Evolution and Control of Photoinduced Transformations In Molecular Materials :
Experiments for Tracking and Understanding their Non-Equilibrium Cooperative and Coherent Dynamics

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Light may direct the functionality of a material through spectacular photoinduced phenomena in the solid state. Due to cooperative interactions between constituents, the medium is active. Positive feedback can trigger the non-equilibrium transformation of the material towards another macroscopic state of different electronic and/or structural order, for instance from non-magnetic to magnetic or from insulator to conductor. Molecular materials constituted of multi-functional molecules which can be switched between two states by electronic excitation are particularly promising.

Two situations occur:

- photosteady instability due to the competition between photon flow and thermal relaxation. This is well illustrated by spin crossover materials, prototypes of molecular bistability in the solid state, and which may present light-induced hysteresis at low temperature.
- ultra-fast phase transformation which may develop after the material is prepared in an excited electronic state by an ultra-short light pulse. The development of this emerging field requires the mastering of three key aspects: light-induced coherent phenomena, intrinsic cooperativity in the material and new processes far away from equilibrium.

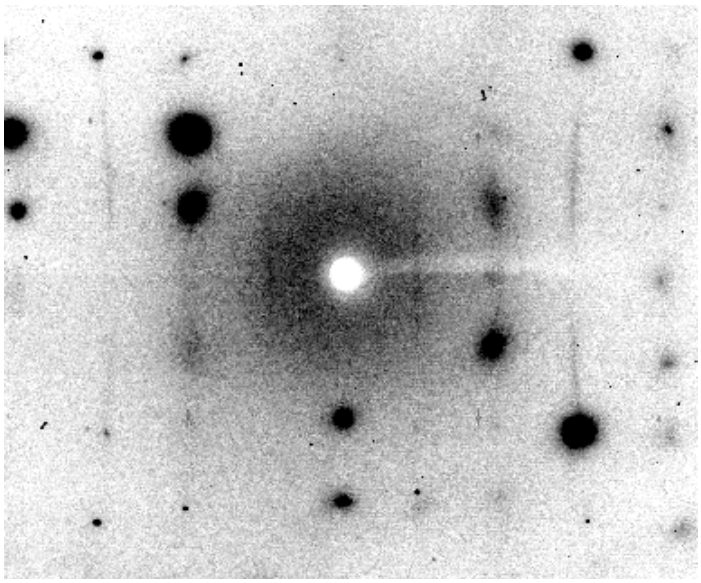
X-ray scattering experiments have the potential to give a global picture of structural changes, at thermal equilibrium as well as out-of-equilibrium. Diffraction experiments are currently performed on photo-steady[1] and long-living non-equilibrium states. More advanced are time-resolved diffraction experiments[2] which give fascinating capabilities not only to observe and understand the elementary dynamic processes in the material but also to watch how it can be directed to a desired outcome.

Recent investigation[3,4] of the structural dynamics in molecular materials by time-resolved x-ray diffraction with 100 ps time resolution on a synchrotron (ESRF and KEK) will be presented. This allows to directly watch the switching dynamics and contribute to our understanding of the physical picture. The key point is that in the solid state different degrees of freedom of different nature play their part on different time scales and the pathway is complex, from the molecular to material length and time scales.

The development of very intense fs x-ray sources opens new opportunity to probe precursor phenomena which precede a photoinduced transformation. For instance:

- time-resolved x-ray diffuse scattering in the case of photo-generation of nano-domains. This is the most suitable method to bring out essential information about the mechanism of a photo-induced phase transition. Thus, preliminary experiment has shown the formation of 1D precursor cluster in a charge transfer (CT) crystal. However, the time resolution of 100 ps precluded to the observation of coherent nucleation dynamics, where fs pulses should be required. Another fascinating question is how these precursor clusters can grow to establish the long range order.
- observation of coherent structural dynamics such as collective optical phonon. In CT molecular solids the formation of 1D nano-domains may induce coherent dimeric displacements. Coherent control of these deterministic vibrational dynamics, for instance by sequencing and tailoring fs laser pulses, is particularly exciting.

The x-ray scattering by a crystal is divided in two parts : Bragg diffraction and diffuse scattering. The former only probes the average periodic structure whereas the latter fingerprints local deviations. It is more or less spread out, depending on the spatial extension of these local deviations (cf. reference 5).



References of presented works

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