## Direct observation of coherent femtosecond solvent reorganization coupled to intramolecular electron transfer

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#### 1 Abstract

It is well known that the solvent plays a critical role in ultrafast electron transfer reactions. However, solvent reorganization occurs on multiple length scales, and selectively measuring short-range solute–solvent interactions at the atomic level with femtosecond time resolution remains a challenge. Here we report femtosecond X-ray scattering and emission measurements following photoinduced charge-transfer excitation in a mixed-valence bimetallic (Fe<sup>II</sup>Ru<sup>III</sup>) complex in water, and their interpretation using non-equilibrium molecular dynamics (MD) simulations. Combined experimental and computational analysis reveals that the charge-transfer excited state has a lifetime of 62 fs and that coherent translational motions of the first solvation shell are coupled to the back electron transfer. Our MD simulations identify that the observed coherent translational motions arise from hydrogen bonding changes between the solute and nearby water molecules upon photoexcitation, and have amplitude of tenths of Å, 120-200 cm<sup>-1</sup> frequency, and ~100 fs relaxation time. This study provides an atomistic view of coherent solvent reorganization mediating ultrafast intramolecular electron transfer.

### 2 Introduction

Ultrafast photoinduced electron transfer reactions are the key steps governing natural and artificial energy conversion processes and are therefore the subject of intense experimental and theoretical studies across several fields of chemistry [1]. A thorough understanding of electron transfer in the condensed phase requires detailing the complex couplings between electronic and atomic degrees of freedom in the solute and the surrounding solvent [2, 3, 4, 5, 6]. Femtosecond electronic and vibrational spectroscopic studies have shown that solute–solvent dynamics critically affect the energetics and the rates of electron transfer [7, 8]. However, the role of specific solute–solvent interactions in ultrafast electron transfer processes remains largely unexplored. This is because time-resolved optical spectroscopy methods measure the solvent reorganization energy in response to a change in electronic charge distribution, often termed dielectric solvation, by averaging over all length-scales in the solvent response and thus obscuring

the detailed nature of the specific solute–solvent interactions [9, 10, 11, 12]. In particular, time-resolved fluorescence Stokes shift measurements have been used extensively to investigate dielectric solvation and have been found to report mostly on the dipolar solvent response [9, 10, 13]. Time-resolved nonlinear IR spectroscopy techniques have advanced our understanding of solute-solvent interactions, but separating the effects of inter- and intra-molecular interactions on experimental observables is demanding, making it difficult to connect solvation dynamics to changes in the vibrational spectrum [14, 15, 16, 17]. To date, an atomic level mechanistic understanding of solvation dynamics upon electron transfer has been derived primarily from molecular dynamics (MD) simulations [13, 18, 19, 20, 21]. Femtosecond X-ray pulses available at X-ray free electron lasers (XFELs) provide a powerful new tool to monitor the photoinduced ultrafast motions of electrons and nuclei in solvated molecular systems. In particular, time-resolved X-ray solution scattering (XSS) at XFELs directly probes, at the atomic spatial and temporal scales, the photoinduced changes of all the atom-pair distances [22, 23]. These observables can be directly compared with the atomic positions calculated by MD simulations, enabling direct tracking of photoinduced structural dynamics and the accompanying changes in the solvation shell structure [24, 25, 26]. In this work, we use femtosecond XSS, in combination with non-equilibrium MD simulations, to provide a real space picture of short-range, specific solvent motions coupled to electron transfer. Our results fill in an important knowledge gap in our understanding of electron transfer reactions in solution.



Figure 1: Mixed-valence complex under study and experimental setup. a) FeRu molecule in water. 800 nm excitation induces metal-to-metal charge-transfer (MMCT) from the Fe to the Ru center, followed by ultrafast back electron transfer (BET). The interatomic distances probed by the elastically scattered X-rays are classified into solute–solute (intramolecular), solute–solvent, and solvent–solvent atom pair distances. b) Schematic of the experimental setup: a combination of a large area detector and a von Hamos emission spectrometer allows for the detection of both elastic scattering and the Fe K $\beta$  fluorescence as a function of laser pump-X-ray probe time delay. Adapted from Ref. [27] with permission from the Royal Society of Chemistry

Cyanide-bridged mixed valence transition metal complexes, like  $[NCFe^{II}(CN)_5(NH_3)_5Ru^{III}]^-$ (FeRu, see Fig. 1a), have served as invaluable platforms for advancing our understanding of electron transfer reactions [1, 3, 8]. In these systems, the metal-to-metal chargetransfer (MMCT) excitation is short-lived (~ 100 fs) and followed by ultrafast back

electron transfer (BET), and the electronic and nuclear dynamics are strongly coupled, as reported by nonlinear optical, infrared and two-dimensional vibrational electronic spectroscopy experiments [8, 28, 29, 30]. In FeRu, 800 nm photoexcitation promotes an electron from the Fe to the Ru center ( $Fe^{II}Ru^{III} \rightarrow Fe^{III}Ru^{II}$ ). Barbara and coworkers observed a BET time of  $\sim 89$  fs in water and found that this value depends on the solvent [29]. Since the BET timescale was found to be slower in deuterated water, the authors concluded that hydrogenic solvent motions, in particular librations, are directly involved in the electron transfer process. However, as discussed in a later work by Barbara and coworkers on a complex similar to FeRu [31], no direct correlation between librations or other solvent motions and electron transfer process could be established, since disentangling the spectroscopic signatures of vibrational relaxation and solvation dynamics is challenging. How specific solute-solvent interactions affect the photoinduced dynamics of FeRu and related mixed valence complexes is an important open question. It is well established that both the cyano and amine ligand groups of FeRu support specific hydrogen bonding interactions with the solvent, causing solvatochromic shifts of their charge-transfer absorption bands [32, 33], and modulating the vibronic and vibrational couplings of the ligands [34, 35]. For FeRu in water, these ligand-solvent hydrogen bonding interactions are expected to be weaker in the MMCT state (Fe<sup>III</sup>Ru<sup>II</sup>) than in the ground state (Fe<sup>II</sup>Ru<sup>III</sup>) [36, 37]. Changes in the specific solute–solvent interactions of hydrogen-bonding molecules like FeRu cannot be properly accounted for using a simple continuum solvation model, and quantitative experimental measurements of these interactions are indispensable.

To track the photoinduced ultrafast motions of electrons and nuclei coupled to the MMCT excitation of FeRu in water, we use a combination of time-resolved X-ray emission spectroscopy (XES) and XSS (Fig. 1b), as in recent experiments [25, 27]. 1s3p K $\beta_{1,3}$  XES reports on the local Fe oxidation and spin state [38], and therefore provides a real time measure of the electron transfer process. The XES measurement can be correlated with the structural information obtained from XSS, since the two signals are recorded simultaneously. By describing the couplings with the solvent through electrostatic interactions in a classical MD framework, we find that the time-dependent XSS signal is dominated by contributions from the water structural reorganization, reflecting large changes in excited-state ligand-solvent interactions and minimal intramolecular structural changes in the excited state of the solute. Ultimately, the combination of femtosecond XSS, XES, and MD simulations enables the direct observation of the solute–solvent reorganization dynamics in response to photoinduced MMCT and subsequent BET in FeRu with femtosecond and sub-Angstrom resolution.

#### **3** Results and Discussion

#### 3.1 Ultrafast BET characterized by Fe K $\beta$ XES

Figure 2a shows the Fe K $\beta$  XES difference spectra measured 50 fs after 800 nm excitation of FeRu in water. This signal can be described by a reference spectrum constructed from the difference between the K $\beta$  spectra of  $[Fe^{II}(CN)_6]^{3-}$  and  $[Fe^{II}(CN)_6]^{4-}$  identifying the changes in electronic structure of FeRu following MMCT excitation. Only the amplitude of measured K $\beta$  signal shows significant time dependence (Supplementary Fig. 4) and a fit of the reference spectrum to the entire dataset (Supplementary Eq. 1) yields the MMCT fraction of molecules at each time-delay, as shown in Fig. 2b. This signal (blue points) is overlaid with a fit (red line) of an exponential decay starting at time-zero, broadened by a Gaussian instrument response function (IRF), and summed to an offset (Supplementary Eq. 2). From the fit, we find an initial excitation fraction of  $25 \pm 4$  %,  $62 \pm 10$  fs MMCT state lifetime, an IRF of ~ 80 fs (FWHM), and a 1 % offset. This offset, corresponding to a minor excitation channel, is further discussed in Supplementary Discussion 4. Barbara and coworkers had previously reported a similar MMCT lifetime ( $89 \pm 10$  fs) [29]. The MMCT excited state lifetime obtained from the analysis of the Fe K $\beta$  XES is used in the interpretation of the XSS data described in the following section.



Figure 2: Fe K $\beta$  XES tracks the MMCT excited state population. (a) Fe K $\beta$  XES difference spectrum (blue) measured 50 fs after excitation. This spectrum is described by the difference of the measured K $\beta$  XES spectra of Fe(III)- and Fe(II)- hexacyanide. (b) The time-dependent fraction of molecules in the MMCT state obtained by fitting the reference spectrum to the time-dependent K $\beta$  data. The red line is a fit of a IRF-broadened exponential decay with lifetime of 62 ± 10 fs plus offset.

# 3.2 Ultrafast solute–solvent interactions dominate the XSS signal

Figure 3a shows the isotropic difference scattering signal  $\Delta S(Q,t)$  measured upon 800 nm photoexcitation of FeRu as a function of pump-probe time delay and scattering vector Q. As detailed in previous work [23, 39, 40], this signal arises from photoinduced changes in the solute–solute, solute–solvent, and solvent–solvent atom pair distances in the sample (examples of which are illustrated in Fig. 1a):

$$\Delta S(Q,t) = \Delta S^{\text{solute-solute}}(Q,t) + \Delta S^{\text{solute-solvent}}(Q,t) + \Delta S^{\text{solvent-solvent}}(Q,t).$$
(1)

The difference scattering signal at  $Q < 1.5 \text{ Å}^{-1}$  arises from changes in solute–solute and solute–solvent distances. In the first 100 fs after excitation, a negative signal develops in the low-Q region (below 0.8 Å<sup>-1</sup>), which is indicative of an increase of atom pair distances [23, 25]. On the same time-scale a positive peak grows in with maximum intensity at ~ 1.3 Å<sup>-1</sup> and shifts towards lower Q value with increasing time delay, yielding an oscillatory feature in the time evolution of the low-Q signal.



Figure 3: The XSS signal. a) Isotropic difference scattering signal measured upon 800 nm excitation of FeRu in water as a function of pump-probe time-delay and scattering vector Q. The signal at  $Q < 1.5 \text{ Å}^{-1}$  arises from changes in intramolecular and solute–solvent distances, while the signal at  $Q < 1.5 \text{ Å}^{-1}$  reports on the increase in temperature of the water. b) Time evolution of both measured and calculated difference scattering signal averaged in a scattering vector range between 0.4 and 0.6 Å<sup>-1</sup>. The calculated signal is the results of non-equilibrium MD simulations (see Fig. 5).

This oscillatory feature is evident in Fig. 3b, which shows a cut at  $Q=0.5 \pm 0.1$  Å<sup>-1</sup> of the measured difference scattering data. This oscillation is indicative of coherent motion involving an expansion of atom-pair distances and subsequent relaxation to the original value. Since the oscillation period (~390 fs, Supplementary Fig. 8) is not attributable to any intramolecular vibrations, and the short lifetime of the MMCT precludes large intramolecular structural rearrangements, we tentatively conclude that the low-Q signal is dominated by solvent reorganization. This conclusion is tested below by comparison with MD simulations.

At  $Q > 1.5 \text{ Å}^{-1}$ , the difference scattering signal develops on the ps timescale and has the same Q-dependence as the signal measured for water when temperature is increased at constant volume [41]. This comprises the  $\Delta S^{\text{solvent-solvent}}(Q,t)$  contribution to Eq. 1 and provides direct access to the energy transfer from the solute to the solvent. The  $\Delta S^{\text{solvent-solvent}}(Q,t)$  component is analyzed and subtracted from the data as described in Supplementary Discussion 3 and it is not further considered here.

We focus our analysis on the difference scattering signal arising from changes in solute–solute and solute–solvent atom pair distances. This is done by comparison of the XSS data with the scattering signals calculated from the solute–solute and solute–solvent radial distribution functions (RDFs) generated by MD simulations ( $\Delta S_{sim}^{solute-solute}$  and  $\Delta S_{sim}^{solute-solvent}$ , respectively). In the MD simulations, we used the solute structure and electrostatic potential (ESP) partial charges in the GS and MMCT state calculated using explicit solvent time-dependent density functional theory (TDDFT). The structures were fixed and embedded in a water box, as described in the Methods.



Figure 4: Difference scattering signals calculated from equilibrium MD simulations of the GS and MMCT state of FeRu in water. The solute–solute signal (blue line), which arises from changes between the GS and MMCT TDDFT calculated FeRu structures, is neglegible with respect to the solute–solvent signal (magenta line). The solute–solvent signal arising from changes in solute structure (mechanical, red crosses) is neglegible with respect to that arising from the response to change in solute partial charges (dielectric, green circles).

Equilibrium MD simulations of the GS and MMCT state of FeRu were initially performed. Fig. 4 shows the  $\Delta S_{sim}^{solute-solute}$  (blue line) and  $\Delta S_{sim}^{solute-solvent}$  (magenta line) signals obtained from the difference of the MMCT and GS scattering simulations. The main distinction between the TDDFT-calculated structures is a ~0.13 Å contraction of the Fe-Ru distance in the MMCT state with respect to the GS. This yields a small positive contribution in the low-Q region of the  $\Delta S_{sim}^{solute-solute}$  signal, inconsistent with the measurements. Further intramolecular structural considerations were also unable to reproduce the experimental data, and are described in Supplementary Discussion 4. In contrast,  $\Delta S_{sim}^{solute-solvent}$  shows a negative signal in the low-Q region, consistent with the measured data, reflecting the increased solute-solvent distances in the excited state compared to the ground state. The magnitude of  $\Delta S_{sim}^{solute-solvent}$  is much larger than that of  $\Delta S_{sim}^{solute-solute}$ , indicating that the measured difference scattering signal at  $Q < 1.5 Å^{-1}$  is dominated by solvent reorganization.

There are two possible contributions to the solute–solvent interactions that dominate the scattering signal: (i) the response of the solvent to the changes in charge distribution (dielectric solvation), and (ii) the response of the solvent to the changes in solute size (mechanical solvation). These contributions can be distinguished through additional equilibrium MD simulations, modelled after previous work [20, 42]. Two distinct excited-state models of FeRu are constructed based on: (i) the GS structure and the MMCT partial charges (purely dielectric), and (ii) the MMCT structure and the GS partial charges (purely mechanical). Fig. 4 shows the difference scattering traces obtained from these two models, making it clear that dielectric contributions dominate and mechanical ones can be neglected. Therefore,  $\Delta S^{\text{solute-solvent}}$  is attributed to photoinduced changes in the electrostatic interaction between FeRu and water molecules. The simulated increase in solute–solvent distances is consistent with the expected weakening of hydrogen bonds in the excited state compared to the ground state, as discussed below.



Figure 5: Non-equilibrium MD simulations describe the measured solvation dynamics. a) Measured difference scattering signal after subtracting the well-characterized  $\Delta S^{solvent-solvent}(Q,t)$  contribution due to the temperature increase of bulk water. A 3-point median filter along the time-axis is applied to the data. b-c-d) Difference scattering signals calculated from non-equilibrium MD simulations and arising from changes in solute–solvent atom pair distances. Five simulations with different t<sub>BET</sub> were performed. As an example, panel c) and d) show the difference scattering signals calculated from non-equilibrium MD simulations with BET at 60 fs and 150 fs, respectively. Panel b) shows the final simulation obtained by a linear combination of the five simulations according to the MMCT state fraction and lifetime, obtained from the analysis of the Fe K $\beta$  data. Calculated signals are convoluted with the IRF.

To describe the solvation dynamics upon 800 nm excitation of FeRu in water, we performed non-equilibrium MD simulations [20, 42, 43, 44]. We aim to reproduce and interpret the measured difference scattering signal after removal of the  $\Delta S^{\text{solvent-solvent}}$ contribution, as shown in Fig. 5a. Based on the above discussion, intramolecular structural changes of FeRu do not contribute significantly to the measured difference scattering signal shown in Fig. 5a and were therefore neglected in the simulations. The non-equilibrium simulations start from 1000 configurations from the equilibrium MD simulation of FeRu in the GS. At t=0, the partial charges of the solute are switched to the MMCT values, creating a non-equilibrium configuration, and the subsequent non-equilibrium dynamics are recorded every 10 fs. After a time delay of  $t=t_{BET}$ , the atomic charges of the solute are switched back to the GS values, mimicking BET. Five non-equilibrium simulations were run with  $t_{BET} = 30, 60, 90, 150, and 210$  fs. Figures 5c,d show the results obtained with BET at 60 and 150 fs, respectively, while the other simulations are presented in Supplementary Fig. 12. Each simulation reproduces the main features observed in the measurements: the negative low-Q signal indicative of expansion of solute–solvent distances, and the positive feature at  $\sim 1.3$  Å<sup>-1</sup> that shifts with increasing time to lower Q values, yielding a time-dependent oscillation in the low-Q signal. The final simulated  $\Delta S(Q,t)$  shown in Fig. 5b is then constructed as a linear combination of the five simulation results, weighted according to the exponential MMCT decay measured by K $\beta$  XES (see Supplementary Fig. 13). This non-equilibrium simulation qualitatively reproduces the measured features both in Q and time, and effectively captures the time-oscillatory feature observed in the low-Q part of the measured scattering signal, as shown in Fig. 3b. The analysis of the MD simulations reveals that collective water translational motions arising from a change in the hydrogen bond strength with FeRu are responsible for the key features of the data, as described in the next section.



Figure 6: Results of non-equilibrium MD simulations. a)  $N_{Fe}$ -O RDF as a function of time, with MMCT excitation at t=0 and BET at t = 60 fs. The RDF of the equilibrated MMCT state is shown for reference (black line). b,c) Time-evolution of the 1st solvation shell peak position for the N<sub>Fe</sub>-O and N<sub>Ru</sub>-O RDFs, respectively. The simulations can be described by a linear fit at early times, before BET (dashed pink line), and by a damped oscillator at later times, after BET (red line). b) The first solvation shell surrounding the N<sub>Fe</sub> atoms expands with an average velocity of 2.5 Å/ps upon MMCT. BET initiates contraction of the solvation shell, which oscillates with a period of 165 ± 2 fs and is damped in 104 ± 9 fs. c) For the first solvation shells surrounding the N<sub>Ru</sub> atoms, the velocity of the initial expansion is 1.8 Å/ps, followed by 174 ± 9 fs oscillations, which are damped in 77 ± 10 fs.

## 3.3 Coherent translational motion of the first solvation shell coupled to BET

Analysis of the MD simulations reveals atomic scale information about solvent reorganization. As detailed in Supplementary Discussion 6, the simulation shows a highly structured and oriented first solvation shell for the electronic ground state of FeRu. This results from hydrogen bonding between water and (1) the H-bond accepting nitrogens of the cyano-ligands bound to Fe (N<sub>Fe</sub>) and (2) the H-bond donating nitrogens of the amines-ligands bound to Ru (N<sub>Ru</sub>). We therefore illustrate the motions of the first solvent shell by the changes in the hydrogen-bonded atom pairs distances. Figure 6a shows the temporal evolution of the N<sub>Fe</sub>-O RDF from the non-equilibrium MD simulation with  $t_{BET} = 60$  fs. This RDF shifts to a higher distance (r) upon MMCT and reverses direction upon BET, overshooting the original position and undergoing a damped oscillation back to the GS position.

The oscillatory motion of the first solvation shell is clearly evident in Figs. 6b,c, which plot the distance (r) corresponding to the maximum of the N<sub>Fe</sub>-O and N<sub>Ru</sub>-O RDFs as a function of time. A linear fit for time delays < 60 fs yields average expansion velocities of 2.5 Å/ps and 1.8 Å/ps of the first solvent shells around the Fe and Ru ligands respectively, upon MMCT. Maximum displacements of 0.15 Å (Fe) and 0.11 Å (Ru) are reached at t=60 fs, where BET is initiated. Using a damped oscillator model to characterize the subsequent temporal evolution, we find that the oscillations of the N<sub>Fe</sub>-O and N<sub>Ru</sub>-O RDFs have a frequency of approximately 200 cm<sup>-1</sup> and 180 cm<sup>-1</sup>, respectively, and relaxation times of ~100 fs. In considering all the non-equilibrium simulations with varying t<sub>BET</sub> (Supplementary Discussion 6), the oscillation frequency varies from 120 cm<sup>-1</sup> to 200 cm<sup>-1</sup>, with the smaller frequency corresponding to later BET, as expected from the anharmonicity of the solute–solvent interaction potential. The observed frequencies are in good agreement with the ~180 cm<sup>-1</sup> peak present in the low-frequency vibrational spectrum of water and assigned to translational motions of the intermolecular hydrogen bonding coordinate [45].

Overall, analysis of the simulated RDFs indicates that: (1) the low-Q difference scattering signal measured at the shortest time delays ( $< t_{BET}$ ) arises from the coherent center-of-mass translation of water molecules away from FeRu as hydrogen bonding is weakened due to the MMCT transition, and (2) the subsequent temporal oscillation in the low-Q difference scattering signal reflects the return of the solvation shell upon BET, as mediated by the intermolecular hydrogen bonding coordinate of water. These solvent translational motions can be described using a classical model that takes into account photoinduced changes in electrostatic interactions between the solute and solvent atoms. These are described in our MD simulations by using different sets of atomic partial charges for the GS and MMCT state of FeRu. An extended analysis (Supplementary Discussion 6) indicates that additional rotational and diffusional motions play a minor role in the structural reorganization of the first solvation shell on the MMCT and BET timescales.

Finally, a quantitative analysis of the solute–solvent interaction energy from the non-equilibrium MD simulations reveals that linear response theory fails to describe the BET process in FeRu (see Supplementary Fig. 21). This observation is in agreement with earlier computational studies of mechanical solvation, where translational motions are found to lead to breakdown of linear response theory [43, 44, 46]. The energetic contributions of the water translational motions observed in our experiment to the overall solvent response upon electron transfer requires a full quantum-mechanical treatment of the solute–solvent interactions, as discussed in Supplementary Discussion 7.

#### 4 Conclusions

We use FeRu as a prototype for studying the influence of the solvent in intramolecular electron transfer reactions. The electron transfer between the Fe and Ru atoms in FeRu changes the oxidation state of the metal centers and, as a consequence of different metal-ligand interactions, the electronic charge distribution on the ligand atoms. This leads to a change both in the molecular dipole moment ( estimated to be 3.5 Debye from the calculated partial charges) and in the strengths of the hydrogen bond interactions between the ligands and the surrounding water molecules. Previous studies of dielectric solvation in water by traditional optical techniques, such as fluorescence Stokes shift experiments, have shown that dipolar solvation is dominated by longrange high-frequency motions (librations) of the water molecules [9]. These studies are, however, relatively insensitive to changes in the hydrogen bonding between the solute and the solvent [13, 47, 48]. Optical pump-probe spectroscopy studies could not directly identify the solvent modes promoting the electron transfer in FeRu and similar mixed-valence systems [29, 31]. In this work, we have exploited the unique sensitivity of time-resolved XSS to changes in solute-solvent distances to capture the first solvation shell reorganization due to changes in the short-range solute-solvent electrostatic interactions upon MMCT excitation of FeRu. By analysing the time-resolved XSS signal in combination with the Fe K $\beta$  XES data recorded simultaneously and with non-equilibrium MD simulations, we found that a large (tenths of Å) coherent  $(\sim 180 \text{ cm}^{-1})$  translational motion of the water molecules hydrogen-bonded to FeRu is coupled to the photoinduced MMCT and subsequent ultrafast (62 fs) BET. We therefore conclude that the observed coherent water translational motions contribute to the reorganization energy of the electron transfer process in FeRu, as well as the water librations and the FeRu intramolecular vibrations previously considered [7, 29, 31]. Our work demonstrates the strong modification of solute–solvent hydrogen bonding induced by electronic excitation of the solute and addresses the long standing question of how specific solute–solvent interactions respond to intramolecular electron transfer.

Translational solvent motions have also been proposed to be important for controlling electron transfer dynamics in non aqueous solvent. For example, they are thought to be responsible for the electron detachment in charge-transfer to solvent excitation of the sodium atom [21, 42]. However, these motions were not directly observed. The ability to directly monitor the local translational motions, and to reveal the detailed nature of the first solvation shell interactions with the solute, paves the way for a mechanistic understanding of solvation processes coupled to charge-transfer reactions in solution, beyond the traditional description based on continuum solvent models and linear response. This will enable systematic and quantitative descriptions of how electron transfer is influenced by both solute and solvent molecular properties, to ultimately control and exploit such processes. Finally, specific hydrogen bonding interactions can play a critical role in biologically relevant chemical reactions, for example influencing the conformational changes critical to protein function [49, 50]. Our method could thus be applied to understand how specific solute–solvent interactions influence a wider range of chemical reactions.

#### 5 Methods

#### 5.1 Data collection and reduction

The experiment was performed at the X-ray pump probe (XPP) instrument at the Linac Coherent Light Source (LCLS) XFEL. A 30 mM aqueous solution of FeRu was delivered through a nozzle producing a 50  $\mu$ m circular liquid jet and recirculated, in a He environment. At t=0, the sample was pumped with 4  $\mu$ J of 800 nm laser pulses of 45 fs (FWHM) duration and 100 x 120  $\mu$ m<sup>2</sup> spot size. After excitation, the sample was probed with 8 keV X-ray pulses (45 fs FWHM) at time delays ranging from -0.4 ps to 1.5 ps at a repetition rate of 120 Hz. The liquid jet pump speed was chosen so that fresh sample was hit for every pump-probe event. The time delay between the laser and the X-ray pulses was determined for every pump-probe event with ~10 fs (FWHM) resolution using the XPP timing-tool [51].

Four cylindrically bent (0.5 m radius) Ge(620) crystal analyzers were arranged in von Hamos geometry to diffract the Fe 3p-1s K $\beta_{1,3}$  fluorescence from the sample onto a 140k Cornell-SLAC Pixel Array Detector (CSPAD) [52], covering a Bragg angle from 78.2° to 80.6° and a energy range from 7.03 eV to 7.08 eV. The total ground state fluorescence spectra were corrected for background and common mode noise and scaled to the ground state spectra of ferrocyanide (as detailed in Supplementary Discussion 1). Reference K $\beta$  fluorescence spectra of ferrocyanide ([Fe(II)(CN)<sub>6</sub>]<sup>4-</sup>) and ferricyanide ([Fe(III)(CN)<sub>6</sub>]<sup>3-</sup>) were measured at beamline 7-ID-D at the APS using the same conditions and emission spectrometer described in reference [37].

At LCLS, elastically scattered X-rays were collected on a 2.3M CSPAD placed after the sample and perpendicular to the propagation direction of the X-ray beam, covering scattering vector Q up to 4.5 Å<sup>-1</sup>. Two-dimensional scattering patterns were corrected for X-ray polarization and solid-angle before extracting one-dimensional isotropic and anisotropic scattering signals, following a procedure previously published [53]. The analysis of the anisotropic part of the scattering signal is presented in Supplementary Discussion 8. The total scattering signals were scaled to the calculated scattering from a liquid unit cell (1 FeRu molecule and approximately 18500 water molecules) yielding signals in electron unit per solute molecule (e.u./molec.).

Difference signals for the XES and the XSS measurements were constructed by subtracting from the full datasets the signal measured from the unexcited sample. Difference signals were sorted accordingly to the time delay measured by the timing tool, and averaged in approximately 30 fs time-bins. Difference scattering signal are of the order of 0.02 % of the total scattering signal, which is dominated by the contribution from the bulk solvent (Supplementary Fig. 3).

#### 5.2 Simulations

First, a quantum mechanics/molecular mechanics (QM/MM) simulation of FeRu was performed in the ground state [37]. After equilibration, a cluster (238 atoms) was extracted comprising FeRu and water molecules contained in a 4Å shell around the complex. Excited state geometries of solvated FeRu cluster were calculated by optimizing this snapshot on the MMCT potential energy surface using TDDFT [54]. The ESP partial atomic charges for the ground and excited state geometries were computed using the corresponding electron densities, respectively. The QM/MM and TDDFT calculations were performed with the PBE0 functional [55] and all calculations were performed with the NWChem computational chemistry program [56]. Both DFT and TDDFT offer the best compromise between accuracy and computational performance for the large explicitly solvated transition metal clusters considered in this study. We have successfully used the same approach in other studies leading up to this work. Further details are provided in the Supplementary Discussion 9.

The resulting GS geometry, with the electron localized on Fe, and the MMCT excited state geometry, with the electron localized on Ru, and corresponding ESP partial atomic charges are then used in classical MD simulations, where the solute structure is fixed in space and embedded in a cubic water box of 60 Å size. In the MD simulations, the intermolecular interactions are represented by site-site Lennard-Jones plus Coulombic potentials with parameters taken from the TIP4P-Ew force field potential [57] for water and OPLS2005 force field [58] for the solute. The MD simulations are carried out in canonical ensemble at an average temperature of 300 K. The simulations of the GS and MMCT state of FeRu are run for 4 ns. From the GS trajectory, equally spaced frames are extracted and used as a starting point for the non-equilibrium simulations described in the Results. RDFs of the atom pair distances are obtained from the MD simulations and used to calculate isotropic scattering signals following the procedure in Ref. 39. The RDFs and corresponding scattering signals, as well as the experimental data, are available from Ref. 59.

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#### 7 Author contributions

Z.W.F., K.S.K., R.A.M., M.C., J.D.G., J.M.G., K.H.,T.K., J.H.L., M.R., D.S., R.W.S., N.G., A.A.C., and M.K. prepared and conducted the experiment at the LCLS. Z.W.F., K.H., J.H.L., G.D., A.M.M., S.H.S., A.A.C. measured the reference iron spectra at the APS. J.M.C. synthesized the sample. E.B. analysed the experimental data and performed the MD simulations. E.B and K.L. analyzed the results from the MD simulations. A.A., Y.Z., S.M., and N.G. performed the QM/MM, DFT and TDDFT calculations. E.B., K.L., C.L.S., K.J.G., R.W.S., N.G., A.A.C., and M.K. interpreted the results. E.B. and A.A.C. wrote the article with contributions from all authors.

#### 8 Competing Interests

The authors declare no competing interests.

## 9 Data Availability

The experimental data and the simulation results that support the findings of this study are available in figshare with the identifier: https://doi.org/10.6084/m9.figshare.13322975 [59].

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