



Experiment title:
Nanosecond dynamics of CH₂I₂ in solution

Experiment number:
CH-1228

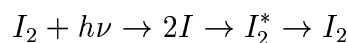
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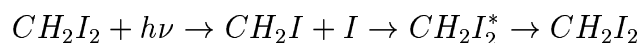
Report:

This experiment aimed to build upon two previously successful experiments, CH-522 and CH-706 which were performed at ID09 of the ESRF in 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 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. The main results from these two previous experiments were published in the fall of 2001 [1].

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



The intermediate species $CH_2I_2^*$ has a life-time of many ns (or even μ s), making it an ideal target for studies at the synchrotron. Furthermore, there is controversy within the literature as to the structure of the long-lived intermediate 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 was initiated by short-wavelength light, and we used the third-harmonic at 267 nm. Approximately 20 μ J/pulse were available. In a previous experiment on this system (SC-810) we found that the stability of a liquid jet was insufficient for these experiments. We therefore passed the sample (50 mMol) through an enclosed flow-cell, as used in the original iodine experiment (CH-522).

This strategy proved to be extremely successful. In combination with a “pink-Laue” (rather than purely monochromatic) data-collection strategy (using the narrow undulator line directly), and the MAR-CCD detector (apparently much more stable than the previous camera at ID09) the improvements in X-ray scattering data were dramatic.

The study of CH_2I_2 in CH_2Cl_2 at first appeared extremely promising, with a strong signal in the μs time-scale which could be identified (by comparison with other studies on liquids using a cryo-stat for heating) as due to thermal heating. The signal could then be optimised by changing the position of the laser focal-spot. On the sub-ns time-scale there was also clearly present a very reproducible signal of a different nature to the thermal signal. However, upon performing the negative test (CH_2Cl_2 by itself without CH_2I_2), virtually the same data were recovered. From this we realised that the third harmonic of the laser was pumping a non-linear optical transition in the solvent, and we were studying the effects of energy relaxation in the solvent alone. While an unexpected result, the data nevertheless is revealing some basic photo-chemistry and requires further analysis.

The experiment was then repeated for CH_2I_2 , but this time dissolved in methanol. The negative tests (methanol alone) gave a negative result, yet the data when CH_2I_2 was dissolved clearly showed significant changes on all time-scales. Analysis of the signal on the μs time-scale shows again the thermal signal. Furthermore, on the sub-ns time-scale, there is (at high-resolution) a clear signal consistent with the presence of a $\text{CH}_2\text{I-I}$ isomer, which is believed to be the most probably candidate for CH_2I_2^* . However, to fully interpret this data we need to model the solvent-changes against the X-ray scattering data recorded at low-resolution. For this we have begun a collaboration with molecular dynamics experts in Gothenburg, but there is work still to be done.

In summary, we believe that this experiment (as with others performed on ID09 during 2002) mark a milestone in so far as the experimental technique has now displayed its true potential. The data are now so reproducible and the signal-to-noise so good, that the possibility of linking the experimental results to a molecular-dynamics level analysis is clearly evident. This was our aim when we began the experimental programme more than four years ago, and we believe that there is much to be done which can build upon these results.

References:

- [1] R. Neutze, R. Wouts, S. Techert, J. Davidsson, M. Kocsis, A. Kirrander, F. Schotte & M. Wulff, Visualizing photochemical dynamics in solution through picosecond X-ray scattering, *Physical Review Letters* 87, 195508-1-195508-4 (2001).