



	Experiment title: Investigation of the excited-state dynamics of tetracyanoplatinum(II) using pump-probe X-ray solution scattering	Experiment number: CH-5619
Beamline: ID09B	Date of experiment: from: 19/09/2018 to: 25/09/2018	Date of report: 26/02/2020 <i>Received at ESRF:</i>
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Report:

We performed time-resolved x-ray solution scattering (TRXSS), which is also known as time-resolved x-ray liquidography (TRXL), on potassium tetracyanoplatinate ($K_2[Pt(CN)_4]$, KCP) at ID09B beamline. The square planar platinum complexes are well-known for their emissive properties upon photoexcitation which originates from the non-covalent interaction between platinum centers, which is termed as platinophilic interaction (Figure 1). However, the exact molecular structures of the photoreaction intermediates that are responsible for the emissive property have been elusive so far. Thanks to its simple cyanide ligands, KCP can be regarded as one of the most basic model systems to investigate the structural dynamics of the photoexcited square-planar platinum complexes and the role of platinophilic interaction in the emission. Hence, we aimed to explore the structural dynamics of KCP using TRXL to reveal the structures of the reaction intermediates which are formed upon photoexcitation.

A typical TRXL experimental setup installed at the beamline was used for the experiment. The aqueous solution of KCP with the concentration of 230 mM was prepared and circulated through a gear pump. A fundamental laser pulse ($\lambda = 800$ nm) from a Ti:Sapphire laser system was converted to the pulse with the wavelength of 300 nm by using an optical parametric amplifier (OPA). The converted laser pulse was used to excite the sample. The x-ray pulse with the central energy of 18.0 keV and the energy bandwidth of ~ 2 % was used to probe the structural change of KCP upon excitation. The scattered x-ray was collected using an area detector (Rayonix CCD detector). To trace

the structural change of KCP along with the progress of the reaction, the scattered images were collected at the following time delays: -3 ns, 100 ps, 300 ps, 1 ns, 3 ns, 10 ns, 30 ns, 100 ns, 300 ns, and 1 μ s.

The resulting TRXL data are shown at Figure 2. The difference scattering curves of KCP showed distinct features which are clearly different from those of the solvent heating signal (Figure 3), indicating that the TRXL data undoubtedly encodes the structural change of KCP after the photoexcitation. Currently, we are analyzing the data to extract the time-dependent structural changes of KCP.

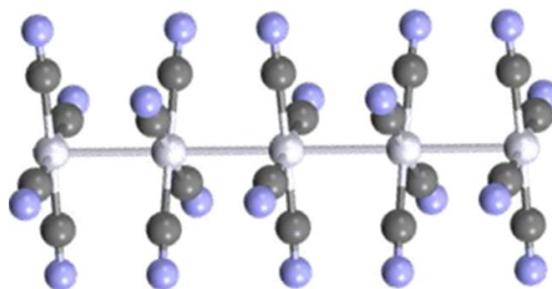


Figure 1. A schematic for the crystal structure of KCP ($K_2[Pt(CN)_4]$). Due to the platinophilic interaction, $[Pt(CN)_4]^{2-}$ anions are located in the vicinity of each other (~ 3.5 \AA for KCP). The short distance between anions is known to be responsible for the emissive property of such square-planar platinum complexes.

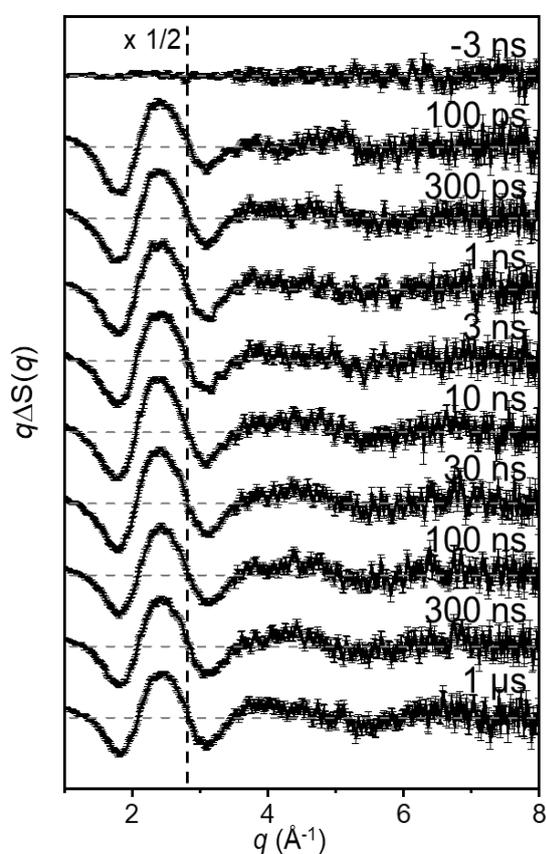


Figure 2. TRXL data of KCP ($K_2[Pt(CN)_4]$) upon photoexcitation.

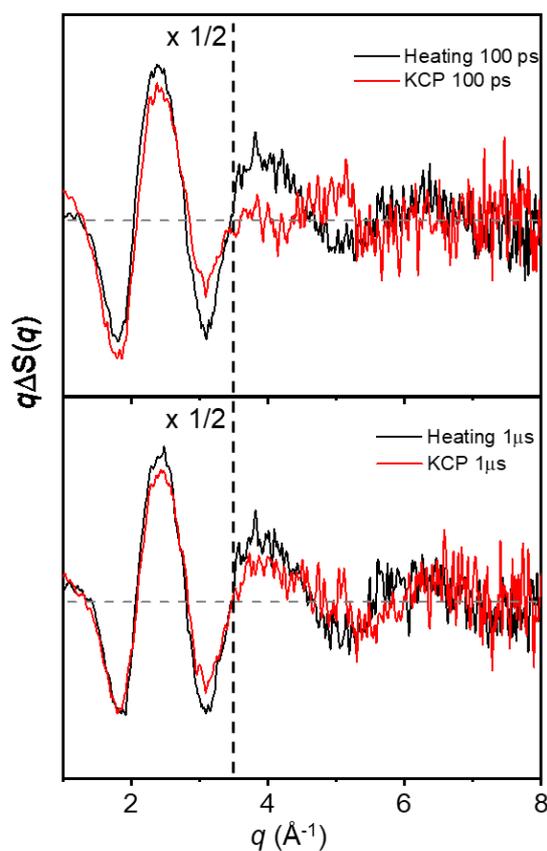


Figure 3. Comparison of the TRXSS data of KCP and heating at 100 ps and 1 μ s.