

PROBING THE FERROCYANIDE AQUATION REACTION WITH NONRESONANT X-RAY EMISSION SPECTROSCOPY

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Observing light-induced reactions in liquids, where much of chemistry happens, and on the timescales during which these reactions occur, has been a long-standing objective. Knowledge of the mechanistic details at the molecular scale can inform rational design of new molecules for applications such as light harvesting and energy conversion and illuminate new means of controlling reactions. We have been exploring how time-resolved x-ray spectroscopy can be used to understand fundamental mechanisms underlying ligand exchange, a reaction common to coordination complexes in solution. Our recent focus has been on the aquation reaction of ferrous hexacyanide in water, where absorption of UV light initiates an exchange of a CN⁻ ligand with a water molecule from the solvent. Using the MHz repetition-rate laser-pump/x-ray-probe capabilities our group has built at the Advanced Photon Source we have investigated the reaction using both absorption spectroscopy at the Fe K-edge and nonresonant Fe 1s emission spectroscopy. Pre-edge resonances sensitive to geometry revealed a 20-ps lived pentacoordinated intermediate species. QM/MM molecular dynamics simulations explain the rather long time for aquation as being due to fluctuations in the geometry of the pentacoordinated complex that leave very short time intervals when there is room for a water molecule to bond. The K alpha, K beta, and valence-to-core emission spectra yield complementary information beyond geometry for the species involved. The measured K beta line confirms the triplet spin state of the pentacoordinated intermediate, and also reveals a subtle spectral difference for the low-spin aquated product compared to the ground state complex. This work was supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.