



	<b>Experiment title:</b> Development of time resolved X-ray Absorption at ESRF	<b>Experiment number:</b> MI1245
<b>Beamline:</b> ID09B	<b>Date of experiment:</b> from: 30/03/2016 to: 05/04/2016	<b>Date of report:</b> 20/09/2016
<b>Shifts:</b> 18	<b>Local contact(s):</b> Gemma Newby	<i>Received at ESRF:</i>
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## Report:

### Aims of the experiment

The aim of the experiment MI1245 was to develop time resolved X-ray absorption (TR-XANES) on ID09B beamline at ESRF. XANES is a powerful tool for extract both electronic (oxidation state) and structural (coordination, metal-ligand distance) information associated with photoinduced phenomena. TR-XANES experiment was carried out in three steps.

Step 1: development of the experimental setup. In this step, we tested different detectors (SDD and MAXIPIX) with different configurations, we developed the macros that can drive the experiment and the data reduction.

Step 2: optimization of the experimental set-up, to find the optimal parameters such as detector-sample distance and angle, x-ray and laser alignment, thickness and concentration of the sample. As test sample we used a solution of Fe(bpy), which was studied extensively in the literature by TR-XANES [1, 2, 3].

Step 3: in this step, we investigated photoinduced phenomena in nanoparticles of prussian blue analogues FeCo by TR-XANES around the Fe K edge and the Co K edge for the tracking electron transfer from Fe to Co responsible for the change of magnetic properties induced by light.

### Experimental setup

We used capillary tubes with different sizes (0.5, 1 and 2 mm) in which the sample solution was cycled using a fast-flowing liquid setup, and was collinearly excited with optical 530 nm laser light. The optical pump had a pulse duration of 150 fs and focal area of  $120 \times 350 \mu\text{m}^2$ . To follow the dynamics after optical pulse excitation a X-ray probe pulse was used, with a pulse duration of 100 ps and focal of  $60 \times 120 \mu\text{m}$ . We detected the total X-ray fluorescence yield to obtain the XANES spectra around the K edge of Fe (7112 eV) and Co (7709 eV). The X-ray fluorescence was collected using MAXIPIX detector positioned at a  $90^\circ$  angle with respect to the X-ray beam propagation direction (Figure 1).

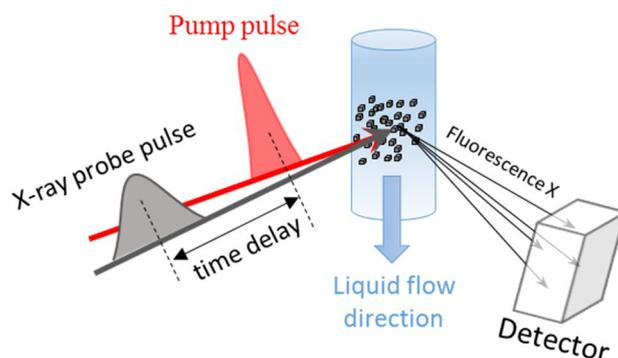


Figure 1 : Schematic representation of time-resolved XANES

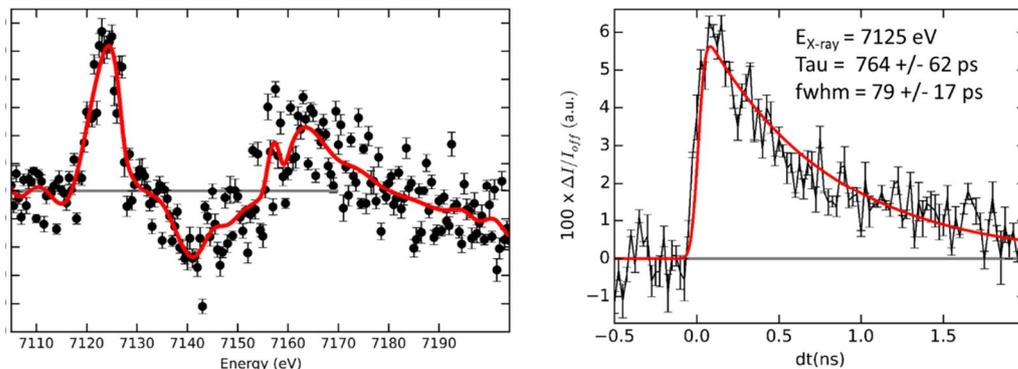
## Results

### - TR-XANES measurements of a Spin-Crossover systems Fe<sup>II</sup>(bpy)

The sample solution of Fe(bpy) was used to perform the first TR-XANES experiment at ID09 beamline. This system switches by light from the low spin LS to the high spin HS states [1,2,3], which is accompanied by a molecular reorganization responsible for the change in the XANES spectrum shown in figure 2 (left). The region ( $E < 7.12$  KeV) called pre-edge is attributed to the change in the electronic configuration and the region above 7.12 KeV is mostly due to the molecule expansion [4]. We could track the lifetime of this transient HS state as shown in Fig. 2 (right)

Figure 2: (left) the transient difference XANES around the Fe K edge in a 14.6 mM aqueous solution of Fe(bpy) recorded 50 ps after laser excitation at 530 nm.

(right) Kinetics of the transient XANES recorded at 7125 eV and the red line is fit to single exponential with time constant  $\tau_{HS-LS} = 764$  ps



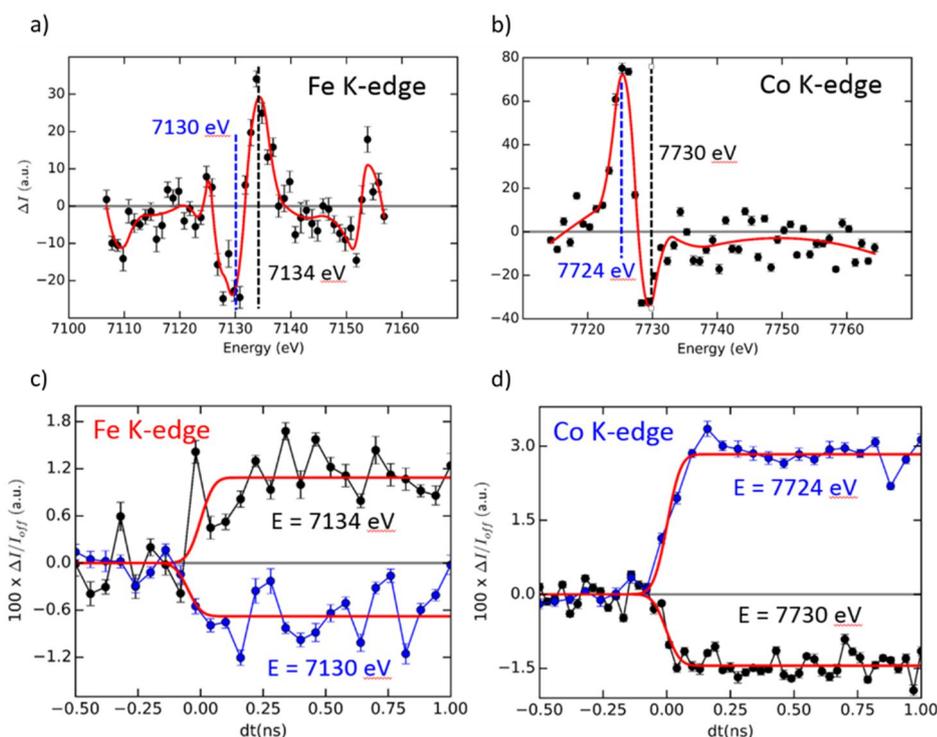
### - TR-XANES measurements of a Prussian Blue Analogue FeCo

Fe-Co Prussian Blue Analogues (PBA) are prototype bistable metallic cubic crystals. Among the great interests of these systems are their bistable chromic and ferromagnetic properties from the low spin (LS) ( $\text{Fe}^{\text{II}}_{\text{LS}} \text{Co}^{\text{III}}_{\text{LS}}$ ) to the high spin (HS) state ( $\text{Fe}^{\text{III}}_{\text{LS}} \text{Co}^{\text{II}}_{\text{HS}}$ ). The switching can be driven by light. With the new TR XANES set-up at ID09, we could perform time-resolved studies of the process. Our data reveal a transient electron transfer from Fe to Co at room temperature, characterized by a chemical shift in opposite directions around the Fe and the Co K-edges (Figure 3). This process occurs within the 100 ps time resolution of the experiment. This measurements are in good agreement with XANES changes observed for long-lived HS state [5].

Figure 3: a) and b) the transient difference XANES around respectively the Fe K-edge and the Co-edge in a 3 mM aqueous solution of CsFeCo recorded 500 ps after laser excitation at 530 nm.

c) Kinetic of the transient XANES recorded at 7134 eV and 7130 eV. d) Kinetic of the transient XANES recorded at 7724 eV and 7730 eV.

The red curve in c) and d) represent step function convoluted by X-ray pulse profile.



## References

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