



	Experiment title: Pump-Probe X-ray Solution Scattering Study of the Photolysis of Triosmium Dodecacarbonyl Cluster in Cyclohexane	Experiment number: CH-3845
Beamline: ID09B	Date of experiment: from: 28/02/2013 to: 05/03/2013	Date of report: 02/03/2015 <i>Received at ESRF:</i>
Shifts: 12	Local contact(s): Michael Wulff	
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Report:

We performed an experiment on photoreactions of triosmium dodecacarbonyl ($\text{Os}_3(\text{CO})_{12}$) compounds at ID09B beamline. We used two different excitation wavelength, 350nm and 400nm, to study the wavelength-dependence of the reaction pathway. In order to investigate complete reaction scheme for each, we collected diffraction data at the following time points; -5ns, 100ps, 178ps, 316ps, 562ps, 1ns, 1.76ns, 3.16ns, 5.62ns, 10ns, 17.8ns, 31.6ns, 56.2ns, 100ns, 178ns, 316ns, 562ns, 1us, 1.78us, and 3.16us.

We used a typical pump-probe setup installed at ID09B for the experiment. The pulses from a femtosecond CPA amplifier ($\lambda = 800 \text{ nm}$) was converted to desired wavelength (400 nm or 350 nm) and used. In order to avoid multi-photon excitations, the pulses were stretched with silica prisms to the pulse length of $\sim 2 \text{ ps}$ before reaching the sample. After the excitation, the reaction was probed using hard X-ray pulses ($E_{\text{photon}} = 18.0 \text{ keV}$). The sample was dissolved in cyclohexane to a final concentration of 1mM and delivered as a liquid jet. Scattering patterns were collected using FReLoN CCD.

Collected diffraction data was

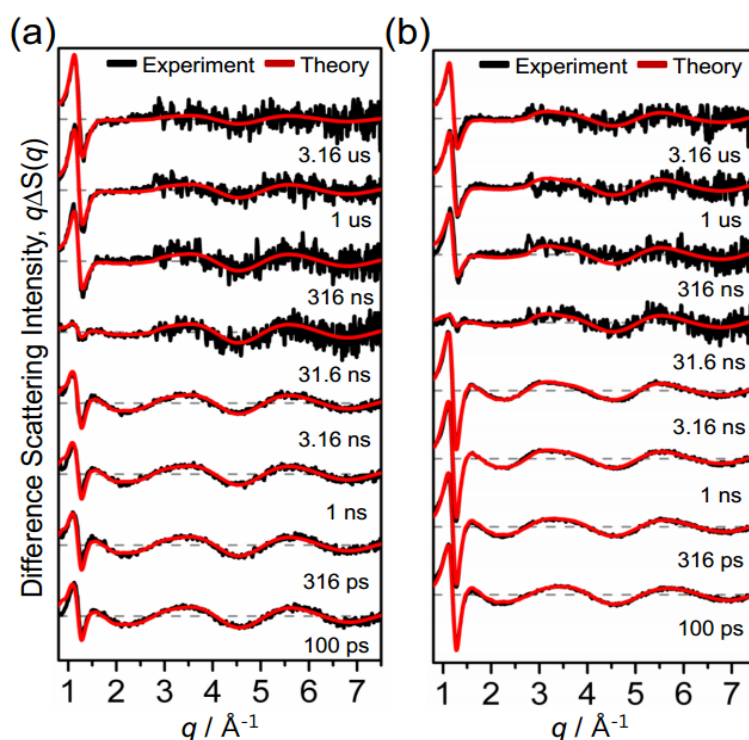


Figure 1 Difference diffraction intensity of the photodissociation of triosmium dodecacarbonyl complex ($\text{Os}_3(\text{CO})_{12}$) at excitation wavelength of 400nm (a) and 350nm (b)

analyzed to extract complete scheme for structural reaction dynamics. Figure 1 shows both experimentally obtained diffraction intensity curve and theoretically calculated diffraction intensity curve. Experimental curves were obtained by radial integration of 2D images to 1D curves followed by subtracting reference curve (diffraction curve obtained at negative time point, -3 ns). Theoretical curves were generated by calculating the diffraction intensities of the solutes from molecular dynamics simulations and the diffraction intensities of the solvent responses due to the temperature and density change. Note that low q regions of curves from 316ns to 3.16 μ s were scaled to 1/3 since the diffraction intensities were too high.

We performed global analysis to extract the whole scheme for structural dynamics from the measured difference scattering curves. As a result, we found that photoreaction pathways of the osmium complex with excitation wavelength of 350nm and 400nm are different each other. Figure 2 shows the photoreaction scheme of $\text{Os}_3(\text{CO})_{12}$ at two different wavelengths.

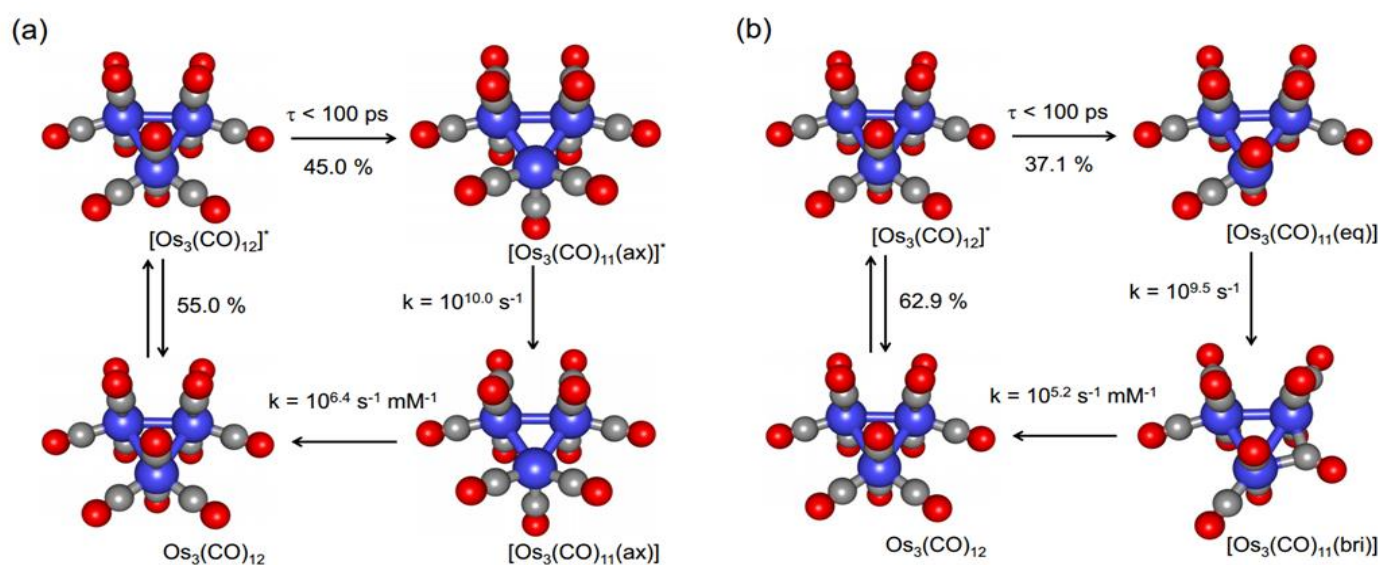


Figure 2 Reaction scheme of triosmium dodecacarbonyl complex in cyclohexane at excitation wavelength of (a) 400nm and (b) 350nm.

In conclusion, we collected time-resolved X-ray solution scattering data of $\text{Os}_3(\text{CO})_{12}$ at several time delays and analyzed to investigate photoreaction dynamics of the molecule. Now we are organizing the result and preparing manuscript for publication.