ESRF	**Experiment title:** Investigation of photocatalytic reaction pathways of a cerium complex by using pump-probe x-ray solution scattering	**Experiment number**: CH-5821
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Report:

We performed a time-resolved x-ray solution scattering (TRXSS) experiment on a cerium hexachloride complex ($[Ce^{III}Cl_6]^{3-}$) at ID09 beamline. According to previous studies, the complex plays a role as a photocatalyst facilitating the activation of the C-I bond of the aryliodide substrates. However, the time-dependent evolution of the molecular structure of photocatalysts and the mechanism of the photocatalytic reaction are still vague. Therefore, we aimed to capture the structures of intermediates using TRXSS, thereby elucidating the reaction mechanism.

We used a typical pump-probe setup installed at ID09 for the experiment. A 330 nm pump pulse was generated using an optical parametric amplifier (OPA) on a fundamental pump pulse (800 nm). We collected the data at the following time delays: -3ns, 50 ps, 100 ps, 215 ps, 464 ps, 1 ns, 2.15 ns, 4.64 ns, 10 ns, 21.5 ns, 46.4 ns, 100 ns, 215 ns, 464 ns, 1 us. A solution of 15 mM cerium complex with 150 mM tetraethylammonium chloride in acetonitrile was used in the overall experiment. To compare the structural dynamics of the cerium complex in photocatalytic reaction pathways with that of simple photoexcitation, we performed the TRXSS experiment on two conditions: No substrate was added for condition **1**, and about 1.7 % (v/v) of 1-fluoro-4-iodobenzene was added as an aryliodide substrate for condition **2**.

The overall difference scattering curves for the cerium cluster are shown in Figure 1a for condition **1** and Figure 1b for condition **2**. The signal obtained from $[Ce^{III}Cl_6]^{3-}$ was clearly different from the heating signal as shown in Figure 1c, indicating that the TRXSS signal undoubtedly encodes the structural change of $[Ce^{III}Cl_6]^{3-}$ after the photoexcitation. Especially, the signals from condition **1** and **2** shows clear difference, which indicates the difference in structural dynamics for the photocatalytic reaction and simple photoexcitation of $[Ce^{III}Cl_6]^{3-}$ (Figure 1d).

Currently, we are analyzing the data to extract the structural dynamics of $[Ce^{III}Cl_6]^{3-}$.

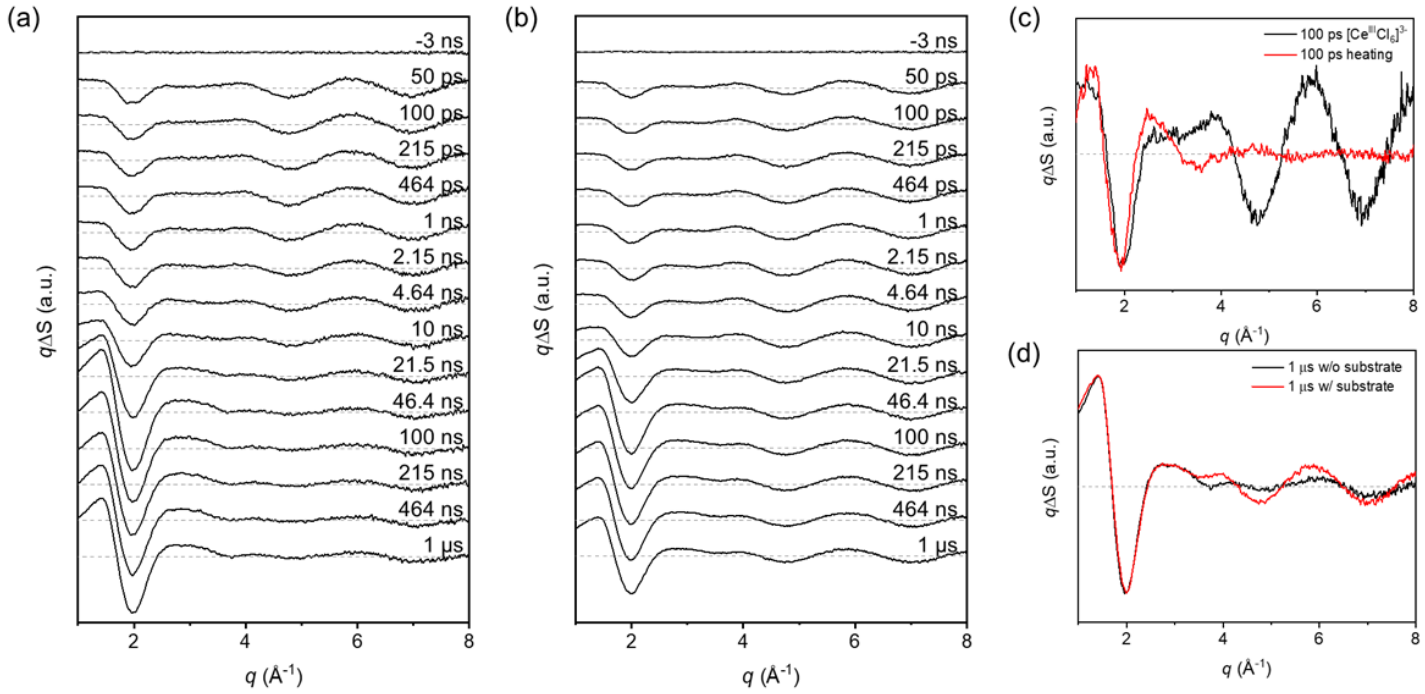

Figure 1. Experimental difference scattering curves collected under (a) condition **1** and (b) condition **2**. (c) Comparison between the diffence scattering curves collected at 100 ps under condition **1** (black) and heating signal collected at 100 ps (red). (d) Comparison between the difference curves collected at 1 µs under condition **1** (black) and condition **2** (red). For (c) and (d), the curves were scaled for comparison.