



	Experiment title: Investigations on the structure of ultrafast intermediates of homogeneous topochemical reactions	Experiment number: CH 2174
Beamline: ID09B	Date of experiment: from: 15 July 2006 to: 18 July 2006 (MDT)	Date of report: 15/08/2006
Shifts: 9	Local contact(s): Dr. Q. Kong	<i>Received at ESRF:</i>
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Report:

Recently we have started a series of studying and characterising photo-induced chemical reactions in organic single crystals with picosecond time-resolved x-ray diffraction (TR-XRD). The results of these studies have been published in [1-5]. Two months ago, in experiment No **CH-2174** we specifically studied the occurrence of structural intermediates during [2+2] photodimerisation processes and its influence on the periodical order of the transforming material, namely whether the reaction is of homogeneous or heterogeneous character.

Due to asbestos problems in the beamline in the begin of 2006, the beamtime for this experiment has been postponed for about 6 months and 9 shifts could be given instead of 15 allocated ones. Due to the delayed and limited experimental time we therefore decided to concentrate on time-resolved x-ray diffraction studies on the [2+2] photodimerisation process of 2-(α -Styryl)pyrylium salts (StyPy) and the *reversible* character of this photodimerisation.

We started the experiments with the working hypothesis that during homogeneous photodimerisation processes short-living intermediates are populated during the photo-transformation which are similar to pi-stackings in organic crystals. These intermediates stabilise the lattice in such a way that the transformation proceeds homogeneously. In StyPy, the population of this intermediate must be reversible meaning that the photo-populated intermediate can be de-populated via thermal processes (temperature) back to the reactant state; the nature of the intermediate state should be a very flat local minimum of the energy hypersurface describing the reaction process.

For the experiment, single crystal layers were used which were grown on a heatable substrate plate. Due to this preparation process we could not probe all Bragg diffractions on the Ewald sphere of StyPy but were limited to about 40 Bragg diffraction peaks. However, about 40 % of the diffractions investigated show more than 10 % of structure factor changes which – squared – results in up to max. 50 % of integral intensity change on the Bragg diffraction. The signs of the changes are positive and negative; they can well be separated from ordinary heating effects.

Figure 1 a) and b) summarises selectively the essential results of this beamtime on two prominent Bragg diffraction peaks:

By using the appropriate temperature where reversible photodimerisation can happen, we can “photo-switch” the crystal from the monomer to the dimer structure by photo-absorption processes. The switching is very fast and essentially limited by the natural halfwidth of the x-ray probe pulse. As been seen, the photoswitching is very efficient if we choose a temperature near the temperature of the reversible process. Note, that spectroscopic measurements suggests that this temperature should lay around $T = 100\text{ }^{\circ}\text{C}$, a temperature, which we can confirm by TR-XRD.

By comparing the measured x-ray diffraction intensity changes with the differences calculated from the known monomer structure factor and the known dimer structure factor, we come to the conclusion that 10 % of all chromophors in the crystal are photoexcited by 5 uJ laser power, and about 30 % if we increase the power to 25 uJ. The found transformation ratios – though they are non-linear- are in absolute agreement with the predicted values taking into account optical reflection and absorption effects (note that the excitation geometry is quasi-parallel between optical pump and x-ray probe pulse, and is therefore far away from the Brewster angle condition and furthermore varies for [002] and [200] Bragg diffraction geometry). Note, that the $F_{[002]}(\text{monomer}) < F_{[002]}(\text{dimer})$ and that $F_{[200]}(\text{dimer}) < F_{[200]}(\text{monomer})$.

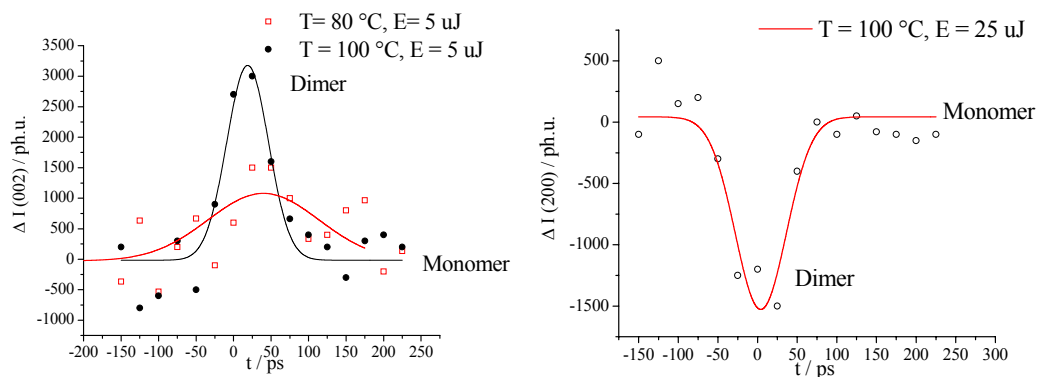


Figure 1: left: Relative intensity changes of the [002] Bragg diffraction peak as a function of temperature and time. Right: Relative intensity changes of the [200] Bragg diffraction peak.

We conclude that in contrast to BBP, the StyPy intermediate minimum is so flat that its population cannot be seen with 80 ps time resolution which furthermore explains consistently the reversibility of this homogeneous [2+2] photodimerisation process. Currently we are performing quantumchemical calculations in order to support this conclusion.

In sum as a result of the beamtime we can state that StyPy can be used as a x-ray photo-scatter-switcher which is triggered by optical light with an ultrafast response function.

To our knowledge this is the first time such switching behaviour has been seen on such a fast time scale without destroying the long-range order of the crystal. At the moment we are preparing the manuscript for this important scientific result and in future we hope to have more possibility of investigating this system with TR-XRD.

References

- [1] J. Davaasambuu, G. Busse, S. Techert, *J. Phys. Chem. A* **110**, 3261-3265 (2006).
- [2] J. Davaasambuu, G. Busse, S. Techert, *J. Phys. D: Appl. Phys.* **38**, A204-A207 (2005).
- [3] J. Davaasambuu, P. Durand, S. Techert, *J. Synchrotron Rad.* **11**, 483-489 (2004).
- [4] S. Techert, *J. Appl. Cryst.* **37**, 445-458 (2004).
- [5] G. Busse, Th. Tschentscher, A. Plech, M. Wulff, B. Frederichs, S. Techert, *Faraday Discuss.* **122**, 105–117 (2002); S. Techert, General Discussion, *Faraday Discuss.* **122**, 392 ff (2002).