

OBSERVING MOLECULAR REACTIONS VIA SIMULTANEOUS ULTRAFAST X-RAY SPECTROSCOPY AND SCATTERING

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Over the past decade ultrafast structural dynamics has been a rapidly growing field aiming to deliver unprecedented detail of understanding the initial steps in complex chemical reactions e.g. during light-induced spin switching, or during a photocatalytic event. Such processes play a vital role in chemistry and biology next to technological applications including efficient charge transport in solar energy converters and ultrafast switchable molecular magnets.

All these processes are either triggered on or occur on a femto- to picosecond timescale, therefore a pump probe technique exploiting ultrashort pulses is mandatory. The other prerequisite is an x-ray tool, which can determine the electronic, spin, and geometric degrees of freedom on the atomic length scale. Transition metal based spin crossover (SCO) systems are of particular interest due to their possible application in quantum-computers, but also in the quest for an efficient artificial solar energy cell. Light induced spin switching systems offer the advantage of an ultrafast trigger for studying their dynamic magnetic properties. In $[\text{Fe}(\text{bpy})_3]^{2+}$, the transition between the low spin (LS) ground and the high spin (HS) excited states is governed by a complex interplay of changes in the electronic and spin configuration next to geometric structural modifications [1]. New charge transfer materials also undergoes such complex processes, whose optimization is highly desirable for photocatalytic applications. We thus investigated a bi-metallic (Ru-Co) compound where the metal atoms are connected through a system of bipyridine (bpy) ligands. The detailed understanding of the charge transport from the Ru donor to the Co acceptor including oxidation (Ru), subsequent reduction (Co), next to geometrical structure changes, and finally the expected spin state changes on the acceptor ion is of high interest for both understanding the mechanism and

finding ways to improve its efficiency. We report on both ps and fs studies of different Fe-based spin transition compounds as well as on a bimetallic Ru-Co compound. These studies were carried out with high S/N, and combining – on a shot-to-shot basis – x-ray emission and x-ray diffuse scattering techniques.

Previous x-ray spectroscopic studies performed at kHz repetition rates yielded results with suitable signal to noise ratios (S/N) after rather long collection times at synchrotrons, which so far prevented a wide scale application of this method. Exploiting MHz laser sources is a straightforward improvement for a much faster data collection rate, and we performed benchmark experiments at the ESRF (ID26) and the APS (7ID) at pump-probe repetition rates up to that of the x-ray source. In order to unravel the complex behavior of photo-excited molecules we implemented a suite of different spectroscopic and scattering techniques. X-ray absorption spectroscopy (XAS) with its sensitivity to local electronic and geometric structural changes [2], 1s x-ray emission spectroscopy (XES) which as a direct probe of the spin state via the exchange interaction between $2p$ and $3d$ orbitals [3], and x-ray diffuse scattering (XDS), which yields complementary information about the local as well as the global structure of the studied molecule.

Among the investigated systems we focus here on $[\text{Fe}(\text{bpy})_3]^{2+}$ and the RuCo molecules. The fs XAS on $[\text{Fe}(\text{bpy})_3]^{2+}$ confirmed an earlier slicing result (using only 10 photons/pulse at 2 kHz) [4], including the switching time, which matches nicely the XES-derived spin switching time, thus determining the HS state formation of $[\text{Fe}(\text{bpy})_3]^{2+}$ directly. The limited time resolution (instrument response) of about 250 fs leaves the issue about the (sequential) order of the elementary steps in spin switching still unsettled.

These experiments were performed simultaneously to the x-ray diffuse scattering patterns (Fig 1.), which reveal a rich variety of changes on the fs, but also few ps time scales. In combination with our ps scattering results on this compound we can enrich our understanding of the geometric structural changes, but now including a first glimpse at the solvent cage dynamics.

While our dynamic studies on the RuCo system at synchrotron sources revealed an x-radiation induced conversion of the RuCo compound, we nevertheless unambiguously confirmed the electron transfer time to 200 ps. Utilizing ultrashort x-ray pulses from LCLS we confirmed this result, but interestingly also discovered a new ultrafast component for the electron transport time on the Co acceptor, which contributes to 1/3 of the total signal. Since

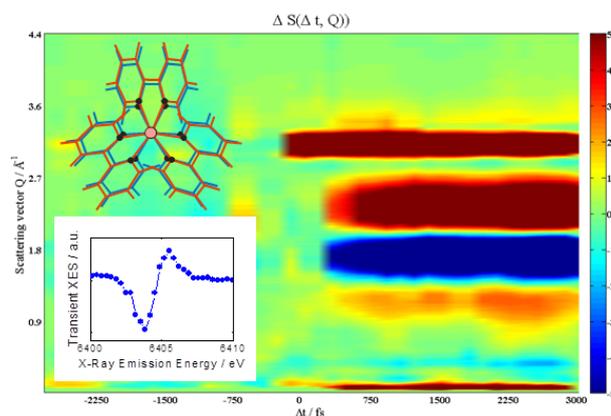


Figure 1: Simultaneous XDS and XES (lower inset) of photoexcited $[\text{Fe}(\text{bpy})_3]^{2+}$ (upper inset illustrating the geometry of low spin in blue and high spin in red) showing different femtosecond modulations for the scattering pattern scanning the pump probe delay and the transient $\text{K}\alpha^1$ XES for a fixed pump probe delay of 500 fs.

we exploited the characteristic XES signal in the Co acceptor, this arrival time also includes an ultrafast SCO process.

Using XES in concert with XDS tools we have investigated a collection of spin transition systems, on both the ps and fs time scales, with hitherto unprecedented S/N. The analysis of these studies should flow into the analysis of more complex compounds, like the bpy-based bimetallic RuCo compound, which revealed at the LCLS its unusual temporal behaviour. As an outlook, these studies should allow a more mature investigation of the dynamic properties in complex molecular systems, which now can include dynamic guest-host interactions in the liquid phase.

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