

IDENTIFYING THE TRIPLET INTERMEDIATE STATE IN THE ULTRAFAST PHOTOINDUCED SPIN-TRANSITION OF LOW-SPIN IRON(II) COMPOUNDS USING FEMTOSECOND $M_{2,3}$ -EDGE ABSORPTION SPECTROSCOPY

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In this work, we perform femtosecond $M_{2,3}$ -edge XANES on low-spin iron complexes using a high harmonic generation (HHG) light source. Low-spin iron complexes hold promise as affordable alternatives to ruthenium-based photosensitizers. Conventional iron complexes with polypyridyl ligands are unsuitable because the excitation energy is dissipated in 200 fs by ultrafast population of the low-lying quintet metastable state. This formally $\Delta S=2$ process is conjectured to proceed through a metal-centered triplet intermediate state, but spectroscopic evidence of such an intermediate has remained elusive. Here we use femtosecond $M_{2,3}$ -edge XANES to elucidate the role of metal-centered intermediate states. The transient response of $\text{Fe}(\text{phen})_3(\text{SCN})_2$ following excitation in the MLCT band clearly shows the presence of a metal-centered 3T_1 state. The transient response also shows oscillations consistent with the evolution of a vibrational wave-packet on the quintet surface. We also recorded the $M_{2,3}$ -edge transient response of $\text{Fe}[(\text{CF}_3)_2\text{bpca}]_2$, a complex with a weaker ligand field. A comparison of the photophysical behaviors of $\text{Fe}(\text{phen})_3(\text{SCN})_2$ and $\text{Fe}[(\text{CF}_3)_2\text{bpca}]_2$ sheds light on the influence of crystal field strength on the relaxation mechanism of the MLCT state. Our findings add a hitherto missing piece to the existing picture of photophysics of iron complexes.