Detailed Characterization of a Nanosecond-Lived Excited State: X-ray and Theoretical Investigation of the Quintet State in Photoexcited [Fe(terpy)(2)](2+) - DTU Orbit (11/11/2019)

Theoretical predictions show that depending on the populations of the Fe 3d(xy), 3d(xz), and 3d(yz) orbitals two possible quintet states can exist for the high-spin state of the photoswitchable model system [Fe(terpy)(2)](2+). The differences in the structure and molecular properties of these B-5(2) and E-5 quintets are very small and pose a substantial challenge for experiments to resolve them. Yet for a better understanding of the physics of this system, which can lead to the design of novel molecules with enhanced photoswitching performance, it is vital to determine which high-spin state is reached in the transitions that follow the light excitation. The quintet state can be prepared with a short laser pulse and can be studied with cutting-edge time-resolved X-ray techniques. Here we report on the application of an extended set of X-ray spectroscopy and scattering techniques applied to investigate the quintet state of [Fe(terpy)(2)](2+) 80 ps after light excitation. High-quality X-ray absorption, nonresonant emission, and resonant emission spectra as well as X-ray diffuse scattering data clearly reflect the formation of the high-spin state of the [Fe(terpy)(2)](2+) molecule; moreover, extended X-ray absorption fine structure spectroscopy resolves the Fe-ligand bond-length variations with unprecedented bond-length accuracy in time-resolved experiments. With ab initio calculations we determine why, in contrast to most related systems, one configurational mode is insufficient for the description of the low-spin (LS)-high-spin (HS) transition. We identify the electronic structure origin of the differences between the two possible quintet modes, and finally, we unambiguously identify the formed quintet state as 5E, in agreement with our theoretical expectations.