ESRF	**Experiment title:** Structural processes in TTF-compounds investigated by time-resolved diffraction in Laue mode	**Experiment number**: CH-2605
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Report:

In order to examine the structural changes in TTF-CA time resolved Laue experiments were performed at ID-09b (ESRF, Grenoble). The experiment was carried out in the 16 bunch mode of the ESRF. With the use of a high speed chopper single X-ray pulses could be isolated, therefore allowing a time resolution of 80 ps.
Given the high flux in polychromatic experiments very small samples (10-20 µm thickness) could be measured with the using about 30 of this single pulses per exposure. The repetition rate for single pulses and laser was limited to 20Hz. Nevertheless the collection of one frame took 18s mainly due to the detector readout. Full data sets consisting of 90degree rotation (1 degree steps) at 6 different time delays could be collected in a matter of just three hours. This allowed for systematic variation of experimental conditions within a reasonable beam time, which were in the present experiment temperature variation (80 - 90K) and optical laser pulse energy variation (11 and 107 uJ (0.5 mm beam)).
Given the relatively modest amount of laser shots needed for an experiment performed in this way we were able to collect several data sets on single samples. Sample degradation due to X-ray exposure could not be observed at all. The limiting fact for the amount of data collectable on a single sample was laser induced cracking of the crystal occurring after more than 10000 laser excitations.
Several reflections in the resulting data sets show very high redundancy, because the Ewald cone is intersecting the reciprocal lattice for several consecutive sample rotations. This results in series of reflections that differ only in the reflecting x-ray wavelength. This feature is especially useful for time resolved experiments, because this high redundancy results in significant measurements during data evaluation even for small observed changes. This allows in principle to use less time points for continuously varying intensities, since the same effects should be observable multiple times allowing the separation of effects from mere fluctuations in the data. In this experiments the resulting data sets consisted of up to 25000 reflections for each delay time. Delay times were varied from 50ps to 1us.
During the course of the experiment the sample temperature and laser power were varied. The temperature range of interest should be around the phase transition (80-90K), but experimental results suggest that all data were from above the phase transition. 80K was the limit of the chosen open flow nitrogen cooling system and the crystal temperature was actually even somewhat higher due to several effects. The laser power was varied between 11 and 107 uJ (0.5mm beam), but there are unfortunately several indications in the data, that the overlap of the laser with the sample was not always the same therefore just allowing the direct comparison of a subset of data collections in regard to the laser power. A clear indication on successful laser excitation can be observed in the collected diffraction patterns for long delay times (10ns/1us). Only

when these data points were showing an easily observable lattice changes (spot shifts or streaking), a good overlap is estimated and significant changes could be found in intensities for shorter time scales.

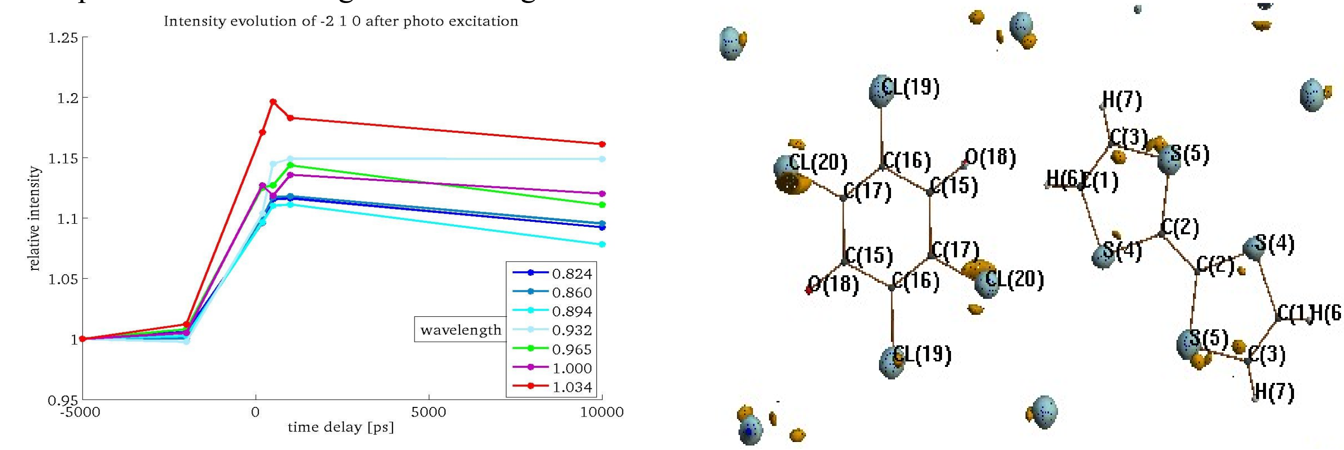

Figure 1: Left: Response of one chosen reflection at different wavelength, right: Overall structural response function for the 500 ps time point.

Illustrated in the left figure is the time evolution of the intensity of (-2 1 0), one of the most remarkably changed reflections. Similar plots can only be generated for a small subset of reflections. Reflections with increasing intensity after laser exposure can be identified as well as reflections with degreasing intensity, while the majority of reflections stays fairly constant. This is consistent with a structural change in the crystal Unfortunately the observed changes are not in accordance with a simple comparison to the difference of neutral/ionic static structures. The constraint of a fixed unit cell might be the main reason for this discrepancy.

Displayed in the right figure is the light induced structural response as seen after 500ps delay (500ps-1ns; 107uJ/pulse laser at 800nm). The figure is generated by applying a difference Fourier synthesis after refining the TTFCA structure for all delays in an identical cell to get a common scaling. The isosurfaces are drawn at 0.3 e/Å^3, blue/red color corresponds to positive/negative density. The main feature (blue surfaces at the heavy atom positions) corresponds to more density in the non exited state than for the photo excited system. It should be noted, that the electron density changes found are of isotropic character. In comparison, the difference maps created from the static crystallographic data at 78 K (phase transition temperature) and 70 K reveal anisotropic electron densities modulations at the heavy atoms (sulphur of TTF and clorine at CA) corresponding to atom position changes. In addition it can be concluded that the unit cell doesn't change up to 1 ns from examination of spot positions, that are unchanged up to 1 ns delay, but clearly shift in the 10ns-1us range, despite the immediate intensity changes observable.
Since there are several delay times measured as well as several temperatures a systematic comparison of difference densities was carried out as well. As explained before for single reflection intensities also the overall photo induced changes show little evolution in the early times 50ps-1ns. Longer delay times show much bigger differences as could be expected since shifts in the spot positions are observed only at long delay times.
We denote this newly found photo-induced structural state, which is formed already within the time-resolution of the ESRF pulses and which decays through following equilibrium processes afterwards (us time scale) as a precursor state to the latter observed lattice changesas expected for the photo-induced phase transition. It can be explained in terms of potential softening on the way of the photo-induced phase transition.

In summary it can be stated that the ID09B beamtime was very successful. It can be concluded that the Laue method is able to give reliable information on structural changes after photo excitation at ID09b. For 20 µm TTFCA single crystals structural changes were observed at 50 ps delay, limited by the ESRF pulse duration which we assign as precursor states to the – slower – photo-induced phase transition in the bulk crystal. At longer delay times >1ns lattice changes are clearly observable. Most remarkably the very intense pink beam allows collection of complete diffraction data sets with a minimal use of the excitation laser. This minimizes crystal decay due to laser irradiation commonly observed for monochromatic time resolved experiments. Therefor this method allows the increase of laser power for the investigation of small structural changes.