



	<b>Experiment title:</b> Unraveling of the origin of unique optical property of a copper cluster using pump-probe X-ray solution scattering	<b>Experiment number:</b> CH-5460
<b>Beamline:</b> ID09B	<b>Date of experiment:</b> from: 01/03/2018                      to: 07/03/2018	<b>Date of report:</b> 26/02/2020
<b>Shifts:</b> 18	<b>Local contact(s):</b> Norman Kretzschmar	<i>Received at ESRF:</i>
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## Report:

We performed a time-resolved x-ray liquidography (TRXL) experiment on a copper complex ( $[\text{Cu}_4\text{I}_4(\text{py})_4]$  (where 'py' refers to pyridine) at ID09B beamline. According to previous studies, the cluster shows two uncoupled photoluminescence bands (see Figure 1). Although decades of research revealed its electronic dynamics with time-resolved spectroscopy, the time-dependent evolution of the molecular structure in solution had been only roughly supported either by the computational calculation or experiments. Hence, we planned to directly observe the structural dynamics with respect to the choice of excitation wavelength by using TRXL.

We used the typical pump-probe setup installed at ID09B for the experiment. A 350 nm pump pulse was generated by using an optical parametric amplifier (OPA) on a fundamental pump pulse (800 nm). To investigate the wavelength dependency of the reaction, we also took the TRXL signal with 267 nm pump wavelength which was provided by triple harmonic generation of the fundamental pump pulse. We collected the data at the following time delays: -3 ns, 100 ps, 178 ps, 316 ps, 562 ps, 1 ns, 1.78 ns, 3.16 ns, 5.62 ns, 10 ns, 17.8 ns, 31.6 ns, 56.2 ns, 100 ns, 178 ns, 562 ns (for 267 nm so far), -3 ns, 100 ps, 316 ps, 1 ns, 3.16 ns, 10 ns, 31.6 ns, 100 ns, 316 ns, 1  $\mu$ s (for 350 nm). A solution of 5 mM  $[\text{Cu}_4\text{I}_4(\text{py})_4]$  in acetonitrile was used in the overall experiment.

The overall difference scattering curves for the copper cluster are shown in Figure 2a for 267 nm and 2b for 350 nm. For both of the figures, the signals collected from the negative time delay, -3 ns, were used as a reference. To eliminate the contributions coming from the heating of solvent, we used the SVD-aided non-orthogonal decomposition (SANOD) method. The result is shown in Figures 3a and 3b. Despite the possibility of exaggerated elimination of the solute signal when using the SANOD method, we can still clearly see the signals irrelevant

with the heating of solvent, indicating that the TRXL signal undoubtedly encodes the structural change of  $[\text{Cu}_4\text{I}_4(\text{py})_4]$  after the photoexcitation.

Currently, we are analyzing the data to extract the structural dynamics of  $[\text{Cu}_4\text{I}_4(\text{py})_4]$  and its wavelength-dependency.

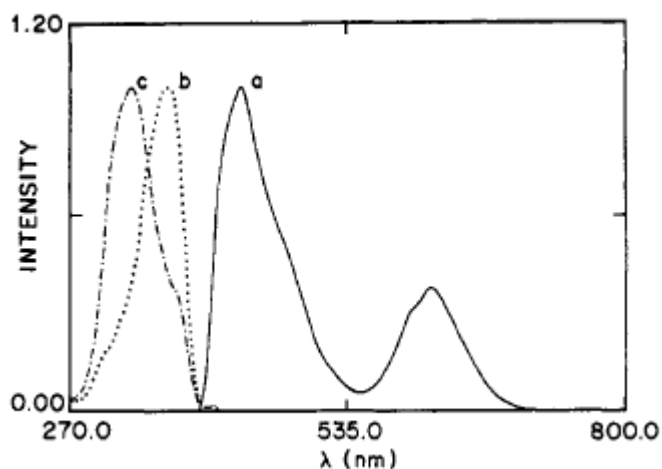


Figure 1. Emission and excitation spectra of solid  $\text{Cu}_4\text{I}_4(\text{py})_4$  at 77 K. (a) emission spectrum ( $\lambda_{\text{max}} = 438$  and  $619$  nm); (b) excitation spectrum monitoring at  $438$  nm ( $\lambda_{\text{max}}^{\text{ex}} = 365$  nm); (c) excitation spectrum monitoring at  $619$  nm ( $\lambda_{\text{max}}^{\text{ex}} = 330$  nm)

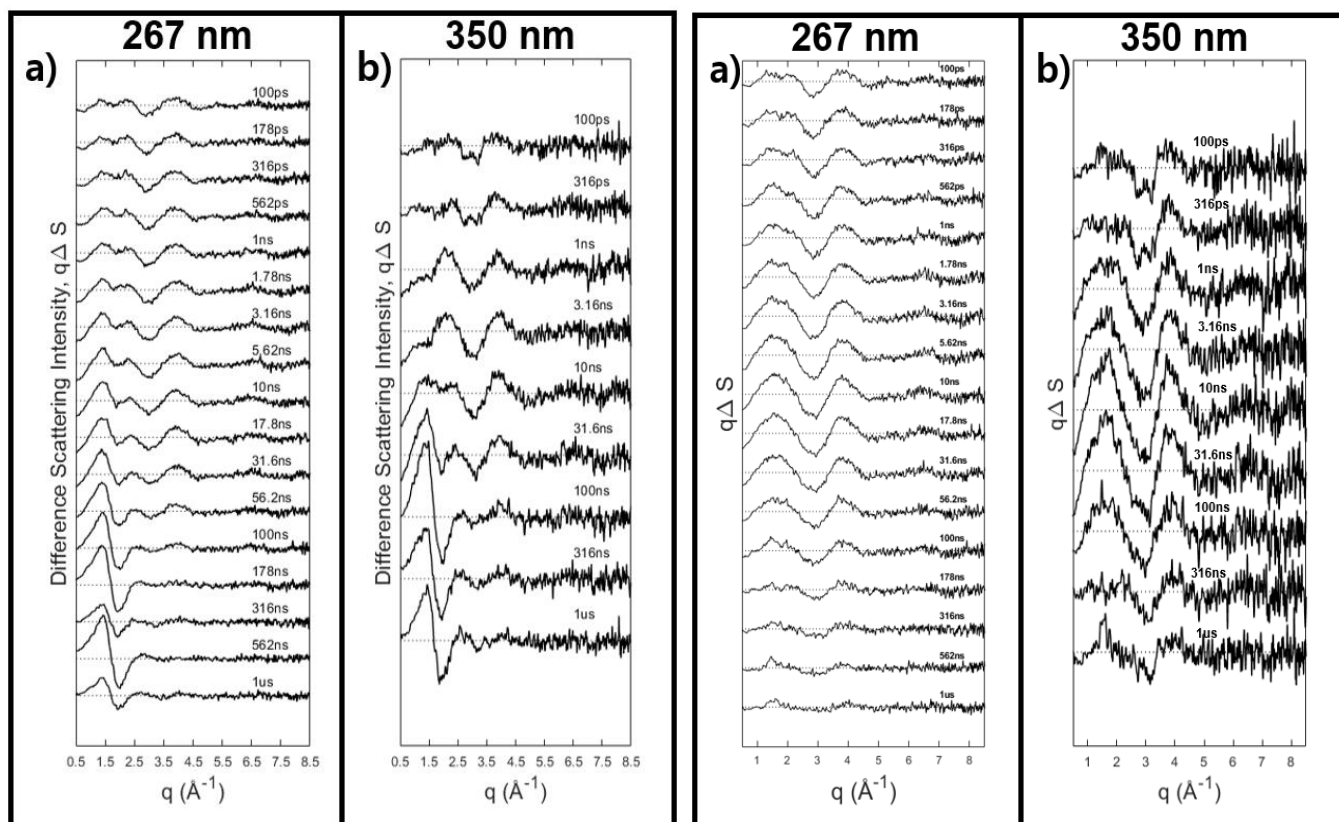


Figure 2. Overall difference scattering signals: a)  $267$  nm b)  $350$  nm.

Figure 3. Difference scattering signals processed by removal of the heat component using SVD-aided non-orthogonal decomposition (SANOD) method. a)  $267$  nm, b)  $350$  nm