

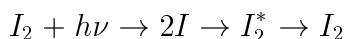
	Experiment title: Visualising the picosecond dynamics of CH ₂ I ₂ in solution.	Experiment number: SC-810
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Shifts: 12	Local contact(s): Dr. Michael Wulff	<i>Received at ESRF:</i>

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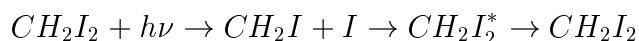
Report:

This experiment aimed to build upon two previously successful experiments, CH-522 and CH-706 which was performed in the fall of 1998 and 1999. Those two experiments followed the recombination dynamics of photo-dissociated iodine in solution. Following photo-excitation by a short (100 fs) green laser pulse ($\lambda = 530$ nm) molecular iodine under goes 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. The two previous experiments succeeded in observing changes in the diffuse X-ray scattering profile from the excited state molecules (as seen on an image intensified CCD camera, Expt. CH-522) and following the time-scale of their relaxation back to the I_2 state (500 ps in the solvent used, CH₂Cl₂, Expt. CH-706). A manuscript describing these two experiments is now at a very advanced stage of review, and it seems likely to be accepted for publication within a few weeks.

In this experiment we set out to perform a similar experiment on CH₂I₂, which has the photo-reaction:



The excited species $CH_2I_2^*$ has a life-time of a few ns, making it an ideal target for studies at the synchrotron. Furthermore, there is controversy within the literature as to the structure of the excited species, and so this system offers an opportunity to extend the earlier proof-of-principle experiments so as to address an open scientific question.

This reaction can be initiated by short-wavelength light, and we used the third-harmonic at 267 nm. Approximately 20 μ J/pulse were available. Due to a relatively low power of the fs laser, we minimised

the sample volume by using an open jet, of approximately 150 μm in diameter. Due to the harsh nature of the solvent and the photo-chemical species, we enclosed the jet in a semi-enclosed cell. However, as described below, the jet itself proved not to be sufficiently stable to succeed with these experiments.

A second methodology development was the use of the Mar CCD camera, whereas previously a Princeton image intensified camera was used. In addition we used a "Pink-Laue" X-ray beam - namely a narrow wavelength spread line of the undulator directly, without using a monochromator. The goal of this approach was to increase the count-rate (by a factor of 50) and therefore decrease the integration time per image. This proved to be quite successful, and a number of technical problems we had previously experienced seemed to have been overcome. Software was written so that everything was automated, and we returned from the synchrotron with a couple of thousand images of diffuse X-ray scattering to analyze.

This analysis has been done over the summer, and it was disappointing. Although the CCD camera appeared to be more stable, there were other experimental artifacts. In particular, the use of an open jet (which minimized the sample volume, so as to compensate for the low photon flux available from the 3rd harmonic of the laser) proved disastrous. There were clearly changes in the diffuse X-ray scattering profile which were at a low level. However, these did not correlate with the laser being on or off. Instead the changes observed could be modeled quite well by changing the relative ratios of the background scatter (from the air, and from gaseous CH_2I_2 within the sample-cell since this solvent is quite volatile) by a few percentage points. As such we conclude that the modified sample environment was not stable enough for this experiment as it was performed. Fortunately our earlier experiments with a CCD camera used a fully enclosed flow-cell rather than a jet, and the nature of the changes in the diffuse X-ray scattering which emerged here were very different to that observed with the iodine experiments.

Despite this disappointment, there were some positive outcomes from this experiment. In the first instance the quantum yield for the third harmonic of the laser was good, and a planned upgrade for the laser system at ID09 should make it possible to obtain really significant improvements in the laser power available for photolysis. As such it seems that the goal to study CH_2I_2 is realistic. Secondly the Mar CCD detector in combination with the Pink-Laue approach seemed to be more stable than the earlier image intensified CCD system. Thirdly, the heat load on the optics did not prove a major problem when increasing fifty-fold the amount of X-ray flux within the experimental hutch in 16 bunch mode by moving over to a Pink-Laue X-ray beam rather than a monochromatic beam. In addition, there were technical developments enabling the timing of the laser and X-ray pulses to be monitored on-line. This development was excellent. However, there is clearly a need to work on the nitty-gritty of the sample environment and the optimal detector strategy (eg. a gas filled detector in combination with a lock-in amplifier was used in CH-706, and may have been a better choice). Until these technical details are ironed out by careful technical development (which would not require the fs laser, nor single-bunch mode) it is difficult to feel confident that the most will be made of the outstanding facilities and X-ray optics available at ID09 for these experiments, which inherently recover only very small light-induced changes in the diffuse X-ray scattering profile.