Discovery of New Excited State Pathways in Transition Metal Carbonyls using Ultrafast Core-Level Spectroscopy

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The coupled electronic and structural dynamics on excited states are fundamental to the photoinduced chemical transformations that underpin processes such as photocatalysis and photovoltaic activity. Of particular interest is the propensity for molecules to undergo ultrafast intersystem crossing, which leads to the formation of triplet species that can significantly influence reaction outcomes. In this talk, I will present our recent joint experimental and theoretical investigation[1] of excited state dynamics in a prototypical photocatalyst, iron pentacarbonyl [$Fe(CO)_5$], whose photochemistry has garnered much interest for decades. By employing ultrafast extreme ultraviolet transient absorption spectroscopy near the Fe $M_{2,3}$-edge (3p-to-valence transitions), our work has spectroscopically detected the fleeting metal-centered excited states responsible for the dissociation of CO ligands after 266 nm excitation. Importantly, our study has also revealed participation of triplet states in mediating CO ligand elimination, with spectral signatures of these triplet states appearing on sub-100 femtosecond time scales. This finding suggests ultrafast intersystem crossing to the triplet manifold despite modest spin-orbit coupling and thus challenges the singlet-only excited state pathways proposed previously for this molecule in the gas phase.

Keywords: transition metal, intersystem crossing, ultrafast spectroscopy, core level spectroscopy, photocatalysis.

[1] J. Troß, J. E. Arias-Martinez, K. Carter-Fenk, N. C. Cole-Filipiak, P. Schrader, L. M. McCaslin, M. Head-Gordon, K. Ramasesha, *Journal of the American Chemical Society*, 146, 22711 (2024)

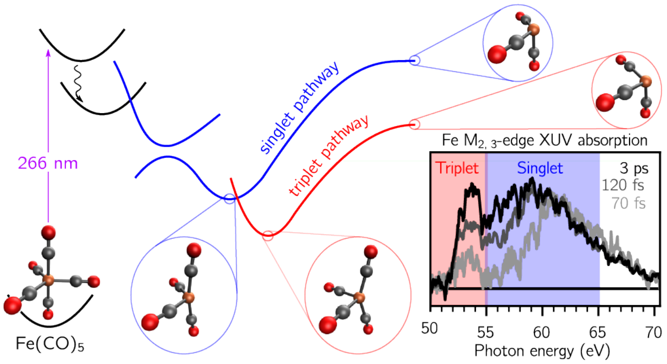

Figure 1. Ultrafast extreme ultraviolet transient absorption spectroscopy of $Fe(CO)_5$ has spectroscopically revealed the involvement of triplet states during UV-induced ligand elimination.