Ultrafast Structural Response of TTF-CA Investigated Using 80 fs X-Ray Pulses at SPPS

C. Blome\textsuperscript{1}, Th. Tschentscher\textsuperscript{1}, J. Davaasambuu\textsuperscript{2}, P. Durand\textsuperscript{2}, J. Hallmann\textsuperscript{2}, W. Quevedo\textsuperscript{2}, S. Techert\textsuperscript{2} and J.B. Hastings\textsuperscript{3} for the SPPS-collaboration

\textsuperscript{1}Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany
\textsuperscript{2}Max-Planck Institut für biophysikalische Chemie, Am Fassberg 11, 37077 Göttingen, Germany
\textsuperscript{3}Stanford Synchrotron Radiation Laboratory/SLAC, Menlo Park, CA 94025

In this project the photo-induced phase transition in tetrathiafulvalene-p-chloranil (TTF-CA, \(C_{12}H_{4}Cl_{4}S_{4}O_{2}\)) was investigated by time resolved X-ray diffraction at the SPPS. TTF-CA is a mixed-stack organic charge transfer crystal which shows a neutral (N)-to-ionic (I) phase transition at 81 K [1]. In the N-phase (room-temperature) the one-dimensional stack consists of alternating donor (TTF) and acceptor (CA) molecules with a spacing of \(~3.42\) Å. In the I-phase lattice relaxation along the stacking-axis leads to a new equilibrium distance between donor and acceptor molecules of 3.461 respectively 3.157 Å, see figure 1. The unit cell in the N-phase contains two undimerized donor-acceptor pairs in space group \(P2_1/n\), the phase transition into the low temperature phase leads to a loss of symmetry (space group \(Pn\)) and therefore to a strong modulation of the X-ray reflectivity for specific orientations \(hkl\).

Figure 5: The left image shows the unit cell of TTF-CA in the neutral phase. The planes on the middle and right side show the 1-dim stacks of alternating TTF and CA molecules in the neutral, resp. ionic phases.

It was shown [2] that the system close to the transition temperature can undergo phase transformation following photo-excitation. For temperatures above the phase transition a N-to-I transition can be observed and for temperatures below the phase transition I-to-N transitions are possible. The studies reported in [2] were limited in time-resolution due to the X-ray pulse duration of synchrotron radiation. However, these studies revealed a delayed onset of the phase transition the reason of which remains unknown. Here we report about experiments using the SPPS at SLAC, Stanford. SPPS delivers \(~10^6\) photons per pulse of \(~80\) fs duration and at a bandwidth of \(~1\%\) [3]. For time-resolved optical laser pump X-ray probe experiments a femtosecond Ti:Sa laser system is synchronized with respect to the master clock of the accelerator. It was shown that the accuracy of this synchronization is of the order of a few picoseconds. For experiments with sub-picosecond time resolution in addition random time sampling using electro-optical measurement of the electron bunch arrival has been implemented. This technique can reach resolution below 100 fs [4].

In order to maximize the signal-to-noise we selected needle like crystals with a diameter of \(~50\) \(\mu\)m and a length of up to \(3\) mm. Proper monitoring of the incident intensity the X-ray beam required to slit down the X-ray beam to \(50\times250\) \(\mu\)m\(^2\). To maximize flux through this aperture we used the existing Be lens system to focus the X-ray beam. An incident X-ray intensity of \(~10^9\) photons/pulse was measured behind the slit by means of a transparent ionisation detector used for monitoring the incident intensity on a pulse-by-pulse basis. A closed-cycle He-cryostat was employed to keep the sample at temperatures near the phase transition. It was carefully verified that the vibrations of the cryostat did not lead to additional signal. Horizontal scattering geometry was employed using a 4-circle goniometer (compare Fig. 2). For the detection of the diffracted X-ray photons a Si diode
with a sensitivity to detect single photons was attached to the detector arm (2 $\Theta$ of the goniometer). The crystalline sample was prealigned and the orientation matrix was measured at a commercial X-ray tube. Using this matrix a software program determined the $\omega$-rotation, the 2$\Theta$-angle for the detector arm and the height of the detector for selected reflections $hkl$.

TTF-CA consists of a number of light elements and has a large unit cell compared to simple solids. Since the number of diffracted photons scales with $(F/V)^2$ (F structure factor and V unit cell volume) the diffraction efficiency is small and a very sensitive detector is required. In Fig. 2 a pulse height histogram of the detector reading is given for accumulation over 5000 pulses, corresponding to $5\times10^8$ incident photons. One observes events corresponding to one up to eight X-ray photons detected. The signal-to-noise level of the detector allowed for detection of single X-ray photons although this is very close to a threshold that had to be set for data acquisition reasons. The mean count rate is three X-ray photons and one obtains that most incident X-ray pulses will lead to a ‘zero’ reading at the detector. Those events are already removed from the plot in Fig. 2. From these numbers it becomes evident that investigations of molecular crystals with large unit cells and low Z atoms at a flux of $\sim10^6$ photons/s are close to being feasible.

The experiment aimed at carrying out the time-resolved measurements near the phase transition at 81 K. We had selected the (-1 0 -1) Bragg reflection since for this reflection the relative change is large while the absolute structure factor at the same time allows observation of this reflection. Since the temperature reading of the cryostat failed during the experiments we needed to measure rocking curves and to compare integrated intensities of the diffracted signal to establish the static phase transition. Nominally close to the phase transition we then carried out time-resolved experiments using the femtosecond laser to pump the system transiently from the I to the N state. The data analysis indicates that we may have observed a change of the integrated intensity indicated a structural response of the system on the few ps time scale. These findings need to be reevaluated in view of the recent measurements of the static phase transition [4].

This work was carried out in the framework of the MoU between DESY and SLAC concerning experiments at the Sub-Picosecond Pulse Source at SLAC, Stanford.

References