



Experiment title: Visualizing the picosecond dynamics of geminate & non-geminate recombination of Iodine in solution.

Experiment number:

CH-706

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9

Local contact(s):

Dr. Michael Wulff* & Dr. Simone Techert*.

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Names and affiliations of applicants (*indicates experimentalists):

Dr. Richard Neutze* (Dept. Biochemistry, Uppsala University, Sweden)

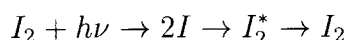
Mr. Remco Wouts* (Dept. Biochemistry, Uppsala University, Sweden)

Doc. Jan Davidsson* (Dept. Physical Chemistry, Uppsala University, Sweden)

Dr. Menhard Kocsis* (ESRF)

Report:

This experiment aimed to build upon our earlier successful experiment, CH-522, which was performed slightly more than twelve 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 undergoes the reaction



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 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 which gave good agreement between experiment and theory. However, in a follow up experiment (CH586, see report) we ran up against the limitations of using a CCD detector as the detection system. It was therefore decided to change strategies with respect to the choice of detector.

Following discussions with Dr. Menhard Kocsis of the ESRF detector group, a new detection system was developed for this purpose, which is illustrated in figure 1. A gas filled detector was fed directly into a pre-amplifier, and then into a lockin amplifier, which was locked-in-to a 130 Hz signal from an optical chopper, which chopped the pump laser pulse at 130 Hz (which differs from the 987 Hz repetition frequency of the laser when mode-locked to the synchrotron ring). This set-up is routine in femtosecond chemistry laboratories (eg. in the laboratory of Doc. Jan Davidsson in Uppsala) and provides a very sensitive way in which to recover a small, noisy signal. The gas-filled detector constructed by Dr. Menhard Kocsis was a key component of the setup.

As with experiment CH522, we chose to work with molecular iodine in dichloromethane. In this solvent the sample has an absorption peak at 510 nm (which we used as the pump wavelength) which forced us to use the OPA. As such a laser power of approximately 20 μJ per pulse was delivered to the sample. A significant advantage of working with dichloromethane, however, is that the time scale of vibrational relaxation of the excited state I_2^* is 400 ps, which proves very convenient when working with a 160 ps X-ray probe.

Three days of 16 bunch mode were allocated to this experiment. On the first day we commissioned the new detector system, and tested certain aspects of its performance. It was apparent that signals of a few tenths of a percent were resolvable with the lockin technique. With the detection setup successfully commissioned, we then proceeded with the experiment.

A pump/probe experiment was then performed on I_2 @ 40 mMol in CH_2Cl_2 . The results from the most successful run are shown in figure 2, which shows the output of the lockin amplifier as a function of the X-ray probe delay relative to the moment of laser photolysis. These data were recorded over a period of two hours immediately prior to a new injection of the storage ring. As expected, the data give a good fit to the theoretical curve obtained by convoluting the 400 ps decay of the excited state of Iodine with the 160 ps X-ray pulse shape.

This result strongly complements the results from experiment CH522, which visualised the differences in atomic spacing between photo-excited iodine and iodine in its ground state. As such we feel that there can be little doubt that the signals seen in both experiments, each observing a different aspect of the same phenomenon using very different detector strategies, arises from the photo-chemistry of Iodine in solution. We also feel that, now that the lockin approach has been successfully implemented, it can be greatly improved. We anticipate that a general experimental strategy, applicable to the study at synchrotron sources of the picosecond dynamics of a variety of photo-chemical systems in solution, can potentially emerge from these initial experiments.

