Energy Dispersive XAFS: Characterization of Electronically Excited States of Copper(I) Complexes

Abstract:
Energy dispersive X-ray absorption spectroscopy (ED-XAS), in which the whole XAS spectrum is acquired simultaneously, has been applied to reduce the real-time for acquisition of spectra of photoinduced excited states by using a germanium microstrip detector gated around one X-ray bunch of the ESRF (100 ps). Cu K-edge XAS was used to investigate the MLCT states of \([\text{Cu(dmp)}(\text{2})](\text{+})\) (dmp =2,9-dimethyl-1,10-phenanthroline) and \([\text{Cu(dbtmp)}(\text{2})](\text{+})\) (dbtmp =2,9-di-n-butyl-3,4,7,8-tetramethyl-1,10-phenanthroline) with the excited states created by excitation at 450 nm (10 Hz). The decay of the longer lived complex with bulky ligands, was monitored for up to 100 ns. DFT calculations of the longer lived MLCT excited state of \([\text{Cu(dbp)}(\text{2})](\text{+})\) (dbp =2,9-di-n-butyl-1,10-phenanthroline) with the builder amine ligands, indicated that the excited state behaves as a Jahn-Teller distorted Cu(H) site, with the interligand dihedral angle changing from 83 to 60 degrees as the tetrahedral coordination geometry flattens and a reduction in the Cu-N distance of 0.03 angstrom.
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