

## PUMPING THE INTERVALLENCE CHARGE TRANSFER AND PROBING ACROSS THE ELECTROMAGNETIC SPECTRUM: DIVERSE SPECTRAL PROBES REVEAL A UNIQUE RELAXATION MECHANISM

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Using transient absorption (TA) spectroscopy with a barrage of spectral probes, we investigate the charge recombination dynamics following intervalence charge transfer (IVCT) excitation of a heterobimetallic Fe(II)Co(III) molecule. Femtosecond optical probes in the near-infrared and visible regions reveal long-lived excited states following IVCT excitation. In order to determine the electronic structure at each metal center in these excited states, we turn to element-specific extreme ultraviolet (XUV) and X-ray techniques. Femtosecond XUV TA at the Fe and Co M<sub>2,3</sub> edges demonstrates that a local, Fe-centered, triplet (d-d) state is formed within 1 picosecond of IVCT excitation. This observation uncovers a unique IVCT relaxation mechanism whereby ultrafast intersystem crossing and back electron transfer populates a local, triplet excited state instead of the singlet ground state. The triplet state then evolves to a long-lived excited state, which we examined with hard and soft X-ray probes from synchrotron sources. Picosecond soft X-ray TA at the Fe and Co L<sub>3</sub> edges shows that this state is also an Fe-centered (d-d) state. Hard X-ray TA at the Fe and Co K-edges reveal large bond length elongations of the Fe coordination sphere that are consistent with a high-spin quintet state. Altogether, these experiments highlight the importance of local, Fe-centered triplet and quintet (d-d) states on the IVCT relaxation dynamics of this heterobimetallic complex. By employing a diverse range of spectral probes, we were able to track charge and spin at each metal center over a broad range of timescales, which enabled the elucidation of this unique IVCT relaxation mechanism.