ESRF	**Experiment title:** The molecular structure of diiodoethyl radical	**Experiment number**: CH-1908
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Report:

We have recently studied the elimination reaction of 1,2-diiodoethane ($C_2H_4I_2$) molecule (CH1646), which after photo-excitation with 267 nm photons gives a short-lived iodoethyl radical ($CH_2ICH_2•$) and iodine atom (I). In that experiment we collected only two sub-nanosecond times at which the early stage of the reaction was probed, 100ps and 300ps. In the newly conducted experiment, (CH1908), we focused on the early temporal window by collecting the following times: -100ps, -75ps, -50ps, -25ps, 0ps, 25ps, 50ps, 75ps, 100ps.

For this purpose we used a pump-probe diffractometer installed at ID09B. The photo-reaction was triggered by pulses delivered from a femtosecond CPA amplifier (λ=800nm) and further converted to third harmonic (267nm, 35μJ/pulse, 1 kHz repetition rate). Before reaching the sample the pulses were stretched with silica prisms to the pulse-length of ~2ps in order to avoid multiphoton excitations. The reaction was probed with the white beam (0.45 keV bandwidth centred at 18.2 keV) produced by U17 undulator. The chromophore was dissolved in methanol and a concentration of 60 mM was chosen to maximize the photoproducts signal while keeping the inter-solute contributions negligible. We used an open jet flow to circulate the solution, which apart from the obvious advantage of refreshing the sample for every laser pulse it also allowed a more efficient use of available laser photons. The damage threshold for glass of which capillaries are made no longer limited the laser spot size, which was consequently tailored to match the size of the X-ray beam.

Time-resolved liquid diffraction does not allow refining molecular structures comparably to single crystal diffraction. Instead, we compare our data to the calculated geometries and use statistical significance, χ^2, for fingerprinting the molecules. Our theoretical approach is built on a model in which all reacting species and the solvent itself enter the equation of state. It should be stressed that the solvent background overwhelmingly dominates the scattering signal. The inclusion of solvent hydrodynamics ensures that the solvent response is appropriately accounted for in the global analysis, and it allows probing the temperature and density of the liquid as they change in time due to ongoing photochemistry. This way the time varying concentrations of reacting chemical species, which translate to time varying energy released to the bulk, are linked to the energy absorbed by liquid, a quantity probed independently through temperature jumps.

The purported bridged structure is short lived, hence the discrimination between this elusive structure and a classical one is particularly sound at the shortest times experimentally available. The figure below shows a result of the fitting procedure, outlined above, using the data collected during the beamtime CH1908. In particular, the inset in the figure provides a convincing evidence of a preferential formation of the bridged structure over the classical anti structure. With greatly improved accuracy these measurements support our earlier conclusions (main plot).

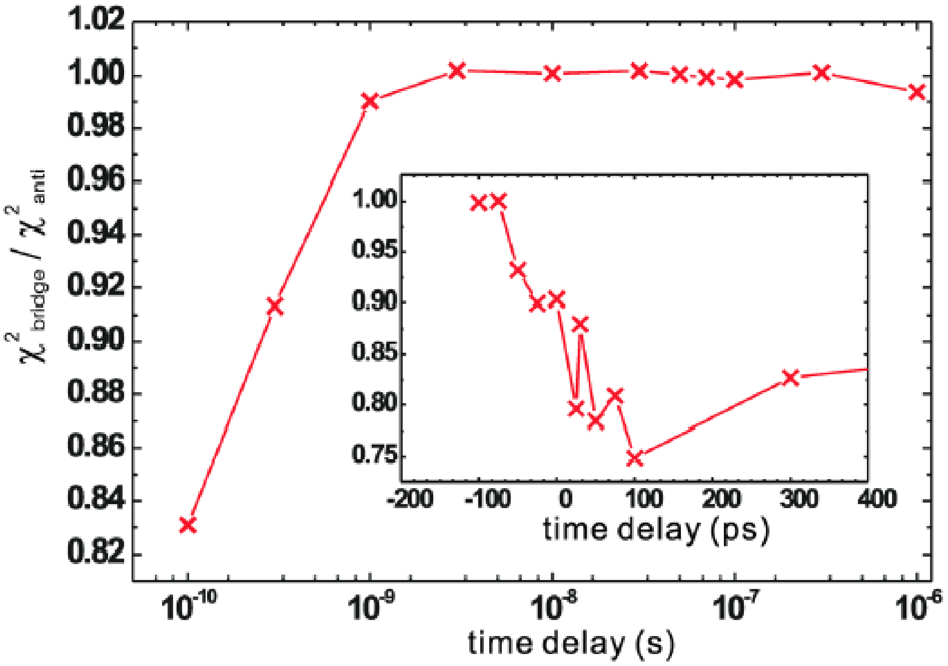

Figure: The bridged model versus the anti model. The data were fit to both models and the final figures of merit are compared as a ratio. Below 1 ns, where the concentration of C2H4I is high, the ratio is significantly below 1, confirming that the bridged model fits the data better than the anti model. The inset shows the results from the time splicing experiment including many more points on a sub-nanosecond scale, which supports the above conclusion.

We would like to stress the fact that the time splicing technique, i.e. probing with slices of an X-ray pulse, offers a significant improvement in time resolution for any time resolved experiment on ID09B station. Already with 25 ps long slice on the rising edge of the X-ray pulse the structural discrimination is evident (see figure).

Finally, we would like to point out the importance of our newly implemented sample circulation system. The open jet has an advantage of dramatically decreased background contaminating the data (when a capillary flow is used half of the scattering signal comes from the glass). Laser triggered signals are subject to meticulous normalisation procedures and having the contribution of parasitic scattering reduced by a factor of 2 is a genuine asset. As mentioned earlier in the report, the open jet allows focusing the laser beam to a size limited by diffraction rather than damage thresholds of materials.