ESRF	**Experiment title:** Visualizing the photo-dissociation of I_3^- in solution by time-resolved X-ray diffraction	**Experiment number**: CH-2176
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Report:

We have recently studied the photodissociation reaction of the triiodide ion (I_3^-). The excitation gives diiodide ion (I_2^-) and iodine atom (I). Previous spectroscopic results reported that the three-body dissociation ($I^- + I + I$) can occur when the excitation energy is high enough. We used both 259 nm and 389 nm photons in order to investigate the excitation energy dependence of the reaction dynamics. To follow the whole process of the reaction, we collected the diffraction data at the following times: -200 ps, 100 ps, 300 ps, 1 ns, 3 ns, 10 ns, 30 ns, 50 ns, 100 ns, 300 ns, 1 μs, and 3 μs.

We used a pump-probe diffractometer installed at ID09B for this purpose. The pulses from a femtosecond CPA amplifier (λ=778nm) was first converted to the second (389 nm, 120 μJ/pulse, 1 kHz repetition rate) and the third harmonic (259 nm, 60 μJ/pulse, 1 kHz repetition rate). The pulses were stretched with silica prisms to the pulse length of ~2 ps before reaching the sample in order to avoid multiphoton excitations, and finally used for the excitation of the molecule. The reaction was probed with the x-ray pulses (5×10^8 photons per 100-ps-long pulse, ~ 3 % of ΔE/E) produced by the U17 undulator. 3.3-mM of iodine (I_2) and 3.3 mM of potassium iodide (KI) were used for making 3 mM triiodide ion (I_3^-) in methanol. This solution was circulated by an open jet system to make a stable liquid sheet. Scattering patterns were detected with MARCCD.

Collected data was analyzed by several steps. At first, 2D images from the CCD detector were integrated to the one dimensional q-space data. And then, the reference data was subtracted in order to magnify the high-q region. Finally, the refined data was used for extracting information about structural changes. Because the liquid phase diffraction cannot

offer high quality information which can be obtained from the single crystal diffraction, other strategy, the global analysis, was used. Theoretical curves were constructed using the scattering intensities of the solutes from molecular dynamics simulations and the scattering intensities of the solvent responses due to the temperature and density change. Every theoretical curve was related by the rate equation and hydrodynamics equation over all time points. The least-squares-fitting was done between experimental data and theoretical model. Figure 1 shows the fitting result.

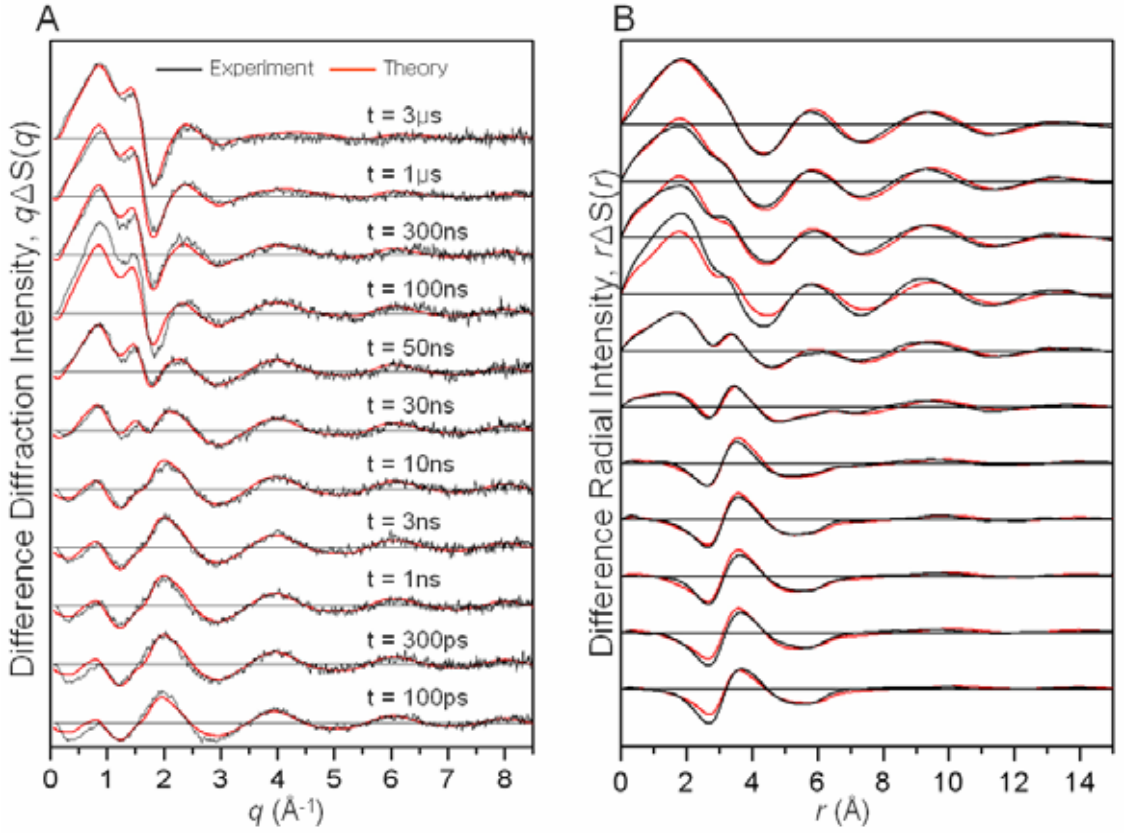

Figure 1: (A) The difference diffraction intensity, $q\Delta S(q)$, of the photodissociation of I3- at the 259nm excitation pulse. (B) The difference radial intensity, $r\Delta S(r)$.

The powerful global analysis gives us rich information about structural dynamics. The most important information is the population change as a function of time (Figure 2).

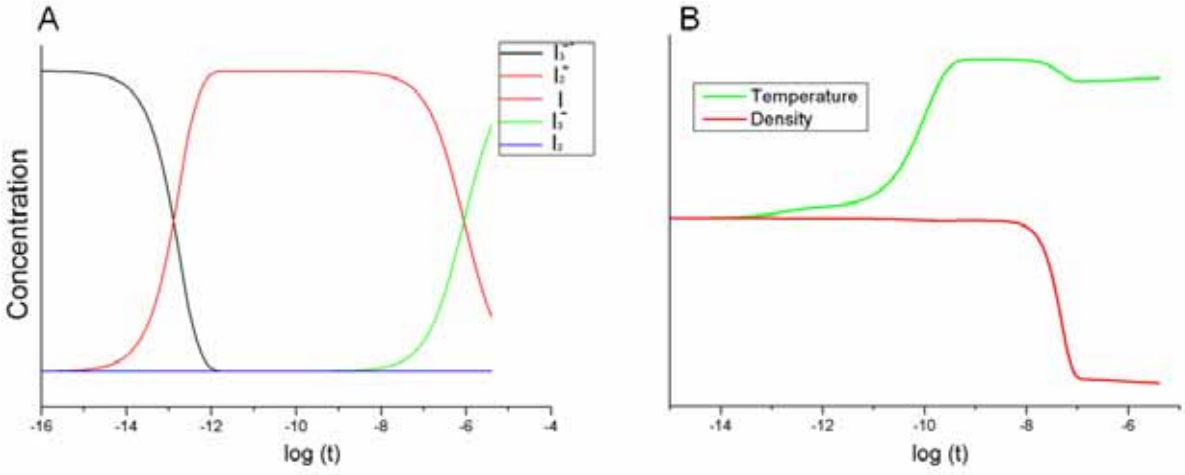

Figure 2: (A) The population change of the I_3^-, I_2^-, I, I_2 as a function of time. (B) The change of the temperature and density of the solvent.

The excited triiodide ion fragmented into the diiodide ion and I atom. The final product was the recombined triiodide ion formed at a few hundred nanoseconds. The iodine molecule was not formed (blue line in Figure 1A).

The other data collected at 389 nm excitation was also analyzed in the same way. The result (not presented here) was almost the same as the 259 nm data except the hydrodynamics (the heat release).

The previous spectroscopic study reported that the three-body dissociation can occurr with a 259 nm excitation. However, the three-body dissociation was not detected at this (CH-2176) experiment. Iodide ion (I^-, the unique product of the three-body dissociation) was not formed. Although we included the reaction pathways of the three-body dissociation, its contribution converged to zero.

Using the data collected at this beam-time, we revealed the photodissociation and nongeminate recombination dynamics of the triiodide ion in methanol.