

MONITORING ELECTRON DELOCALIZATION IN A MIXED VALENCE RU DIMER USING TRANSIENT RU L-EDGE X-RAY AND INFRARED SPECTROSCOPIES

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Recent spectro-electrochemical studies have shown that the Ru-Ru dimer, $[\text{Ru}(\text{tpy})(\text{bpy})(\mu\text{-CN})\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})]^{3+}$ (tpy = terpyridine, bpy = bipyridine), exhibits Class III mixed valency (complete delocalization between metal centers) upon one electron oxidation. Photochemically, this could be achieved by metal-to-ligand-charge transfer (MLCT) excitation where one Ru center is oxidized while one of the polypyridine ligands is reduced. Characterizing the extent of electron delocalization on the excited states of donor-bridge-acceptor complexes remains an important target in the field of mixed-valence chemistry. Transient X-ray spectroscopies are well suited to investigate electron delocalization processes as they offer element and orbital specific probes of local electronic and atomic structure. Here, we utilized solution phase, femtosecond, Ru L₃-edge resonant inelastic X-ray scattering, performed at the Alvrá Prime end station of the Swiss X-ray Free Electron Laser, to probe valence electron and hole motions during the ultrafast delocalization process following MLCT excitation. A complementary study using transient Infrared spectroscopy was done to determine role of the CN bridge in the delocalization process. Additionally, TD-DFT calculations of spectroscopic observables were performed to help interpret and describe the X-ray and infrared experiments.