



	Experiment title: Excited-State Structure of CHI_3 in Solution Studied by Picosecond X-ray Diffraction	Experiment number: CH-2063
Beamline:	Date of experiment: from: 29/09/2005 to: 03/10/2005	Date of report: 21/08/2006
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Report:

We have recently studied the photodissociation reaction of iodoform (CHI_3) in methanol. The photo-excitation from the nonbonding electron of C-I bond to the antibonding by 267 nm photons lead bond-breaking in one C-I bond of iodoform. Photoproducts of this reaction were the diiodomethyl radical ($\text{CHI}_2\bullet$) and an iodine atom. Previous spectroscopic results reported that the diiodomethane ($\text{CHI}_2\bullet$) radical and iodine (I) atom recombined to form iso-iodoform whose lifetime is about a few microseconds. Therefore it was of great interest to investigate whether time-resolve x-ray diffraction captures this isomer. To resolve this issue, in our experiment (CH-2063) we tried to capture the structural changes of the excited iodoform molecules at several time delays: -100 ps, 100 ps, 300 ps, 1 ns, 3 ns, 6 ns, 10 ns, 30 ns, 45 ns, 60 ns, 100 ns, 300 ns, 600 ns, 1 μs and 3 μs .

Time-resolved x-ray diffraction data were collected using an optical-pump and x-ray-probe diffractometer in the beamline ID09B. 20 mM iodoform (Aldrich, 99.5 %) passing through sapphire slit nozzle (300 μm thickness) formed a stable liquid sheet. An optical-pump was provided by a Ti:Sapphire laser system, synchronized with the single pulse of x-ray. The third harmonic of amplified femtosecond laser ($\lambda = 267$ nm, 35 $\mu\text{J/pulse}$, 1 kHz repetition rate), which was stretched to 2 ps, triggered the photodissociation reaction. As a probe, x-ray pulse was used. Polychromatic x-ray pulses (5×10^8 photons per 100-ps-long pulse, ~ 3 % of $\Delta E/E$) were diffracted by the liquid sample sheet after precisely controlled time delay from the striking of the pump pulse. Scattered photons were collected with MARCCD.

2D images collected with the CCD detector were integrated to produce 1D data, momentum transfer, q (\AA^{-1}), vs. scattering intensity, $S(q)$ (e.u.) by FIT2D program. To enhance the real structural changes of interest, all scattering intensities were subtracted by using reference data collected at -3 ns. The difference scattering intensities (which was the result of subtraction) could not give us intuitive information. After taking sine Fourier

transformation of the scattering intensities, we can get the difference radial intensities, containing information about bond formation and bond cleavage. Figure 1 shows these two curves.

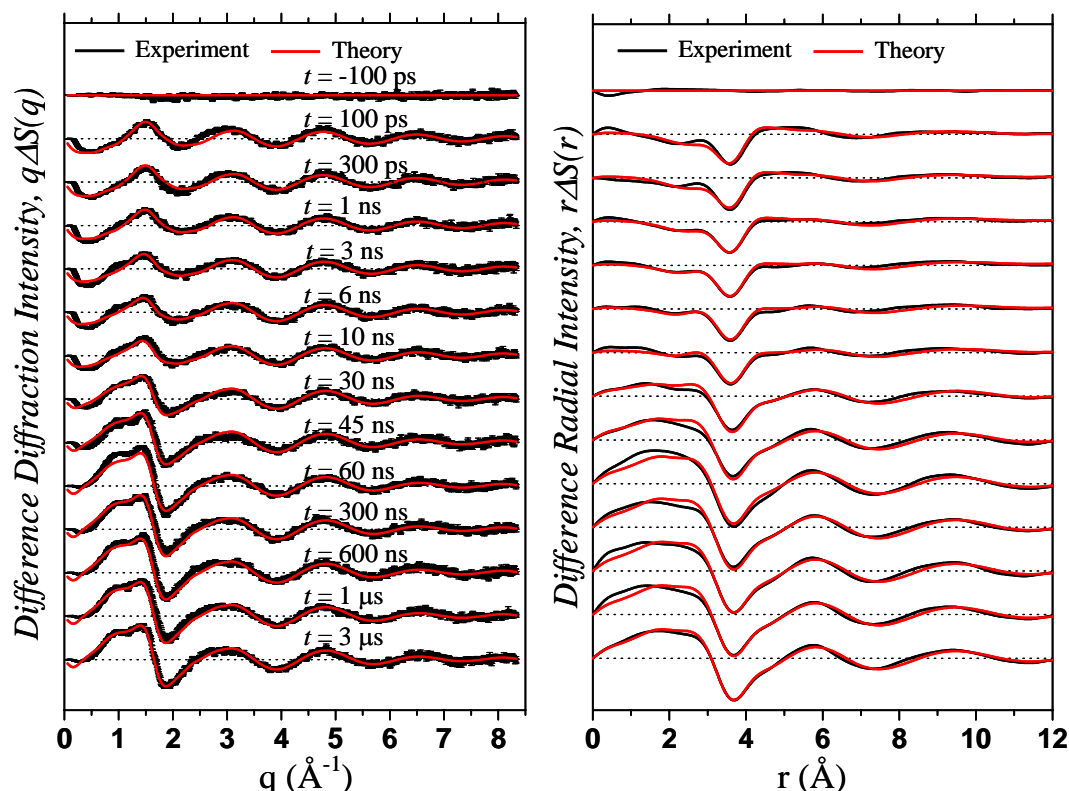


Figure 1: Left: the difference diffraction intensities, $q\Delta S(q)$. Right: the difference radial intensities, $r\Delta S(r)$. Black curves were experimental data. Error bars indicates experimental error in difference diffraction intensities. Red curves were the least-square fit to theoretical model.

A least-squares global analysis was used to fit experimental data with the theoretical model. Theoretical models comprise the scattering intensities from molecular dynamics (MD) simulation about iodoform and its photo products, and the scattering curves of solvent response for the temperature and density change. Each theoretical component was related with reaction rate equations (for solute) or hydrodynamics equations (for temperature and density change).

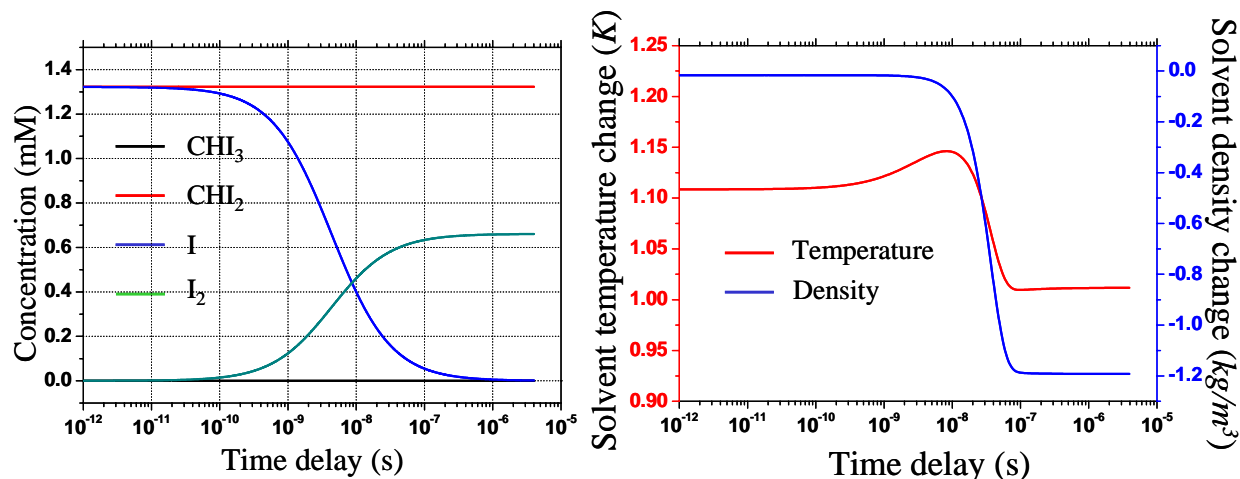


Figure 2: Left one is the population change of the CHI_3 , CHI_2 , I , and I_2 as a function of time delay. Right one is the change in the solvent density and the solvent temperature.

Figure 2 shows the global analysis result. Among 20 mM of iodoform, 4.8 mM was excited by photon. 3.46 mM of excited molecule came back to its ground state through a fast vibrational cooling process. Other 1.34 mM of iodoform lost one iodine atom, then CHI_2 radical and I atom were formed. The final products were the CHI_2 radical and the I_2 molecule. The CHI_2 radical was the first photo-dissociation product, and I_2 molecule was formed from the collision of two I atoms via non-geminate recombination with the bimolecular rate constant of $3.1 (\pm 0.5) \times 10^{10}$. The rate constant for the non-geminate recombination of I_2 molecule is similar to that of I_2 in CCl_4 solution from optical spectroscopy. The temperature change at 10 ns is 1.15 K and finally it becomes 1.02 K after equilibrium. The density change after 1 μs is about -1.2 kg/m^3 .

Previous spectroscopic results reported that diiodomethane ($\text{CHI}_2\bullet$) radical and iodine (I) atom recombined to form iso-iodoform. The lifetime of iso-iodoform was approximately a few micro seconds. To check the validity of this proposed channel, we included the reaction channel of isomer formation in the global analysis. However the χ^2 value from the reaction with isomer formation was much larger than that from the reaction without it. This indicates that the isomer channel is not a major one or that the previous spectroscopic interpretation was erroneous.

Time-resolved x-ray diffraction can reveal the structural dynamics reaction pathway in solution. The photodissociation reaction of iodoform in methanol was studied in this beam-time. Our results show us the reaction dynamics as well as hydrodynamics followed by photodissociation.