ESRF	Experiment title: **ULTRA-FAST TIME RESOLVED CRYSTALLOGRAPHIC STUDY OF THE PHOTO-INDUCED NEUTRAL-IONIC PHASE TRANSFORMATIONS : COOPERATIVE MULTI-ELECTRON TRANSFER.**	**Experiment number**: CH-1230
Beamline: ID09B	**Date of experiment**: from: 10th 07 02 to: 15th 07 02	**Date of report**: 15th 08 02
Shifts: 15	**Local contact(s)**: M. Wullf	*Received at ESRF:*

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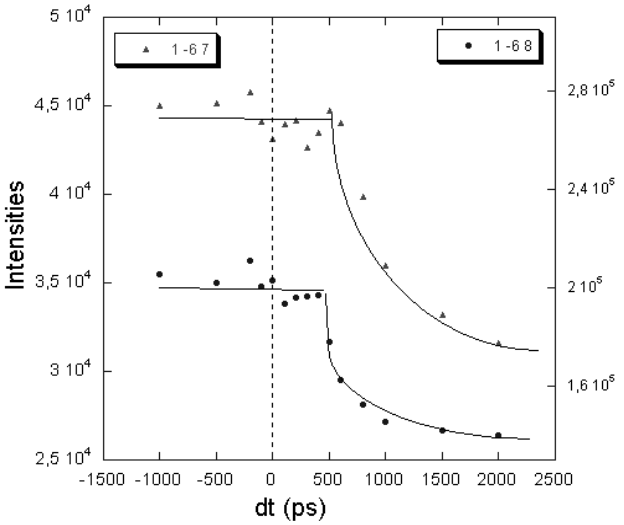
Report:

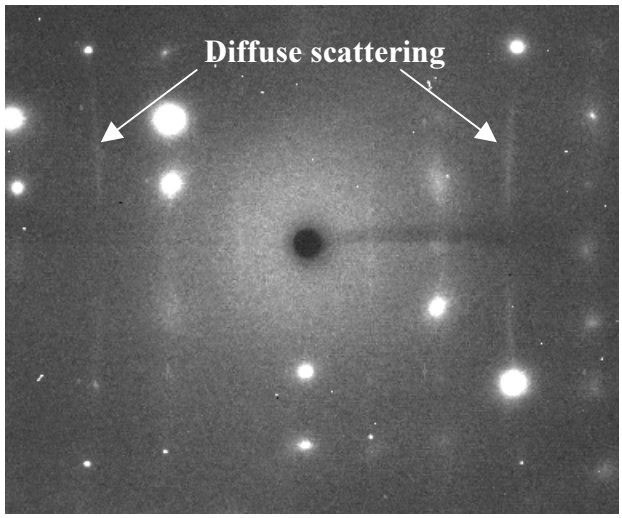
In some unconventionally photo-active materials the relaxation of optically excited states results in drastic structural changes involving a large number of atoms and electrons. The situation is carried to extremes in the case of photo-induced phase transformations, i.e. when the light triggers a complete macroscopic phase change. TTF-CA is the prototype compound for charge-transfer (CT) solids which exhibit the so-called neutral-ionic (N-I) transition, an unusual phase transition where the electronic and structural aspects are strongly coupled. It occurs in some one-dimensional CT organic crystals with a mixed stack architecture (alternation of electron donor (D) and electron acceptor (A) molecules along chains). The electron transfer manifests itself by a change of molecular ionicity, i.e. the degree of CT, and by a dimerization process with the formation of (D^+A^-) pairs along the stack in the I phase. With regards to the regular N chains, the dimerization distortion for the I chains is associated with the inversion center loss and then leads to two degenerated ferroelectric states. At finite temperature, charge transfer exciton-strings (made of hundreds of adjacent (D^+A^-) excited pairs) may be thermally activated [1]. They may also condense and become ordered [2]. The photo-induced N-I transition in TTF-CA has been experimentally evidenced from irradiation with ultra-short laser pulses, and can be discussed in terms of structural relaxation of CT excitations and of cooperativity [3]. The "I to N" transformation at low temperature (77 K), as well as the "N to I" transformation at high temperature (100 K), have been observed excluding simple laser heating effects (the phase transition temperature is ≅ 82 K). In particular cooperative effects express by the fact that hundreds of DA pairs may be transformed per photon. Recently [4] we have observed, around the time-resolved X-rays study of the photo-induced N-to-I transition, that light triggers a 3D ferroelectric long range ordering of the photo-induced dimers. The photo-induced structure could be solved

indicating structural changes at the molecular level. After a long time consuming adaptation of software [4], it is now possible to treat completely the data obtained for monochromatic diffraction on single crystal.

In the last experiment CH-1230 we have performed the study of the opposite photo-induced transformation starting from the low temperature phase at 70 K, thanks to the Helijet cooling device now available on the beamline. A long time was devoted to find the optimal conditions for cooling down samples. We could collecte complete data, now under treatment, in the stable and photo-induced states and also we have measured a clear delay dependence of many Bragg peak intensities, including the (030) Bragg reflection characteristic of the ferroelectric order in the I low temperature phase, which present important changes. The X-ray data indicate a 2 step mechanism associated with the I_{ferro}-to-N_{para} tranformation with at first a disordering phenomena, followed by structural rearrangement, in agreement with the physical picture we proposed from optical measurements [5]. At the present stage we focus on the complex data treatment, since the signal is the superposition of two : one from photoinduced N macroscopic domains and one from the unconverted I_{ferro} one.

The other important observation is the diffuse scattering signal observed with the 100 ps time resolution (Figure). It is associated with the formation of condensed 1D CT excitations. An accurate study of this diffuse scattering opens the way to the deep understanding of the physical mechanisim of photo-induced phase transitions by measuring the delay dependence of the size and concentration of the excitations after the laser pulse, as successfully done around the thermally-induced phase transition at the ESRF [1].





Left: Delay dependence of the intensity of some Bragg reflections. The decrease correspond to the relative transformed part (few 10 %). The reflection intensity changes correspond to the molecular reorganization in the N state, completed within 1 ns. Other Bragg reflections seem to indicate a disordering phenomenon occuring before 500 ps.

Right: Diffuse scattering observed with 100 ps time resolution. It is associated with the 1D charge-transfer excitations existing around thermo and photo-induced transitions.

[1] E. Collet, MH. Lemée-Cailleau, M. Buron, H. Cailleau *et al,* Europhys. Lett 57 (2002).

[2] M.H. Lemée-Cailleau, M. Le Cointe, H. Cailleau, et al., Phys. Rev. Lett. **79**, 1690 (1997).

[3] S. Koshihara et al., J. Phys. Chem. **103**(14) 2592 (1999)

[4] E. Collet, MH. Lemée-Cailleau, M. Buron, H. Cailleau, S. Techert, M. Wulff et al, submitted

[5] T. Luty, H. Cailleau, S. Koshihara E. Collet *et al*, Europhys. Lett. **59**, 619 (2002).