

# Dynamics of Aqueous Ferrocyanide Solvent Interaction Revealed by High Repetition Rate Laser Pump / X-ray Probe Technique

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Understanding the role of a solvent in influencing the rate and/or selectivity of a reaction is of great importance to chemistry. In general, solvent effects may be classified into two distinct groups; passive or active. Active solvents are directly involved during the course of the chemical reaction by forming an explicit interaction with the reacting species. In such cases, these interactions generally result in mechanistic changes and the formation of new reaction channels. A case in point, is the photochemistry of aqueous hexacyanoferrate (ferro- and ferricyanide) ions. Previous studies have determined the photochemical dynamics of aqueous ferrocyanide can be separated into photooxidation ( $[\text{FeII}(\text{CN})_6]^{4-} \rightarrow [\text{FeIII}(\text{CN})_6]^{3-} + e^-$ ) and photoaquation ( $[\text{FeII}(\text{CN})_6]^{4-} \rightarrow [\text{FeII}(\text{CN})_5\text{H}_2\text{O}]^{3-} + \text{CN}^-$ ) [1], however little is known about the dynamics of these processes or their geometric structure. While numerous time-resolved optical studies of the photooxidation process exist, getting information on the photoaquation dynamics proved difficult, as it is related to the population of intramolecular states with low extinction coefficients. In addition, while the relaxation pathway towards photooxidation or photoaquation strongly depends on the excitation wavelength, the photoaquation tends to be obscured by intramolecular MLCT and intermolecular CTTS transitions, making separate studies of photooxidation and photoaquation challenging.

To shed light on the different dynamics, we used our recently developed high repetition rate laser pump / x-ray probe setup [2] at different laser excitation wavelengths while probing with x-rays at the Fe K-edge. Our transient x-ray spectra (pumped sample x-ray absorption spectrum minus unpumped sample x-ray absorption spectrum) upon 266 nm and 355 nm excitation show unique fingerprints for each pump wavelength, which can be directly linked to photooxidation and photoaquation respectively. While 266 nm excitation into a charge transfer to solvent state (CTTS) results in a characteristic edge shift of the excited state due to the oxidation state change of the metal, upon 355 nm excitation simulations of the photoaquated species are in good agreement with the experimental transient spectrum. This allows a differentiated view into the dynamics involved.

[1] M. Shirom et al., J. Chem. Phys. 1971 55(7), 3372–3382

[2] F. Lima et al., Rev. Sci. Instrum. 2011, 82, 063111.

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