

NRIXS on High Valent Iron Complexes Relevant to Small Molecular Activation

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High valent Iron-oxo/hydroxo ($\text{Fe}=\text{O}/\text{Fe}-\text{OH}$) species have been identified as the key reactive intermediates to carry out numerous oxidative transformations in biology, such as oxidative oxygenation and halogenation reactions. Some of these transformations are key chemical steps in many biological pathways, such as DNA/RNA repair, gene regulation, O_2 sensing, and natural product biosynthesis. In order to design synthetic catalysts that can harvest the strong oxidizing power from the iron-oxo/hydroxo species in a controlled fashion, it is necessary to obtain a thorough molecular level description of the $\text{Fe}=\text{O}/\text{Fe}-\text{OH}$ moiety and its interactions with the supporting ligands, as well as with the local environment. In the past decades, experimental and theoretical efforts have brought significant progress on the understandings of electronic structure and reactivity relationships of $\text{Fe}=\text{O}/\text{Fe}-\text{OH}$ species. However, detailed spectroscopic studies on $\text{Fe}=\text{O}/\text{Fe}-\text{OH}$ moieties that are in different oxidation states but supported by similar ligand systems having tunable hydrogen bonding interactions are rare. By using synchrotron radiation based ^{57}Fe Nuclear Resonant Inelastic X-ray Scattering (^{57}Fe NRIXS) together with $^{16}\text{O}/^{18}\text{O}$ isotope labeling, we have revealed the vibrational signatures of $\text{Fe}=\text{O}$ and $\text{Fe}-\text{OH}$ moieties in a series of mono-iron synthetic complexes in different oxidation states (Fe^{III} or Fe^{IV}), and showed that subtle changes of the hydrogen bonding interactions to the $\text{Fe}=\text{O}/\text{Fe}-\text{OH}$ moieties can significantly affect their vibrational features. Based on these vibrational data and density functional theory (DFT) calculations, we will discuss the electronic effects of the iron oxidation state, the supporting ligand, and the local environment to the bonding interactions of $\text{Fe}=\text{O}/\text{Fe}-\text{OH}$ moieties. We will also extend our discussion to a series of high valent (Fe^{IV} or Fe^{V}) iron-imido ($\text{Fe}=\text{NR}$) complexes, which are supported by *N*-heterocyclic carbene ligand and exhibit parallel chemical reactivities as those of $\text{Fe}^{\text{IV}}=\text{O}$ species. ^{57}Fe NRIXS data revealed the vibrational features associated with $\text{Fe}^{\text{IV}}=\text{NR}/\text{Fe}^{\text{V}}=\text{NR}$ moieties in these complexes. Based on these observations, a comparison between $\text{Fe}^{\text{IV}}=\text{NR}$ and $\text{Fe}^{\text{V}}=\text{NR}$, and $\text{Fe}^{\text{IV}}=\text{O}$ units will be given.