



Experiment title: Pump-Probe X-ray Solution Scattering Study for UV-Induced Photolysis of Triosmium Dodecacarbonyl Cluster in Cyclohexane	Experiment number: CH-4565
Beamline: ID09B	Date of experiment: from: 09/09/2015 to: 13/09/2015
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Report:

We proposed to unveil the structural dynamics of $\text{Os}_3(\text{CO})_{12}$ cluster after UV irradiation using time-resolved X-ray solution scattering. Especially, the goal of the experiment was to elucidate the early reaction following the 267-nm excitation. We used a pump-probe device installed at ID09B for this purpose. A total of 12 shifts were allocated during 9th to 13th of September, 2015. To probe the fast dynamics, we collected the scattering data from 8 time delays (50 ps, 100 ps, 178 ps, 316 ps, 562 ps, 1 ns, 3.16 ns, and 10 ns). The intense X-ray pulses (5×10^8 photons per 100 ps pulse) from U17 undulator is directly used (pink beam) to probe the reaction. 1 mM solution of $\text{Os}_3(\text{CO})_{12}$ in cyclohexane is prepared and circulated by an open jet system to make a stable liquid sheet. Scattering patterns were detected with FReLoN CCD detector. Collected images were processed through a conventional method to yield the difference scattering curves, $q\Delta S(q, t)$. Structural information of the reaction intermediates were extracted by analyzing the difference scattering curves. The curves are shown in **Figure 1**.

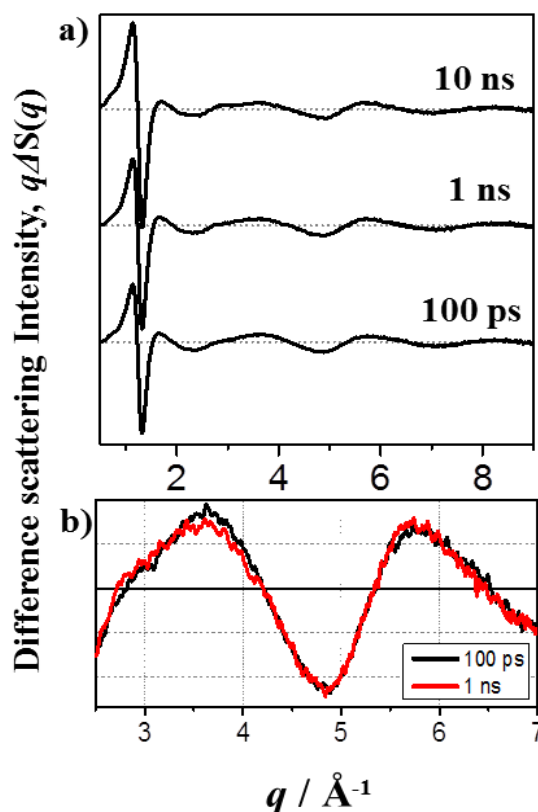


Figure 1. a) The time-resolved difference scattering curves obtained from the solution of $\text{Os}_3(\text{CO})_{12}$ after 267-nm excitation. b) The comparison of the two difference curves at time delays 100ps and 1 ns.

In the kinetic point of view, the shape of difference curves remains constant from time delays of 50 ps to 10 ns, except a really minor change occurring from 100 ps to 1 ns. From the analysis, it was revealed that the major reaction pathway is the dissociation of a ligand, and the major reaction intermediate is axial-vacant $\text{Os}_3(\text{CO})_{11}$. The intermediate is formed so fast to be captured within the time window of this experimental setup, and remains to 10 ns without showing any sign of decay. It can be noted that the assignment of the major intermediate, the axial-vacant complex, coincides with the previous time-resolved IR study.

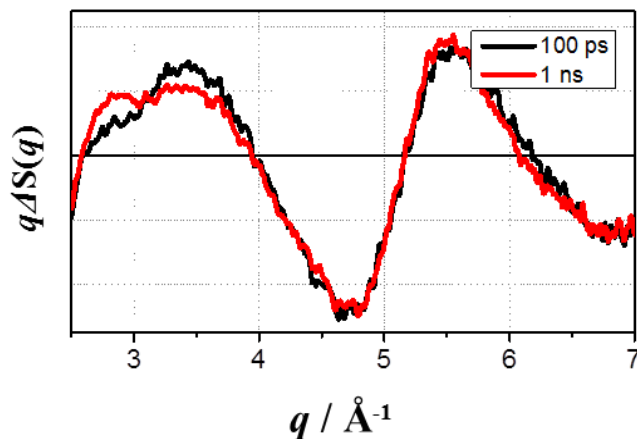


Figure 2 The comparison of the two difference curves at time delays of 100 ps and 1 ns after 267-nm excitation. The scattering signal is obtained from multilayer-reflected X-ray beam.

One more point to be noticed is that the scattering curve at 100 ps time delay is slightly different from that of 1 ns (See **Figure 1b**), which means that there might be another, minor reaction pathway. To clarify the minor pathway, additional experiment was performed using multilayer X-ray mirror to probe the reaction using more monochromatic X-ray. The result is shown in **Figure 2**. The difference between the two curves at 100 ps and 1 ns was clearly visualized as the result of less spectral broadening. The curves were analyzed and it was confirmed that the minor pathway is also the dissociation of a ligand from the complex.

However, in contrast to the major pathway, a different isomer is formed as a result of the dissociation in this minor pathway. It turned out that the reaction between 100 ps and 1 ns is the bridging isomerization of a CO ligand, following the formation of equatorial-vacant $\text{Os}_3(\text{CO})_{11}$ which occurs within 100 ps (See **Figure 3**). To the best to our knowledge, the formation of equatorial-vacant $\text{Os}_3(\text{CO})_{11}$ and its isomerization has never been reported from the previous spectroscopic studies.

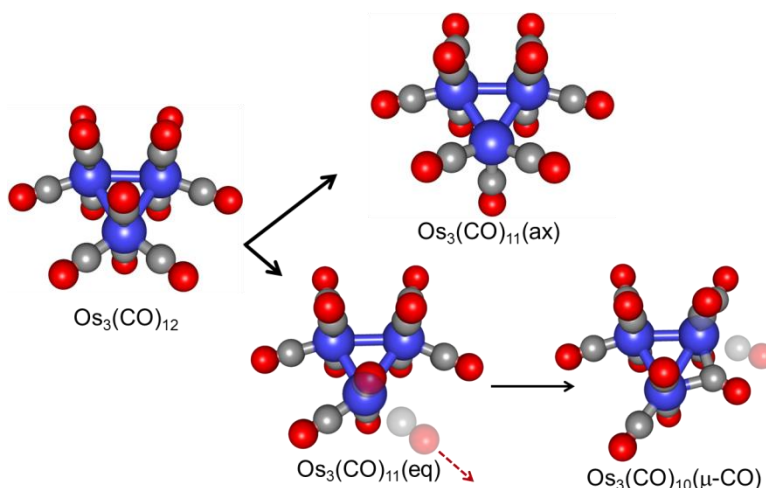


Figure 3 The schematic illustration of the proposed reaction pathway of $\text{Os}_3(\text{CO})_{12}$ after 267-nm excitation. The longer arrow means the major reaction pathway.

In summary, the photoreaction of $\text{Os}_3(\text{CO})_{12}$ upon 267-nm excitation is investigated using time-resolved X-ray solution scattering method. As a result, it is confirmed that axial-vacant $\text{Os}_3(\text{CO})_{11}$ is formed as the major reaction intermediate. In addition, it is claimed that there is a minor pathway which involves equatorial-vacant $\text{Os}_3(\text{CO})_{11}$. To the best to our knowledge, this minor pathway has never been suggested from previous spectroscopic studies on the osmium complex.