ESRF	Experiment title: Deconvoluting structural dynamics: picosecond resolution in solution studies of the photo-dissociation and geminate recombination of Iodine.	Experiment number: CH-586
Beamline: ID09	**Date of Experiment:** from: 5th April 99 to: 8th April 99	**Date of Report:** 25 February 2000
Shifts: 9	**Local contact(s):** Dr. Michael Wulff* & Dr. Simone Techert*.	*Received at ESRF:* 28 FEV 2000

Names and affiliations of applicants (*indicates experimentalists):

Dr. Richard Neutze* (Dept. Biochemistry, Uppsala University, Sweden)
Mr. Remco Wouts* (Dept. Biochemistry, Uppsala University, Sweden)
Mr. Adam Kirrander* (Dept. Biochemistry, Uppsala University, Sweden)

Report:

This experiment aimed to build upon our earlier successful experiment, CH-522, which was performed five months earlier. In experiment CH-522 we succeeded in capturing the changes in the diffuse scattering profile of a simple photochemical system when photo-excited. The system of study in the earlier experiment was Iodine in dichloromethane. Following photo-excitation by a short (100 fs) green laser pulse ($\lambda = 530$ nm) molecular iodine under goes the reaction

$$I_2 + h\nu \rightarrow 2I \rightarrow I_2^* \rightarrow I_2$$

where the $*$ denotes an excited state of molecular iodine. The excited state of iodine, I_2^*, has a larger separation between the two atoms than the ground state. Upon spherical averaging of the X-ray scattering, due to the random orientations taken by all atoms within the sample, the diffuse scattering profile of the photo-excited sample appears slightly changed from that of the un-excited sample.

In the earlier experiment, as with this experiment, we used an image-intensified CCD detector to record the diffuse scattering profile from the sample. We then integrated the recorded image in rings before subtracting two integrated images from each other. This protocol enabled us to observe an oscillation in the diffuse scattering profile (figure 1) which gave good agreement between experiment and theory.

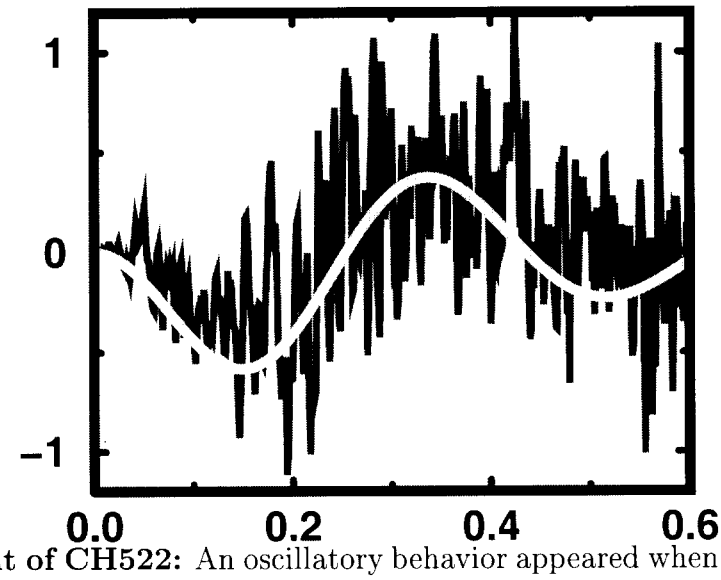
The earlier experiment, however, was hampered by the relatively small signal and the large statistical noise. In particular, we recorded X-ray images for fifteen minutes before reading the detector. It was very difficult to achieve a stability to the order of 0.1 % from one image to the next, and this severely restricted the potential of these experiments when using this approach. So as to address this issue, we made one significant change in this experiment. The decision was made to move from a pump wavelength of 530 nm, which required the OPA so as generate green light, to a pump wavelength of 400 nm, which is the second harmonic of the laser system. This in itself achieved a five fold gain (approximately) in the amount of light which could be delivered onto the sample, and we felt that this gain could improve the stability of the entire experimental set-up.

Once again the system of study was chosen to be Iodine in solution. However, the solvent was changed from dichloromethane to ethylene glycole. In this solvent molecular iodine has a strong absorbance at 400 nm. Unfortunately, however, there was a cost in changing this solvent. Whereas the excited state I_2^* has a lifetime of 400 ps in dichloromethane, the lifetime of the excited state of iodine in ethylene glycole was measured by Dr. Jan Davidsson, prior to traveling to Grenoble and using the fs laser in Uppsala, to be only 20 ps.

Three days were allocated to this experiment: one day normal filling (which was used for beam alignment, and for installing the CCD detector), a machine day (which was used for optimising the fs laser) and then two days of single bunch. Apart from some troubles with the interlock system, which appeared to affect the laser's mode-locking to the synchrotron ring, we were very happy with the performance of the beamline and all the components. The staff at ID09 provided a very professional service, and by the early afternoon on the first day of single buch all aspects were ready such that we could pursue the experiment.

Ultimately, however, the cost in terms of the signal strength (reduced when a 20 ps sample response is convoluted with the 160 ps X-ray probe pulse) and the critical need for accurate timing, caused this experiment to be unsuccessful. Despite the extra power available from the laser in going to a 400 nm pump wavelength, the results from this experiment we no more conclusive than the earlier experiment.

The most valuable result to come from this experiment, therefore, was the recognition that the detector strategy (using an image intensified CCD detector and integrating for fifteen minutes prior to reading each image) was not optimal for such critical experiments. In the months which followed, discussions with Dr. Menhard Kocsis of the ESRF detector group were initiated. From these discussions a decision was made to abandon the CCD detector, and to construct a gas filled detector which could be coupled to a lockin amplifier. As such a lockin detection system well suited to the needs of this experiment was developed, and was utilised in the follow up experiment CH-706 (see experimental report). This strategy proved very successful.



Experimental result of CH522: An oscillatory behavior appeared when the diffuse scattering profile (after integrating in rings) of iodine in solution was subtracted from the diffuse scattering profile of photo-excited iodine in solution,