ESRF	**Experiment title:** **ULTRA-FAST TIME RESOLVED CRYSTALLOGRAPHIC STUDY OF THE PHOTO-INDUCED NEUTRAL-IONIC PHASE TRANSFORMATIONS : COOPERATIVE MULTI-ELECTRON TRANSFER**	**Experiment number**: CH-1441
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Shifts: 18	**Local contact(s)**: Michael Wulff	*Received at ESRF:*

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Report:

In some photo-active materials, the structural relaxations of the electronic excited states following the absorption of photons are not independent processes, as in conventional excitonic or photo-chemical processes. It results in drastic electronic-structural changes involving a large number of electrons and molecules. Strong intermolecular cooperative processes still further lead to a photoinduced phase transition towards a new structure and electronic state. Therefore, new possibilities appear to drive with light new self-organized long-range ordering (structural, magnetic, ferroelectric,…), opening the way to controlled ultrafast photo-switching of macroscopic physical properties of materials. In that frame, molecular charge-transfer (CT) insulating materials are exemplary since they are readily tuned between competing neutral (N) and ionic (I) ground states on a picosecond timescale. The mixed-stack sequence of alternating donor and acceptor molecules stimulates cooperative intermolecular electron transfer, which gives rise to a chain multistability between one regular N state and two degenerate and polar dimerized I states. The photoinduced phase transition mechanism can be governed by the formation of lattice-relaxed CT strings along the stack, i.e. of sequences of I dimers within a N chain or vice-versa, which strongly interact with each other [1].

Previously, we have observed, around the time-resolved X-ray study of the photo-induced N-to-I transition, that the light triggers a 3D ferroelectric long-range ordering of the photo-induced dimers from the N high temperature phase [2]. The photo-induced structure has been solved indicating structural changes at the molecular level [2]. We investigated as well, thanks to the Helijet cooling system, the I-to-N transition. The X-ray data (fig.1) indicate a 2-step mechanism associated with the I_{ferro}-to-N_{para} transformation with at first a disordering phenomena, followed by structural rearrangement, in agreement with the physical picture we proposed from optical measurements [1]. These results will be published soon in a special issue of chemical physics : Ultrafast Science with X-ray and Electrons [3].

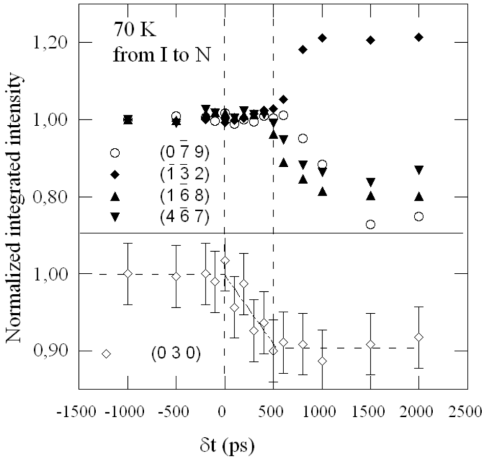

Figure 1 : Normalized intensity dependence of some Bragg reflections with the delay between the laser pump and the x-ray probe pulses. This is associated with the photoinduced transformation of the I phase to the N one. General reflections (top) are modified after an incubation time of about 500 ps, whereas the intensity of the (030) reflection starts to decrease just after the laser pulse excitation (bottom), indicating a two steps mechanism.

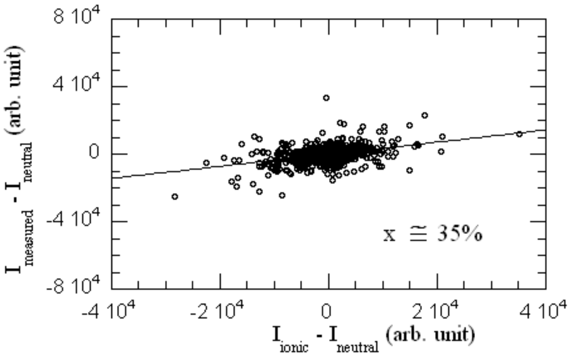

Figure 2 : Dependence of the variation of the intensity of more than 6000 Bragg reflections between the measurements in the photoinduced experiment and the neutral state ($I_{measured}$ - $I_{neutral}$) with the variation of the intensity between the neutral and ionic phases (I_{ionic} - $I_{neutral}$). The slope gives an estimation of the transformation rate around 35 %.

In the last experiment CH1441, we investigated the photo-induced N-to-I transformation and I-to-N in TTF-CA. A long time was devoted to search for optimal conditions for the crystal orientation and for setting-up the laser power irradiation on the sample. We wanted also to check the quality of the x-ray data and the signal/noise ratio by investigating the weak structural signatures in the low temperature phase associated with the phase transition (@82 K). The Helijet cooling system was used for this purpose. Unfortunately, the temperature regulation of the Helijet system was difficult to reach due to a technical problems (the temperature varied within a range of 30K). Furthermore, ice block hit the sample and important oscillation of the sample associated with variation of the He gas pressure have damaged many samples. Nevertheless, several data collections could be performed providing only partial results because of the cryogenic troubles, since the sample travelling during the data collection from one phase to the other one under the effect of temperature oscillations.

We would like to underline that, besides the experimental time itself, we spent a lot of time developing software and we can now treat online the complete data obtained for monochromatic diffraction on single crystal. Data reduction and the reconstruction of the scattered intensities in the reciprocal space can now be performed. Many tools were also developed to compare data collection as a function of delay between the laser and X-ray pulses and it is then possible to rapidly evidence photoinduced transformation signatures that can then be studied with more accurate measurements. Furthermore, the complex treatment of data where two macroscopic phases coexist, the photoinduced and the stable, is now achieved. It is now possible to evaluate the transformation rate (fig. 2) and to refine the photoinduced structure. All these developments will make it possible to realize future experiments in the best conditions.

References

[1] T.Luty et al, *Europhys. Lett.*59, 619 (2002).
[2] E.Collet et al., *Science* **300**, 612 (2003)
[3] L. Guérin et al., *Chemical physics*, in press.