state^{13,21–24}. Ideally, spectroscopic information from specific atomic sites would allow following and characterizing the relaxation from the initially

excited charge-transfer excitation to localized partial charge densities, i.e. an electron-hole pair determined by Coulomb and covalent metal-ligand interactions.

Atomic site-sensitivity can be provided by X-ray spectroscopy. By projecting a highly localized core orbital onto delocalized valence orbitals in an X-ray absorption process, the chemical environment around the absorbing atomic species can be characterized. Picosecond X-ray absorption experiments at the Ru K and L-edge of $[\text{Ru}(\text{bpy})_3]^{2+}$ and similar systems established subtle changes in metal-ligand bond lengths as a result of the formation of the $^3\text{MLCT}$ state^{25,26}.

More importantly, changes in the local valence electronic structure and the ligand field around the Ru center, which result from the metal-center's photo-induced oxidation, could be determined using L-edge absorption spectroscopy^{8,25}. However, with the underlying metal $2p \rightarrow 4d$ transitions primarily being sensitive to the hole in the metal d orbitals, L-edge absorption spectroscopy is limited in providing information on the transferred electron. The latter is only indirectly observed through changes in covalent metal-ligand interactions which modulate the Coulomb and exchange interactions that influence the L-edge line shape. An ultrafast spectroscopic probe that can adapt both, a metal- and ligand-centered view, within one process would indeed provide the necessary information on the transient charge density of an intra-molecular electron-hole pair.

We present femtosecond resonant inelastic soft X-ray scattering²⁷ (RIXS) at the K-edge of ligand atoms, specifically at the Nitrogen K-edge^{28–32}, as such a probe: Resonant N 1s core-excitations, which promote ligand core-electrons to unoccupied metal-centered orbitals with subsequent resonant emission from ligand-centered valence electrons, report on the charge density of the ligand modulated by charge density changes at the metal. This provides simultaneous information on the transferred electron as well as the hole on the metal and is manifested in valence excitation spectra deep into the vacuum ultraviolet regime specific to certain chemical sites^{33,34}. Due to the

underlying spin selection rules governing the dipole transitions of the RIXS process in the soft X-ray photon range, the contained spectral information also gives information on different spin states, since specific valence excited final states are only dipole-allowed in specific spin configurations of the system.

Thus far, time-resolved RIXS in the soft X-ray regime has been employed in L-edge measurements on iron complexes in order to follow the evolution of the valence electronic structure locally at the metal center during ligand-exchange^{35–37} and charge-transfer dynamics^{38,39}. At the N K-edge, however, only time-resolved X-ray absorption studies on transition metal complexes have previously been realized^{32,40,41}, while time-resolved RIXS has only been used to study the transiently deprotonated N site in an organic molecule³⁴. In the case of charge-transfer excited $[\text{Ru}(\text{bpy})_3]^{2+}$, time-resolved N K-edge RIXS allows one to directly access, distinguish and evaluate the valence electronic structure of the different bpy groups (electron-accepting and non-electron-accepting) and follow the electron-hole pair in time since the spectroscopic probe also includes the metal valence charge density. Thereby, our results and analysis provide a robust temporal upper limit for electron and hole localization by exploiting the sensitivity of our experimental method to the dynamics of charge-transfer excitations for both, electron and hole. We utilize the spin-selection rules of N K-edge RIXS to demonstrate how such ultrafast measurements can follow the spin crossover associated with the MLCT excitation.

Figure 1 shows the molecular structure as well as steady-state RIXS data of $[\text{Ru}(\text{bpy})_3]^{2+}$ measured at the N K-edge. The data is acquired by simultaneously scanning the incident energy and pump-probe delay. By integrating over all pump-probe delays $t < 0$, the steady-state RIXS map is generated. The RIXS map is displayed as a function of the energy transfer, which corresponds to the energy of the valence-excited final states of the RIXS process. By integrating

along the energy transfer axis, the partial fluorescence yield (PFY) X-ray absorption spectrum (XAS) can be generated. It is dominated by a single intense transition at 399.6 eV, which can be assigned to the elevation of a N 1s core-electron into the unoccupied bpy π^* manifold. In the two-step approximation of the RIXS process, the core-excitation is followed by a resonant emission step, whose spectrum is additionally shown on the left in Fig. 1. It is acquired by integrating the RIXS map along the incident energy axis across the main absorption resonance between 399.15 eV and 399.85 eV. The resonant emission spectrum exhibits a feature at 0 eV energy transfer corresponding to elastic scattering. The most intense feature is located at 7 eV energy transfer followed by additional features with lower intensity up until 25 eV energy transfer. The general shape of the spectrum is similar to previous measurements on $[\text{Fe}(\text{bpy})_3]^{2+}$, where the resonant emission originated mostly from the recombination of electrons occupying ligand-centered orbitals of the bpy ligand with the N 1s core-hole²⁸.

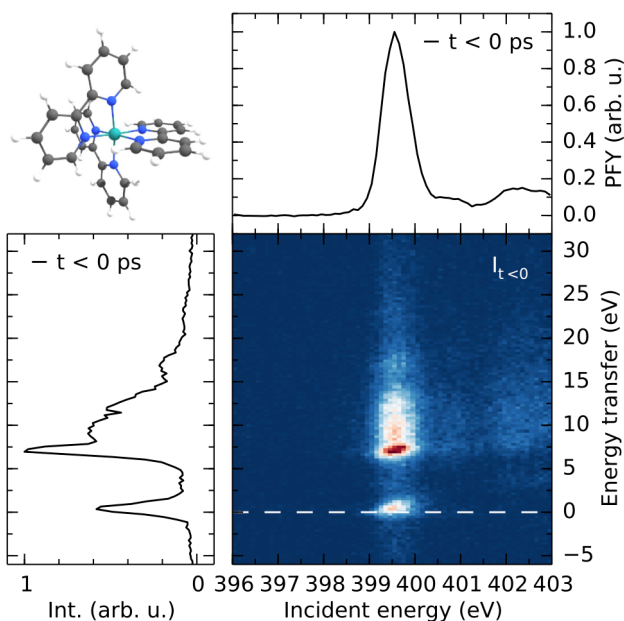


Fig. 1. DFT-optimized molecular structure and steady-state N K-edge RIXS map of aqueous $[\text{Ru}(\text{bpy})_3]^{2+}$. By Integrating along the energy transfer axis, the PFY spectrum (shown on top) is acquired. On the left, a resonant emission spectrum is displayed, which is acquired by integrating across the main absorption line.

Figure 2a shows the PFY XAS spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ for positive and negative pump-probe delays. The individual spectra are normalized to the number of FEL shots, which are included in the respective delay range. The spectra are then scaled so that the maximum of the ground state spectrum is unity to visualize the relative magnitude of the spectral changes upon laser excitation. The absorption of an optical photon causes a decrease of the main X-ray absorption resonance as well as an intensity increase before and after the main resonance. To isolate the laser-induced changes in the PFY spectrum, Fig. 2b shows the difference between the two spectra from Fig. 2a. The observed spectral changes upon photo-excitation are well described by the calculated difference spectrum. The calculation is based on time-dependent density functional theory (TD-

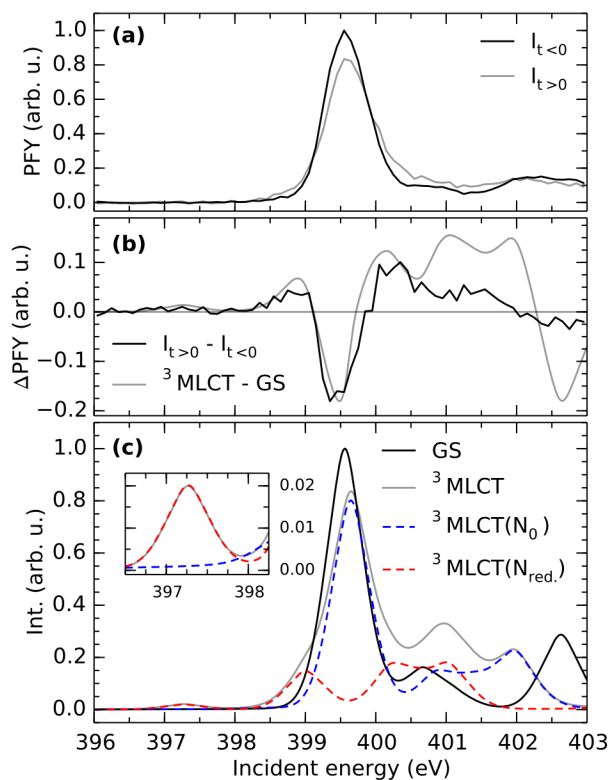


Fig. 2. (a) PFY XAS of $[\text{Ru}(\text{bpy})_3]^{2+}$ for negative and positive pump-probe delays in the range of -1.5 to +1.5 ps. (b) Difference PFY between the two spectra from (a) compared to a calculated difference spectrum between the $^3\text{MLCT}$ state and the ground state of $[\text{Ru}(\text{bpy})_3]^{2+}$. (c) Calculated spectra of the ground state (GS) and the $^3\text{MLCT}$. The spectrum of the $^3\text{MLCT}$ state is further broken down into contributions from the two N_{red} atoms of the electron-accepting bpy ligand and the four N_0 sites of the spectator ligands.

DFT) and carried out for each unique N atom. In the case of the ground state, the molecule is sufficiently symmetric that the XAS spectrum resulting from creation of a core-hole on any one of the N atoms is equivalent. Due to the symmetry reduction associated with the MLCT excitation, however, the spectrum of the $^3\text{MLCT}$ is the sum of six TD-DFT spectra. The calculated difference spectrum is then generated as the weighted difference between the excited and ground state spectrum and scaled to the maximum of the depletion in the experimental data at 399.45 eV. The calculation shows very good agreement with the experiment, reproducing the depletion of the main absorption line at 399.45 eV and the signal increase below and above the main absorption line.

In order to rationalize the dominant core-excitations causing the spectral trends observed in the experimental PFY spectrum, Fig. 2c shows the simulated spectra of the ground state and the $^3\text{MLCT}$ state as well as a breakdown of the $^3\text{MLCT}$ spectrum into contributions from different ligands. The spectrum of the $^3\text{MLCT}$ can be divided into contributions from the electron-accepting reduced bpy group (denoted as N_{red}) and the two other bpy groups (denoted as N_0), which merely act as spectators of the charge-transfer excitation. This distinction is motivated by the observation that the orbital of the transferred electron is clearly localized at a single bpy group (see Supporting information). The good agreement of such a description with experiment reinforces previous notions of a localized electron in the $^3\text{MLCT}$ state¹⁹ and for the first time ties the associated reduction of symmetry to differences in the underlying electronic structure between the two types of ligands.

The general character of the spectrum of the N_0 sites is very similar to the ground state spectrum, however slightly shifted to higher energies. This is due to the N_0 sites mainly experiencing the effective oxidation of the Ru center as a result of the charge-transfer excitation. The depopulation of the Ru t_{2g} orbitals reduces the Coulomb-repulsion between the N_0 ligands and the metal. This

leads to an increase in σ -donation, a relation, which has previously been observed also for other charge-transfer excitations^{39,42}. These changes in covalency cause the N 1s core-level energies to drop by on average 0.4 eV at the N₀ sites, which shifts the transitions to higher energy^{32,43}.

A completely different spectral behavior can be observed for the N_{red.} sites. There, the intensity of the main π^* resonance is drastically reduced and shifted to lower energy (see Supporting information for associated difference density) causing the emergence of the pre-edge feature at 398.8 eV in the experimental difference spectrum in Fig. 2b. The energetic shift, however, can be associated with the increase of electron density on the ligand caused by the MLCT process and results in a 0.5 eV increase in the N 1s orbital energy. The decrease in intensity can be attributed to the fact that the lowest-lying π^* orbital is half-filled in the MLCT state. Additionally, the calculations in Fig. 2c suggest a new low-energy resonance to appear for the N_{red.} sites at 397.3 eV. The character of this resonance can be clearly assigned to a N 1s \rightarrow Ru t_{2g} excitation (see Supporting information). This feature becomes visible in the N_{red.} spectrum because the increase in the N_{red.} 1s orbital energy and the presence of the t_{2g} hole yield a lowered excitation energy, which is separated from the rest of the N K-edge XAS spectrum. Secondly, while the N 1s \rightarrow Ru t_{2g} transition is formally forbidden, the Ru-based t_{2g} acceptor orbital exhibits a small amount ($\sim 2\%$) of N_{red.} p-character providing dipole intensity. The new transition therefore constitutes a direct fingerprint for the depopulation of metal d orbitals and thus local oxidation of the metal center by the MLCT excitation as seen from the N K-edge⁴¹. It should be noted, that the experimental difference PFY spectrum shows no significant intensity increase in the range of 397.3 eV. However, in the following, we provide unambiguous experimental evidence for the presence of this transition, which allows one to selectively access the reduced bpy ligand of the ³MLCT state and extract the corresponding site-specific RIXS spectrum.

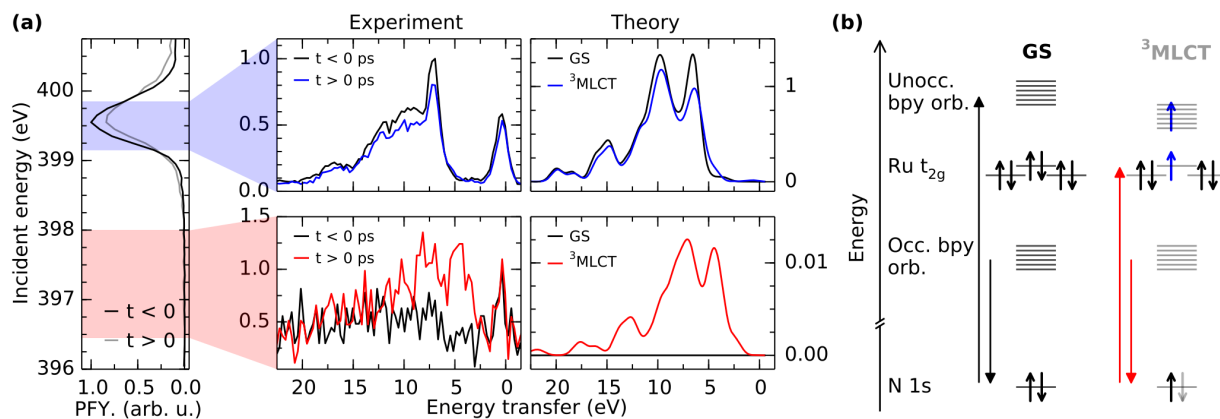


Fig. 3. (a) Experimental RIXS spectra for negative and positive pump-probe delays compared to calculated RIXS spectra. The experimental spectra are acquired by integrating the incident energy across the regions marked in the PFY spectrum displayed on the left. The calculated spectra are based on the single-electron approximation and evaluated for excitation energies within the experimental incident energy regions. **(b)** Schematic representation of the observed RIXS transitions based on a single-electron picture.

Fig. 3a shows experimental RIXS spectra integrated over the incident energy region of the ground state π^* resonance (marked blue) as well as the t_{2g} resonance (marked red) for positive and negative pump-probe delays. Most importantly, the latter shows an emergence of intensity after at energy transfers between 3 eV and 13 eV following the optical excitation. The detected fluorescence in this range clearly demonstrates the presence of a resonant excitation for the $^3\text{MLCT}$ state at this incident energy as predicted by the calculations in Fig. 2c. This is despite the resonance not rising above the noise level in the experimental PFY difference spectrum in Fig. 2b, because it is acquired by integrating over a wide range of energy transfers. In the RIXS spectrum recorded at the ground state π^* resonance, a uniform decrease of intensity up until 20 eV energy transfer can be observed reflecting the overall decrease of the main absorption line in the PFY spectrum upon optical excitation.

In order to rationalize the spectral features in the transient RIXS spectra, calculated RIXS spectra based on a one-electron picture (see Supporting information) are additionally presented in Fig. 3a. The calculated RIXS spectra show good qualitative agreement with the experiment. The overall decrease in intensity at the ground state π^* resonance is reproduced as well as the emergence of fluorescence in the range of the t_{2g} resonance which is absent before the optical excitation. It should be emphasized that, despite minor variations, the general shape of the RIXS spectra is maintained after the optical excitation and is very similar at the two different excitation energies. This indicates that the orbitals and their energies involved in the X-ray emission step of the RIXS process largely remain the same and the variations in final state energies can for the most part be rationalized by the underlying differences in X-ray excitation energies in the different incident energy regions. This is illustrated by the molecular orbital diagram displayed in Fig. 3b. As has been mentioned previously, the ground state RIXS spectrum following an excitation at the π^* resonance is characterized by electronic decays dominantly from occupied bpy orbitals resulting in ligand-centered valence-excited final states²⁸. In the case of at the newly opened t_{2g} resonance, however, the system is core-excited at lower incident energy. With emission energies remaining constant, this creates new low-energy valence excited final states of dominantly ligand-to-metal charge-transfer (LMCT) character.

Additionally, due the half-filled Ru t_{2g} level in the $^3\text{MLCT}$ state (compare Fig. 3b), core-excitation at the t_{2g} resonance creates exclusively spin-down core-holes. The Pauli exclusion principle for Fermions and spin selection rules of dipole transitions ($\Delta S = 0$) therefore dictate that only spin-down electrons can subsequently fill the N 1s core-hole following the core-excitation. This allows one to retrieve information about the spin state of the system from the spectra measured at the t_{2g} resonance, since the spin-up electron occupying the bpy π^* orbital in the $^3\text{MLCT}$ state

cannot recombine with the spin-down N 1s core-hole, although the two orbitals have significant overlap. Such a transition is, however, allowed as long as the system is in the initially populated ¹MLCT configuration. Exploiting these selection rules therefore introduces sensitivity to the spin state of the charge-transfer excited state. As will be shown in the following, this opens up novel opportunities to temporally follow the earliest transients involved in the charge-transfer dynamics.

The spectral changes discussed so far were averaged over all negative and positive delays and have been assigned to dominantly correspond to the presence of the ground and the ³MLCT state, respectively. To follow the spectral changes as a function of pump-probe delay, Fig. 4 shows the full difference RIXS map with the experimental PFY difference spectrum from Fig. 2b above. Incident energy regions A and C correspond to the regions discussed in Fig. 3, while B and D cover regions before and after the main edge. To increase the signal-to-noise ratio, region A is restricted to the area for which an increase in intensity could be observed in Fig. 3 (elastic scattering as well as positive energy losses). Area A' is additionally introduced as a spectral region which will be discussed separately. By integrating the scattered photons within the marked regions for time intervals of 70 fs, the time traces shown on the right of Fig. 4 can be extracted (errors deduced from \sqrt{N} of detected photons within a spectral region). To visualize the relative magnitude of the spectral changes in the individual regions, the traces are normalized to the integrated signal of region C before time-zero (intensity of the ground state π^* -resonance). The relative changes detected in the regions A to D are modeled by a step-function, which is broadened by a Gaussian. The good description of the data by the fit demonstrates that the dominant signal changes happen synchronously and within the (250 ± 40) fs rise-time of the step-function. This assessment again confirms the previously drawn conclusion that the ³MLCT state is the species dominantly contributing to the observed spectral changes. Furthermore, due to the good description of the

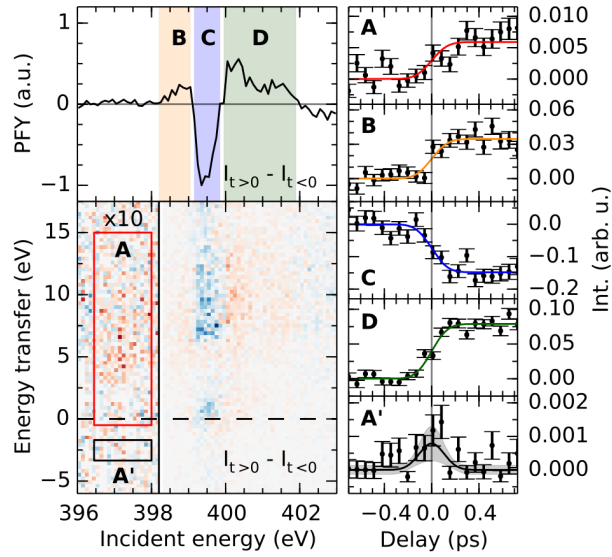


Fig. 4. Delay traces acquired by integration over spectral ranges in the difference PFY spectrum as well as the difference RIXS map. The temporal evolution of the spectral signatures can for the most part be described by the emergence of the $^3\text{MLCT}$ state within the time-resolution of the experiment.

observed spectral changes by a localized $^3\text{MLCT}$ state, the retrieved rise-time of 250 fs can be established as an upper limit for electron localization in $[\text{Ru}(\text{bpy})_3]^{2+}$ in agreement with previous transient absorption experiments^{19,20}.

Traces of an additional species can be identified which do not correspond to the formation of the $^3\text{MLCT}$ state, but instead point towards the short-lived $^1\text{MLCT}$ state. For a discussion of this observation, we turn to region A', which is located at the t_{2g} resonance of the $^3\text{MLCT}$ state and at negative energy transfer (compare Fig. 4). As discussed previously, the core-excitation at the t_{2g} resonance only creates spin-down Nitrogen-1s core-holes. Due to spin selection rules, this core-hole can therefore only be efficiently filled by the decay of the transferred electron via a dipole transition as long as the system is in the initial $^1\text{MLCT}$ state with a singlet spin configuration right after the optical excitation. Region A' is thus centered at a negative energy transfer which exactly corresponds to the energy of the optical excitation (see Experimental details). Conceptually, this

can be understood as energy, which is deposited in the system by absorption of an optical photon and subsequently added to the energy of the core-excitation. An Anti-Stokes transition³⁷ then results in a net gain in energy of the emitted X-rays and the final state character of this transition therefore corresponds to the singlet ground state of $[\text{Ru}(\text{bpy})_3]^{2+}$. Such Anti-Stokes transitions have been previously observed in L-edge RIXS measurements^{35–37} and calculations³⁸, where they have been characterized to constitute unique spectroscopic fingerprints of short-lived transient intermediates during photochemical reactions. The delay trace derived from region A', however, cannot be considered statistically significant evidence for an Anti-Stokes line. This is not surprising given that the lifetime of the $^1\text{MLCT}$ state has been reported to be on the order of 20 fs by theory⁴⁴ as well as experiment¹⁶. Still, the increase in intensity around time-zero points towards the presence of such a feature. To guide the eye, the delay trace retrieved from region A', is therefore fitted with a Gaussian function (shaded area refers to 95% confidence interval), whose temporal width corresponds to the previously determined signal rise-time and exceeds the $^1\text{MLCT}$ lifetime by one order of magnitude. While the data presented here does not constitute an unambiguous detection of the $^1\text{MLCT}$ state, it provides a template for the design of future experiments with the improved time-resolution and count rates at upcoming high-repetition rate XFEL facilities.

In summary, we have shown how time-resolved RIXS at the ligand K-edge can be a powerful tool to follow charge-transfer dynamics in transition metal complexes. In particular, by directly evaluating the differences in the electronic structure between the electron-accepting and non-electron-accepting ligands, the method confirms the localized nature of the $^3\text{MLCT}$ state of $[\text{Ru}(\text{bpy})_3]^{2+}$ on time-scales upward of 250 fs and uniquely provides valence excitation spectra specific to the reduced ligand. Furthermore, by exploiting the stringent selection rules of the RIXS

process, new experimental schemes could be proposed which would allow to capture and characterize the elusive primary $^1\text{MLCT}$ state. Such experiments, which are expected to be routinely performed at upcoming high-repetition rate X-ray free electron lasers, would nicely complement studies using femtosecond $\text{K}\beta$ X-ray emission spectroscopy, a technique, which is powerful in terms of determining the spin-state of the metal center but, due to its purely metal-centric character, struggles to distinguish between $^1\text{MLCT}$ and $^3\text{MLCT}$ states^{45–48}.

ASSOCIATED CONTENT

Chemicals and materials, experimental and computation details, isosurfaces of selected molecular orbitals (Figure S1) transition orbitals (Figure S2) as well as additional RIXS data (S3) not shown in the main text.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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