



Experiment title: Ultrafast X-ray investigation of the Photoinduced spin transition.

Experiment number:
CH-2599

Beamline: ID9B	Date of experiment: from: 12/06/2008 to: 16/06/2008	Date of report: 29/09/2008
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Report: Tuning by light the macroscopic state of molecular crystals represents a fascinating fundamental feature for the out-of equilibrium science and, may moreover lead to the photo-control of physical properties of materials: optical, magnetic, conduction... This involves changes in the molecular identity, such as charge or spin between degenerate or quasi-degenerate ground states. In some systems, the coupling with the lattice degrees of freedom is strong enough to generate photo-induced cooperative phenomena leading to macroscopic phase transitions (new electronic and structural order with new physical properties). These are very different in nature from independent photochemical processes.

The photoinduced spin transition is a prototype of the molecular multi-stability driven by light, which is present and very efficient in a variety of molecular solids [1]. In such systems, Fe ions in a nearly octahedral field possess two possible spin states: high spin (HS) or low spin (LS). Until now, they have been mainly investigated under continuous laser irradiation at very low temperature where permanent states are reached [1-6]. All the structural analysis we performed on different compounds [2, 3, 5, 6], show strong structural signatures, associated with the spin state change. The aim of our experiment at ID09B was to investigate the dynamics of such transformation in real time. We focussed on the [(TPA)Fe(TCC)]PF₆ ferric catecholate spin crossover system which presents the advantage of a short relaxation time (~ 1 ms) well adapted to the repetition rate of the laser pump and RX chopper (~1kHz) at ID09B. Prerequisite ultra-fast optical pump-probe experiments had been performed in Rennes.

We investigated the structural signatures associated with the photoinduced transition from LS state to the HS, by generating the HS with a laser flash and probed its evolution/relaxation with a pulse of X-rays. In order to maximize the transformation rate, we used a double laser excitation (incidence 180°) on 10 μm thick needle-shaped crystals, on the monoclinic polymorph of this system we recently evidenced. This monoclinic polymorph has the advantage to present a more regular shape than the orthorhombic one which grows into plate-like shape. The needle-like shape of the monoclinic polymorph allows a quite homogeneous laser irradiation of the sample during the complete diffraction data collections (rotation of the crystal along its axis). The laser was polarized along the crystal axis for which the penetration depth is larger (≈ 5μm). We collected partial and complete diffraction data from which structures were solved and refined at different delays with good quality and in agreement with the structures obtained in our laboratory at thermal equilibrium. Partial data collections are used to follow the time evolution of volume unit-cell and lattice parameters. Thereby we could demonstrate that different processes on different length and time scales are involved [8].

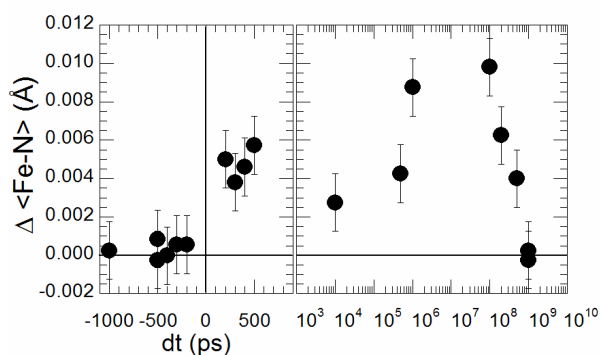


Fig. 1. Time evolution of average Fe-N bond length

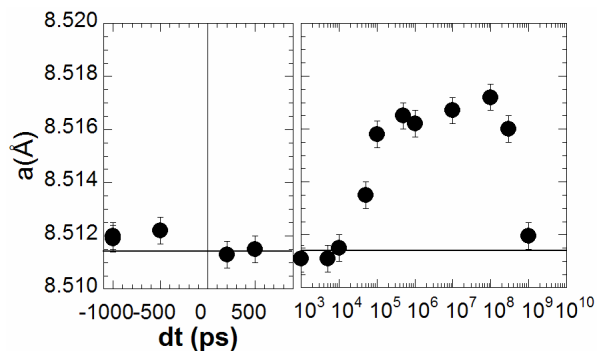


Fig. 2. Time evolution of lattice parameter *a*

The main results we obtained can be summarized in three points:

- The variation of $\langle Fe-N \rangle$ (Fig. 1a) occurs on the ps plateau (here on 200 ps as limited by the temporal resolution). Such an increase is characteristic of the LS to HS state change during thermal conversion. It provides here a structural evidence of the photogeneration of HS molecular states in the early stage of the phototransformation. $\langle Fe-N \rangle$ is even higher on μs scale (see point 3).
- Lattice parameter *a* of the crystal – *rotation axis measured with the best resolution*- (and therefore the unit-cell volume) (Fig. 2), increases only after a lapse of about 50 ns. The same expansion around 50 ns is observed at other temperatures (120 & 160 K) and for a weaker excitation density. It corresponds to the time required for acoustic wave propagation (order of 1000m/s).
- The high energy deposited (~ 1.5 eV) in comparison with the energy difference between LS and HS states (tens of meV) must result in some heat diffusion at some stage. Analysis of changes of the Debye-Waller factor in the time-domain show significant variations in the μs time scale [8] associated with a heating by 10-20 K. This laser heating leads to an additional thermal switch of HS molecules.

During CH-2559 we succeed in identifying three main steps during the transformation pathway: i) the sub-picosecond and therefore non-thermal molecular switching, ii) unit cell volume expansion on 10 ns time scale and iii) significant thermal effect on μs time scale. The recovery to thermal equilibrium with the environment (cryostat) occurs on ms time scale, as observed in the experiment.

These promising results benchmark our future optical pump-RX probe experiments on spin-crossover systems. Improving the experimental set-up so as to assure the same laser irradiation conditions irrespective of the rotation angle of the sample will allow studying the plate-like crystals, the orthorhombic polymorph of the present system for example. Besides, the study of highly cooperative spin-crossover systems will be essential in future, in particular to test the possibility of coherent nucleation through elastic interaction [9] and we are currently looking into potential candidates.

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