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| | Experiment title: COOPERATIVE MULTI-ELECTRON TRANSFER : PHOTO-INDUCED NEUTRAL-IONIC PHASE TRANSFORMATION | Experiment number: CH-807 |
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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^+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 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 $\cong 82$ K). Cooperative effects manifest by the fact that one photon transforms hundreds of DA pairs.

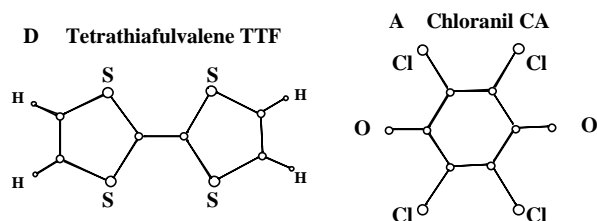


Fig. 1 : TTF-CA compound

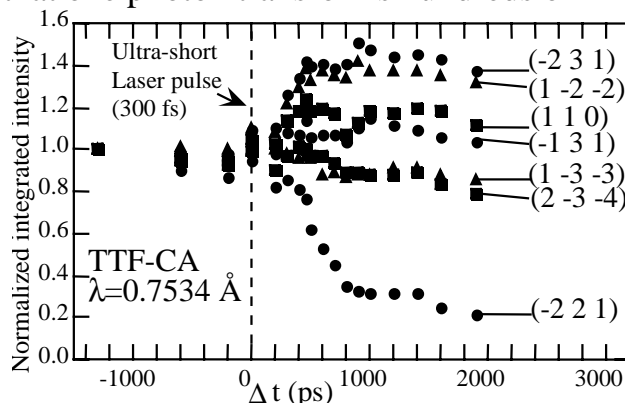


Fig. 2 : Time resolved intensities behaviour showing structural evidences of photo-induced transformation.

We have performed an ultra-fast time-resolved structural study of the photo-induced "N to I" transformation at 93 K using the pump-probe method. It was successfully 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) with low power (20 mW). A CCD detector (2θ limited at 31°) recorded the diffraction pattern from a delayed X-ray monochromatic ($\lambda = 0.7534 \text{ \AA}$) pulse beam of 150 ps width. This sequence was repeated at 900 Hz accumulating 2 s for an oscillation of the sample of 2° . Several data sets were accumulated for different delay time between -1.5 and $+1.7$ ns. Structural signatures are shown in the drastic changes of Bragg reflections intensity. Some are decreasing but some are increasing, what is directly characteristic of a phase transformation (figure 2). The transformation of the photo-irradiated part is realized within 1 ns (the recovery to thermal equilibrium is in the range μs -ms). The changes in intensities allow to estimate that the converted fraction of the sample is at least $3/4$. The photon efficiency is very large since from the laser power it is also estimated that 1 photon transforms thousands of molecules (present experiment). This is a strong signature of important cooperative effects in those systems. The close-connection between the phase transition phenomena at thermal equilibrium and the out-of-equilibrium photo-induced phase transformation has recently been established : the photo-irradiation of I ferro phase induces at first a disordering process[2] of I species which afterwards transform in N. The experimental set up used did not allow to reach such low temperature neither to perform a full structure refinement or to conclude about ordering of the I photo-induced species. However, a model to describe the here observed photo-induced metastable phase is in processing. The observed structural signatures give a kinetics in perfect agreement with the one observed by optical methods[2].

This preliminary result opens the way to study ultra-fast photo-induced structural phase transformations, and to watch at atomic rearrangements at the 100 ps scale. Concerning our project, the next step is to study ordering and disordering processes and to solve the photo-generated phases. To our knowledge, this study constitute the first monochromatic time resolved structural study on single crystal for such ultra-fast photo-induced transformations.

[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)