

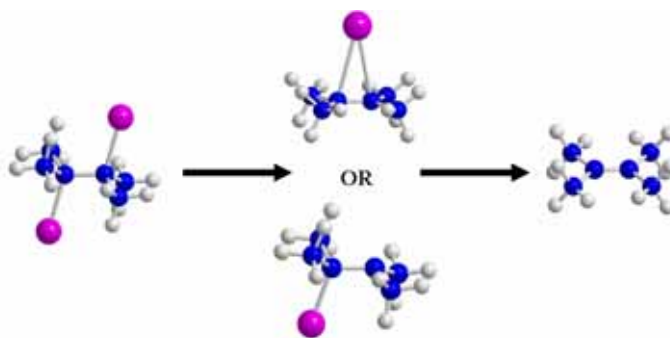


	<b>Experiment title:</b> Capturing the bridged structure of an excited diiodoethane derivative in solution	<b>Experiment number:</b> CH-2060
<b>Beamline:</b>	<b>Date of experiment:</b> from: 03/10/2005 to: 07/10/2005	<b>Date of report:</b> 21/08/2006
<b>Shifts:</b>	<b>Local contact(s):</b> Michael Wulff	<i>Received at ESRF:</i>
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## Report:

The experiment CH2060 aimed at determining the “bridged structure” radical of a small organic system triggered by a photo-reaction. This bridged radical has been believed to control stereochemical selectivity in the halogen elimination reaction. We have recently investigated the structural dynamics of  $C_2H_4I_2$  and  $C_2F_4I_2$  in methanol using time-resolved x-ray scattering. Whereas the  $CH_2ICH_2$  radical has a bridged structure, the  $CF_2ICF_2$  radical is in an anti conformation. This fact implies that the substitution of atoms can alter the structure of the radical. The underlying idea was to probe the structure of the radical (bridged or anti conformers) in the photodissociation of 2,3-iodo-2,3-dimethylbutane ( $C(CH_3)_2I-C(CH_3)_2I$ ) in methanol/cyclohexane. Our preliminary DFT calculation results show that the bridged structure of the  $C(CH_3)_2I-C(CH_3)_2$  radical is more stable than the anti conformer. Another idea was that the enhanced contrast of scattering intensity between the bridged and anti radicals by substitution of H atoms by  $CH_3$  group from the  $C_2H_4I_2$ . The use of higher contrast was expected to facilitate the structural identification of the transient radical. The schematic proposed for the structural change of this molecule is summarized in Figure 1.

For the elucidation of the radical structure, we used a laser pump and x-ray probe scheme available at the ID09B beamline. The photodissociation of the sample was initiated by a laser pulse (267 nm, 2 ps pulse width, 35  $\mu J$ /pulse, and 100  $\mu m^2$  at the sample) and was probed with a white x-ray beam (3 % bandwidth centered at 18.2 keV) produced by a U17 undulator.



**Figure 1:** Proposed structural dynamics in the photodissociation of  $\text{C}(\text{CH}_3)_2\text{I}-\text{C}(\text{CH}_3)_2\text{I}$  in solution

$\text{C}(\text{CH}_3)_2\text{Br}-\text{C}(\text{CH}_3)_2\text{Br}$  was used in place of  $\text{C}(\text{CH}_3)_2\text{I}-\text{C}(\text{CH}_3)_2\text{I}$  due to the challenge of synthesizing the latter. It has been suggested that the bromine compound also has a bridged structure, but this bridged structure could not be observed directly. Usage of this cousin bromine molecule also provides a good chance to test the signal-to-noise ratio of time-resolved liquid x-ray diffraction.

We used an open jet flow to circulate the solution. This approach allows us a more efficient use of laser photon and a replacement of sample for every laser shot (CH1746 and CH1908). The chromophore was dissolved in methanol and a 150 mM concentration was chosen to maximize the signal of the photoproduct by considering the low absorption coefficient near 267 nm. To check the data-collection quality, we preliminary measured difference scattering data at selected time-delays (100 ps, 300 ps, 1 ns, 3 ns, and 1 us). All measured data was in disagreement with our models due to the instability of the sample jet system. Some solute powders were stuck on the output widow of the high-pressure sapphire open-jet nozzle. This powder blocked the flow of the jet. We also tried to perform measurements using the diluted sample solution (100 mM), but the results were the same. We believe that this problem is caused by the decreased solubility of the solute. The decreasing of the solubility can originate from the laser heating and/or the sudden pressure changes of the solution through the open-jet nozzle. Since we spent all available solutes, we could not launch further experiments. The remaining beam-time was devoted to collect solvent (methanol and water) response signals at selected time-delays (100 ps and 1 us) by IR excitation. Using IR excitation of pure solvent molecules, we can measure the solvent response signal experimentally without any chemical structural changes.

Although we could not collect reasonable time-resolved data from the photodissociation of the target molecule, we consider that our preliminary attempt gave us valuable results. To unravel effects of a substitution and an electronic energy on the radical structure (anti or bridged), we need more beam-time to investigate a different molecule of interest. The systematic understanding of radical structures of various systems during photodissociation will help explain the stereochemical selectivity in chemical reactions.