ESRF	**Experiment title:** Exploring solvation dynamics involved in vibrational relaxation of mercury(II) iodide using pump-probe X-ray solution scattering	**Experiment number**: CH-4004
Beamline: ID09B	**Date of experiment**: from: 11/09/2013 to: 16/09/2013	**Date of report**: 09/09/2016
Shifts: 12	**Local contact(s)**: Dmitry Khakhulin	*Received at ESRF:*

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Report:

We performed an experiment on photoreactions of mercury iodide (HgI_2) compounds at ID09B beamline. It is known that 267 nm excitation of the compound leads to dissociation of a Hg-I bond, and simultaneously, vibrational excitation of the remaining Hg-I bond. The goal of the experiment was to see the kinetics and structural dynamics how the excited Hg-I bond relaxes. More specifically, we expected to see the ultrafast change of Hg-I bond distance and the rearrangement of surrounding solvent cage due to the vibrational relaxation.

We used a typical pump-probe setup installed at ID09B for the experiment. The pulses from a femtosecond CPA amplifier (λ = 800 nm) was converted to desired wavelength (267 nm) and used. In order to avoid multiphoton excitations, the pulses were stretched with silica prisms to the pulse length of ~2 ps before reaching the sample. After the excitation, the reaction was probed using hard X-ray pulses (E_{photon} = 18.0 keV). The sample was dissolved in methanol to a final concentration of 15 mM and delivered as a liquid jet. Scattering patterns were collected using FReLoN CCD.

Time-resolved x-ray scattering signals were obtained at various time points; -3ns, -100ps, 0, 100ps, 178ps, 316ps, 562ps, 1ns, 1.78ns, 3.16ns, 5.62ns, 10ns, 17.8ns, 31.6ns, 56.2ns, 100ns, 178ns, 316ns, 562ns, 1us, 1.78us and 3.16us. (Figure 1) We could successfully obtain characteristic difference signals of HgI_2.

Time-slicing experiment was also performed to capture ultrafast vibrational relaxation of HgI intermediate. We collected diffraction data at the following time points; -5ns, from -100 ps to 150 ps with 10 ps intervals, 150 ps to 250 ps with 20 ps intervals, and 250 ps to 400 ps with 30 ps intervals. (Figure 2) We could see that positive peak at ~2Å^{-1} started to grow from -70ps.

We measured methanol heating signals at 100ps and 1us from 267nm-excitation by using 2mM of dye (4’-diethylamino-2-methoxy-4-nitroazobenzene, CAS No. 6373-95-1) solution. (Figure 2 inset)

In conclusion, we collected time-resolved X-ray solution scattering data of mercury iodide at several time delays including time-slicing experiment to investigate photoreaction dynamics of the molecule. As a result, difference curves with an extremely high signal to noise ratio was obtained. However, it was unable to retrieve any signal originating from the fast vibrational relaxation of Hg-I bond despite the high quality of data. From the result, we concluded that the vibrational relaxation occurs much faster than the temporal resolution of the time-slicing experiment, 10 ps.

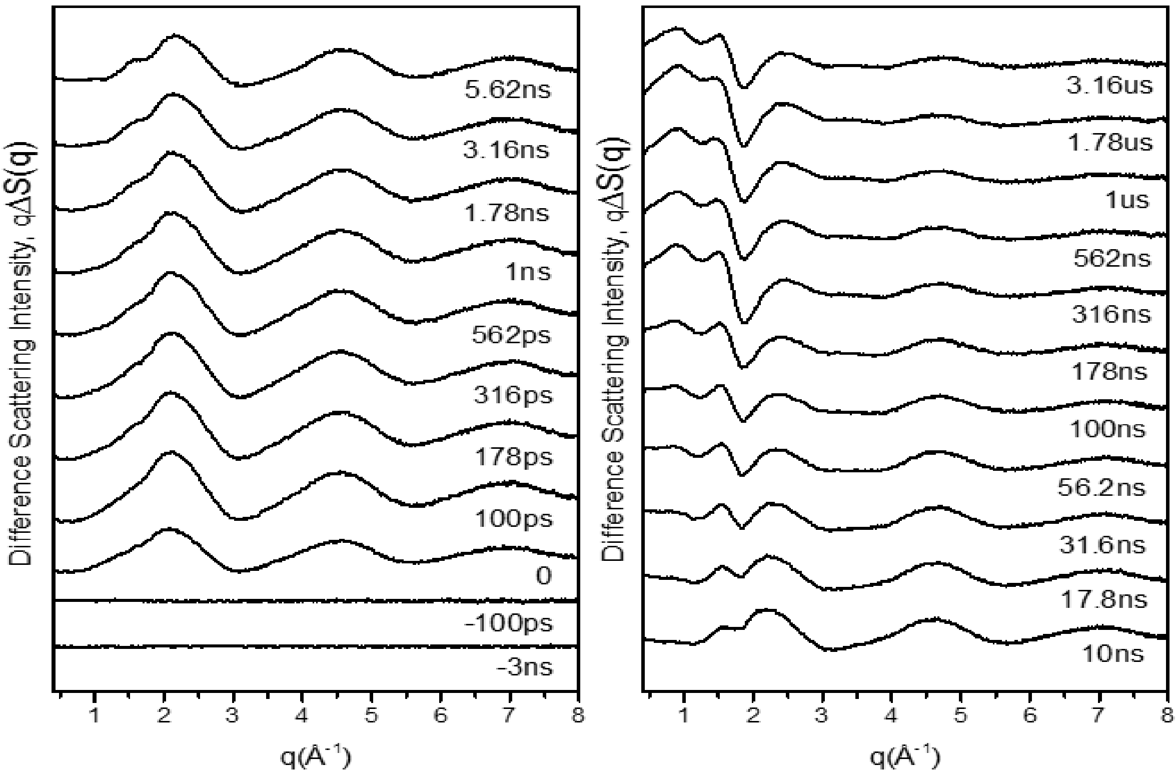

Figure 1 Time-resolved difference scattering signals from photoreactions of the mercury iodide (HgI_2) at excitation wavelength of 267nm.

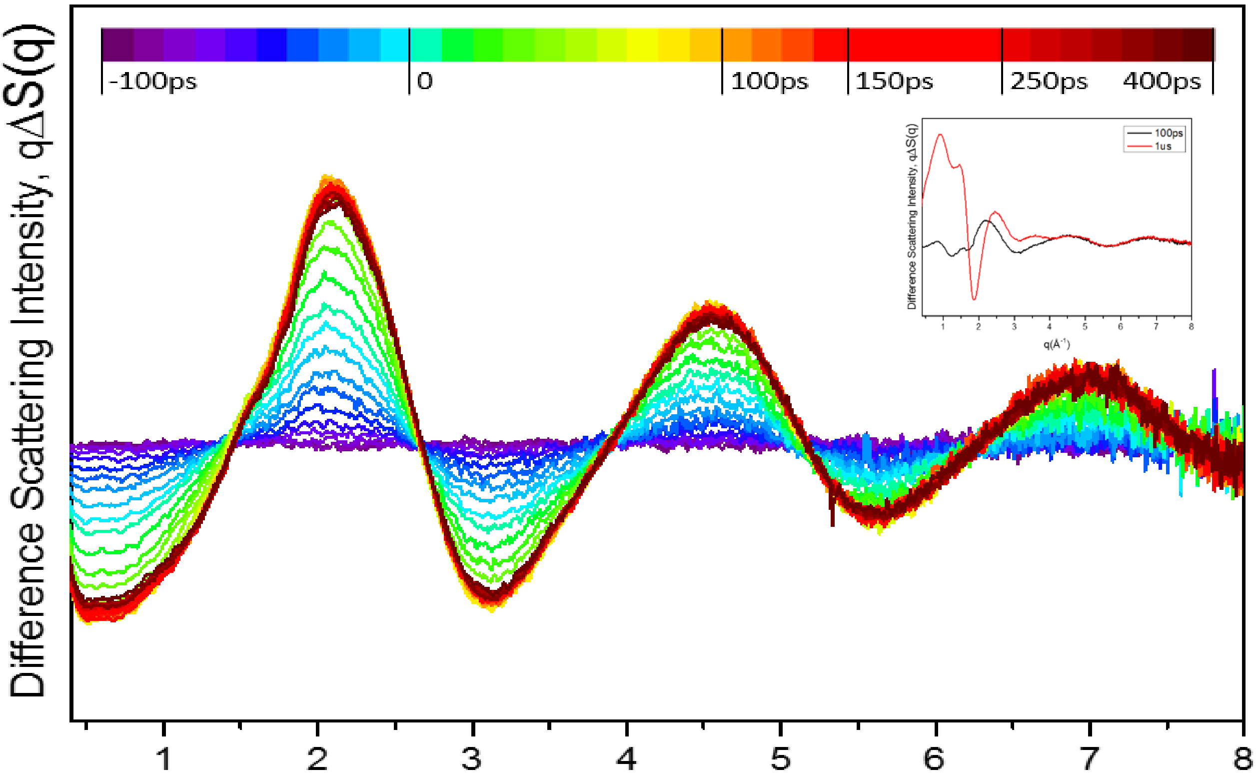

Figure 2 Difference scattering intensity curves from time-slicing experiment. Methanol heating signals are also plotted.