PHOTOPHYSICS OF EXCITED STATES IN THE Co_4O_4 CUBANE CATALYST FOLLOWED VIA FEMTOSECOND $M_{2,3}$-EDGE ABSORPTION SPECTROSCOPY

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The Co_4O_4 cubane and its oxidized derivatives are molecular models of heterogeneous cobalt-based oxygen evolution reaction catalysts and are structural cognates of the oxygen evolving center in plant life. Insight into these latter systems is garnered through study of the high-valent states achieved in oxidized cubane. The oxidized cubane species is generated transiently through photoinduced electron transfer to a laser-excited pendant perylene bisimide chromophore and interrogated via extreme ultraviolet (XUV) spectroscopy. The XUV probe effects transitions at the $M_{2,3}$ edge (3p→3d) in the cobalt centers and is sensitive to changes in e.g. oxidation and spin states. However, spectroscopic characterization of the high-valent states achieved in through this charge separation is hindered by the concurrent population of metal-centered excited states via energy transfer. Once populated, these states undergo further evolution via intersystem crossing and/or relaxation back into the charge separated state, imparting significant ambiguity into the observed XUV signals. This work clarifies these results through further studies into the ultrafast dynamics of excited cubane molecules, as well as synthetic strategies toward manipulation of the electronics and energetics of the pendant chromophore. As probed by our tabletop high-harmonic generation (HHG) XUV instrument, the excitation energy in this system is followed as it cascades through metal-centered states in the cubane manifold vs. the formation of charge separated states.