



**Experiment title:** Deconvoluting Ultrafast Dynamics: picosecond resolution in solution studies of the photo-dissociation and geminate recombination of Iodine.

**Experiment number:**  
CH-522

**Beamline:**  
ID09

**Date of Experiment:**  
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**Date of Report:**  
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**Shifts:**  
12

**Local contact(s):**  
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*Received at ESRF:*

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**Report:**

This experiment attempted to establish two distinct methodologies:

- that photochemical processes in solution can be visualised using a fs laser pump and a 100 ps X-ray probe;
- that, from the differences observed in a series of evenly spaced time points, the X-ray pulse can be deconvoluted out so as to improve the temporal resolution beyond the 100 ps X-ray pulse duration.

To facilitate these goals the review committee generously allocated 21 shifts to this experiment. This, however, was reduced to 12 shifts because of pressure on the beamline's schedule, and further reduced to approximately 8 shifts as laser experts from Coherent had to work on the fs laser system during our scheduled beamtime. Other technical and software failures meant we had approximately 2 shifts with both the laser optimised and the single X-ray bunch of hybrid mode being selected. Nevertheless, this time proved sufficient to achieve the first goal of this experiment, but not to achieve the second.

Our experiment utilized a simple flow-cell, constructed in Uppsala, whereby solutions flowed through an X-ray capillary in the region of interaction with the X-ray/laser pulse. Reliable measurements of the optical spectra of our samples in this flow-cell, taken using our microphotospectrometer, showed that light scatter from the capillary walls was minimal (<10 %) when the capillary diameter was  $\approx 300 \mu\text{m}$ . Each solution was circulated through this capillary using a peristaltic pump. The fact that this flow cell could be mounted directly on the goniometer head provided a simple procedure for aligning both the X-ray beam and the laser beam at the sample position.

So as to establish that intensity differences could be observed arising (primarily) from a difference in the separation of atoms within solution, we initially collected static images from both  $\text{I}_2$  (20 mMol) and  $\text{Li}^+\text{I}^-$  (40 mMol) in ethanol. Fig. 1 gives the measured intensity differences as a function of the pixel radius from the beam centre, after X-ray scattering data recorded using the on-line CCD was integrated in rings and normalised. A strong periodic (almost sinusoidal) variation of intensity with

radius arises, due (primarily) to the difference in X-ray scattering interference effects between the Iodine atoms (ions) of the respective solutions: in the  $I_2$  solution the distance from one Iodine atom to its nearest neighbouring Iodine atom is  $2.72 \text{ \AA}$  (due to these sharing a covalent bond), yet this distance is some tens of Angstroms in the  $L^+I^-$  solution. Additional structure at low resolution reflects X-ray interference effects between the Iodine atoms and the surrounding solvent.

A pump/probe experiment was then performed on  $I_2$  @ 40 mMol in  $CH_2Cl_2$ . In this solvent the measured lifetime of the excited A state (atomic spacing  $3.1 \text{ \AA}$ ) is  $\sim 200 \text{ ps}$  [Harris *et al. Ann. Rev. Phys. Chem.* **39** 341 (1987)], making this an ideal candidate for this proof of principle experiment. The output power of the fs laser downstream of the OPA @  $\lambda = 530 \text{ nm}$  (green light) peaked at  $\approx 25 \mu\text{J}$  per pulse, but typically fell by 50 % over one shift. After trialing a number of optical configurations, the laser spot when focussed to a diameter  $\approx 150 \mu\text{m}$ , and using an X-ray spot of  $80 \mu\text{m} \times 100 \mu\text{m}$ , gave the best results. With the laser pulse set to coincide with the rising edge of the X-ray pulse, a laser induced intensity difference, shown in Figure 2, was observed. This reflects that the X-ray interference between the Iodine atoms is changed due to sample photolysis, whereby the atoms become further separated. The dark line shows a simple theoretical model neglecting (at this point) the Iodine atom's interference with the surrounding solvent, and assuming only the A-state and the X-state are populated. Theoretical development of this model is currently being pursued.

This interpretable intensity difference was corroborated with a second laser-pumped image recorded under identical conditions. However, the intensity differences for further time points are empty, due to this very small laser spot walking off the X-ray spot. Figure 3 shows the differences between two equivalent measurements after making small corrections for the CCD dark current (varying by a fraction of a count per pixel from one reading to the next) and a slight non-linear response of the detector. This shows (and was always seen) that two equivalent measurements give a flat baseline (within noise) and our observation cannot be interpreted as due to drift within the X-ray detection system.

A final experiment pumped Iodine in ethanol at the second harmonic ( $\lambda = 400 \text{ nm}$ ) as this provided approximately  $150 \mu\text{J/pulse}$ : a six to ten fold increase in power essential for stable photo-excitation. Five time points were collected, each 50 ps apart, the laser being walked through the X-ray pulse as advocated within our deconvolution protocol. This experiment was unsuccessful. Follow up experiments in Uppsala have shown that water is also required to give a strong absorption @ 400 nm for Iodine in ethanol (we used 99.8 % dry ethanol in Grenoble) and a series of fs laser studies exploring this observation have been initiated.

In summary, this experiment yielded the first demonstration that picosecond time scale photo-induced structural changes on simple systems in solution can be observed with synchrotron generated X-rays. We anticipate that the signal to noise ratio will be improved approximately four fold following the planned undulator optimization and the move from hybrid bunch mode to single bunch mode. We therefore believe that this field shows a high degree of promise, but we strongly encourage initiatives to increase the available laser power per pulse. The efforts of the beamline staff above and beyond the call of duty, particularly Dr. Simone Techert and Dr. Michael Wulff, played a crucial role in the success of this experiment.

