

Tracking the photoswitching dynamics of bistable spin-crossover molecules at solid state

Maciej Lorenc

Institute of Physics of Rennes, UMR CNRS-University Rennes 1, Campus Beaulieu, Rennes, 35042, France

Controlling molecular states in a solid material with an ultrashort laser pulse poses a new challenge to the ultrafast science, ensuing the now established field of femtochemistry. Molecular materials offer the possibility to be directed between different macroscopic states by using appropriate electronic excitations. By contrast to a dilute solute in a passive solvent, all molecules that make up the solid are active and can be switched. This opens bright perspectives for the light-control of various photoswitchable functions (magnetic, optical, conduction...). Spin-crossover compounds are prototypes of molecular bistability between low spin and high spin states. Yet, the pertinent time scales for photo-switching processes in these materials are unknown as previous investigations dealt mainly with the kinetics of recovery to the thermally stable state. In solids, we can expect the dynamics to follow a complex pathway from molecular to material scale through a sequence of processes. We hope to have shed more light on this problem with the time-resolved studies of photoinduced spin-state switching in a new monoclinic polymorph of catecholato-Fe(III) solid [(TPA)Fe(III)(TCC)]PF₆ [2]. At thermal equilibrium this solid undergoes a spin-crossover from the low temperature LS ($S=1/2$) to the high temperature HS ($S=5/2$) state. By combining time-resolved optical and X-ray diffraction techniques, we were able to identify 3 main steps during the transformation pathway: i) the sub-picosecond molecular switching, ii) unit cell volume expansion on 10 ns time scale and iii) significant thermal effect on μ s time scale. The recovery to thermal equilibrium with the environment is complete within ms. The recovery to thermal equilibrium with the sample environment occurs within milliseconds. All of these steps bear their imprints on the time course of the molecular fraction of HS molecules. Based on these results we attempt a mechanistic description which differs from the case of delocalized electronic photo-excitation (semi-conductors, for example) where structural relaxation is governed by collective and coherent optical phonons. In the present case of long-lived trapping of molecular excited state on different lattice sites, there exists a complex relaxation pathway from the molecular level onto the material scale [3].

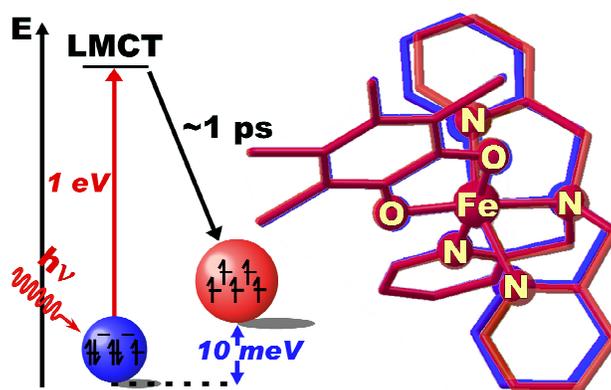


Fig. 1. Schematic representation of the photoinduced spin state switching and concurrent structural reorganization probed by 100 ps x-ray diffraction

References

- 1) E. Collet *et al.*, *Z. Kristallog.* **223** (2008) 272
- 2) E. Collet *et al.*, *Acta Cryst. B* **65** (2009) 474
- 3) M. Lorenc *et al.*, *PRL* **103** (2009) 028301