



**Experiment title: ULTRA-FAST TIME-RESOLVED CRYSTALLOGRAPHIC STUDIES OF THE PHOTO-INDUCED NEUTRAL-IONIC TRANSFORMATIONS**

**Experiment number:**  
CH909

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**Report:**

The transfer of electron is fundamental to many chemical and biological processes in nature. In solid, the electron transfer reaction may be highly cooperative; it is more complex and less understood. Beside many insulating solids where an electron excited by a photon induces a local structural distortion, 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, like in TTF-CA (FIG. 1). TTF-CA is the prototype compound for (quasi-one-dimensional) 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 quasi-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<sup>+</sup>A<sup>-</sup>) 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<sup>+</sup>A<sup>-</sup>) excited pairs) may be thermally induced. They may also condense and become ordered. In this way, three phases are observed in the (P,T) phase diagram of TTF-CA. The first one, where the concentration in I fluctuating CT exciton-strings is low, is the N paraelectric (Npara). The second one, where the concentration in I fluctuating CT exciton-strings is high, is the Ipara. The third Iferro phase is characterized by a ferroelectric ordering between I species[1]. The photo-induced N-I transition in TTF-CA has been experimentally evidenced by irradiation with ultra-short laser pulses, and can be discussed in terms of structural

relaxation of CT excitations and of cooperativity [2]. 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  $\sim 82$  K). Cooperative effects manifest by the fact that one photon transforms hundreds of DA pairs.

During CH807, we have performed a first ultra-fast time-resolved structural study of the photo-induced "N to I" transformation at 93 K using the pump-probe method. It was performed on a single crystal of prismatic shape ( $80 \times 160 \times 1500 \mu\text{m}^3$ ), irradiated with about 300 fs width laser pulses (800 nm wavelength). A CCD detector ( $2\theta$  limited at to  $31^\circ$ ) recorded the diffraction pattern from a delayed monochromatic ( $\lambda=0.7534 \text{ \AA}$ ) X-ray pulse of 150 ps width, with a repetition rate of 900Hz. Several data sets were accumulated for different delay times between  $-1.5$  and  $+1.7$  ns showing drastic changes of some Bragg reflexion intensity which allowed to estimate that  $\frac{3}{4}$  of the irradiated part is transformed with low laser power. The photon efficiency is therefore extremely large : 1 photon can transform about thousands of molecules at once. The treatment of the complete data sets collected at several time points was carried to its limits. Unfortunately if large angular frames were well adapted for the first part of the experiment, it was not for structure analysis, the assignation of Bragg peaks being impossible in that case.

A test of data collection was performed in July, in order to check the quality of the measurement and to develop as soon as possible the crystallographic software to treat the images. Some troubles in the goniometer positioning were evidenced, possibly due to a too large oscillation speed. This made impossible the development at this time of the software required to treat the data, i.e. to obtain sets of (hkl) and intensities necessary to solve the structure.

A new experiment CH909 was therefore carried out during November 2000, in conditions now well established. We have made full data collections on similar shaped crystals cooled at 90 K with always 300 fs width laser pulses at 800nm. A new MAR detector, with a  $2\theta$  limit of  $45^\circ$ , has allowed to record diffraction patterns from a delayed  $\lambda=0.7534 \text{ \AA}$  X-ray pulse of 150 ps width, always with a repetition rate of 900Hz. Data collection were performed for two delay times, one before ( $-1$  ns) and one after ( $+2$  ns) irradiation, in order to solve the structures, i.e. to directly access to structural informations at the atomic scale on the photo-induced effects. In that sense a without laser data collection was also performed. These type of clean data collection is very time consuming and we were able to collect complete data for only two different laser power (before and after irradiation) : 18 mW and 5 mW. The quality of the measurements was checked during data collections with a home made software and the reduction of data is now under test with an adapted software.

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

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