

NO is a classic non-innocent ligand and iron nitrosyls can have different electronic structure descriptions depending on their spin-state and coordination environment. These highly covalent systems are found in proteins and are also used as models for Fe-O₂ systems. This study utilizes iron L-edge X-ray absorption spectroscopy, interpreted using a valence bond configuration interaction multiplet model, to directly experimentally probe the electronic structure of the S=0 {FeNO}⁶ compound [Fe(PaPy₃)NO]²⁺ (PaPy₃ = N,N-bis(2-pyridylmethyl)amine-N-ethyl-2-pyridine-2-carboxamide) and the S=0 [Fe(PaPy₃)CO]⁺ reference compound. This method allows separation of the σ-donation and π-acceptor interactions of the ligand through ligand-to-metal and metal-to-ligand charge transfer mixing pathways. The analysis shows that the {FeNO}⁶ electronic structure is best described as Fe^{III}-NO(neutral), with no localized electron in an NO π* orbital or electron hole in an Fe dπ orbital. This delocalization comes from a large energy gap between the Fe-NO π-bonding and antibonding molecular orbitals relative to the exchange interaction between electrons in these orbitals.