

*Iron(III, IV, V)-oxo complexes studied by nuclear resonance vibrational spectroscopy*Yisong Guo¹, Andrew Weitz¹, Michael Hendrich¹¹Chemistry Department, Carnegie Mellon University, Pittsburgh, United States

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High-valent iron-oxo (FeIV=O, FeV=O) species have been identified as the key reactive intermediate to carry out numerous oxidative transformations in biology, which include hydroxylation, halogenation, desaturation, epoxidation, endoperoxidation, ring expansion and ring contraction. Some of these transformations are key chemical steps in many biological pathways, such as DNA/RNA repair, gene regulation, O₂ sensing, and natural product biosynthesis. Very recently, high-valent iron-oxo species have also been hypothesized to be involved in water splitting in iron-based synthetic catalysts. In order to design synthetic catalysts that can harvest the strong oxidizing power demonstrated by iron-oxo species in a controlled fashion, it is necessary to obtain a thorough molecular level description of the bonding interactions in the Fe=O moiety and its interaction with the supporting ligand. In the past decades, experimental and theoretical efforts have brought significant progress on the understandings of electronic structure and reactivity relation in iron-oxo species. However, detailed spectroscopic studies on Fe=O moieties that are in different oxidation states but supported by similar ligand systems are rare. By using synchrotron radiation based ⁵⁷Fe nuclear resonance vibrational spectroscopy (NRVS, nuclear resonance inelastic x-ray scattering, NRIXS) together with ¹⁶O/¹⁸O isotope labeling, we have revealed the vibrational signatures of Fe=O moieties in three different oxidation state (FeIII, FeIV and FeV). Based on these vibrational data, we are able to extract the electronic effects of the iron oxidation state and the supporting ligand to the bonding interaction and thus the intrinsic reactivity of the Fe=O moiety.

Keywords: [high valent iron-oxo](#), [nuclear resonance inelastic x-ray scattering](#)