

MEASURING CHARGE DELOCALIZATION IN MIXED-VALANCE COMPLEXES USING ULTRAFAST X-RAY SPECTROSCOPY

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One of the challenging problems in the field of mixed valence complexes is determining the extent of electronic delocalization between metal centers in the ground and excited states. In this study, we applied femtosecond transient Fe K-edge X-ray absorption spectroscopy measurement on a tri-metallic, mixed valence complex, $[\text{L}_4\text{Ru}^{\text{II}}(\text{NC-Fe}^{\text{III}}(\text{CN})_5)_2]^{4-}$ (L=pyridine and 4-methoxypyridine), in methanol. The experiment was performed at X-ray Pump Probe end station of Linac Coherent Light Source. We observed 0.3 eV and 1.5 eV red shifts for the Fe 1s to 3d e_g and ligand π^* transition, confirming the delocalized nature of the excited metal-to-metal charge transfer state. The appearance of a spectral feature at 7107.5 eV in the excited state was first reported, suggesting that a short-lived transition was enabled unique to the trimer system. Complementary TD-DFT calculations were performed to visualize the transition orbitals and interpret experimental results.