



	Experiment title: Topochemical photodimerisation of cinnamic acid imaged by in situ IXS	Experiment number: CH-4040
Beamline: ID20	Date of experiment: from: 25 June 2014 to: 1 July 2014	Date of report: 13 October 2014
Shifts: 18	Local contact(s): Christoph Sahle	<i>Received at ESRF:</i>
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Report:

We measured non-resonant inelastic X-ray scattering spectra from the carbon *K*-edge of cinnamic acid (CA) and its dimerisation product, truxillic acid (TA) crystals. In addition, the timeseries of the spectra show evolution of an X-ray induced chemical reaction. The main aim of the experiment was to obtain information on the development of the dimerisation reaction in CA, which is usually initiated by irradiation with UV light. This reaction is a canonical, so-called [2+2] photodimerisation reaction, where two CA monomer molecules bind together to form a CA dimer, truxillic acid molecule [1].

The spectra were obtained with the X-ray Raman Scattering spectrometer of the beamline ID20 using its imaging capability. The incident beam was monochromatized with a Si(111) premonochromator and a Si(311) channel-cut monochromator, and focused to the sample to a size $135 \times 800 \mu\text{m}$ (V×H). The large width of the beam was used to enable imaging a large region. The sample crystals were mounted on a He-flow cryostat and cooled to ~ 10 K to slow the X-ray induced reaction. The TA crystals were produced from CA crystals by illuminating them under an UV lamp.

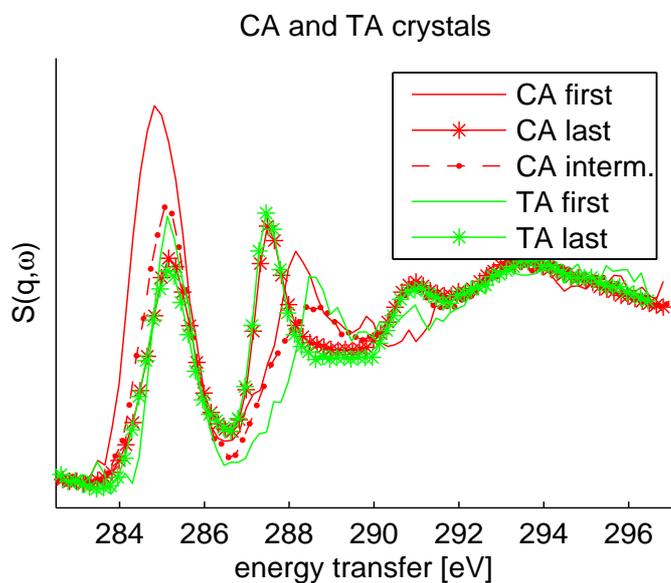


Figure 1: The first and last spectrum from the timeseries from cinnamic and truxillic acid crystals, and one intermediate spectrum from the cinnamic acid timeseries.

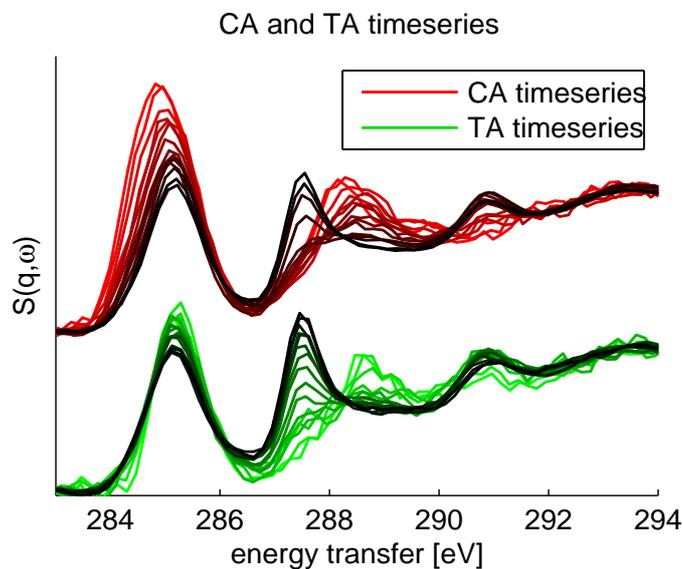


Figure 2: Comparison of the timeseries of the spectra from cinnamic and truxillic acid crystals. Darkening of the spectra corresponds to later time.

The measured spectra from the CA and TA crystals show the effect of dimerisation as a shift and decrease of the main peak (see in Fig. 1 the 'CA first' and 'TA first' spectra). The effect arises because in the dimerisation the intramolecular double C=C bonds in CA are transformed to single bonds and new single bonds are formed between two CA molecules producing TA molecule.

The timeseries of spectra (Fig. 2) show an evolution of the spectrum due a chemical reaction induced by the probing X-rays. In the case of CA there exists a two-step process. In the first step the spectrum changes to closely resemble the initial TA spectrum (in Fig. 1 'CA interm.' vs. 'TA first'), suggesting that the X-rays induce the same dimerization reaction as UV light, producing TA.

In the second step, a pronounced new peak forms at 287.5 eV. This occurs also in the case of the TA, and the last spectra from the CA and TA timeseries are nearly identical (Fig. 1 'CA last' vs. 'TA last'), which supports the view that the product of the first step in CA is TA. This second step change occurs with much longer time scale than the first step, hinting that reaction mechanism is also different.

Detailed analysis of the spectra and publication preparation are currently underway. In the analysis the imaging technique is exploited to examine possible spatial inhomogeneities on chemical structure.

References:

[1] M. D. Cohen *et al.*, 384. Topochemistry. Part II. The Photochemistry of *trans*-cinnamic acid, J. Chem. Soc., 2000 (1964).