

# Mononuclear Non-Heme Fe(IV)=O Systems: Electronic Structures and Comparison to Heme and Copper Species

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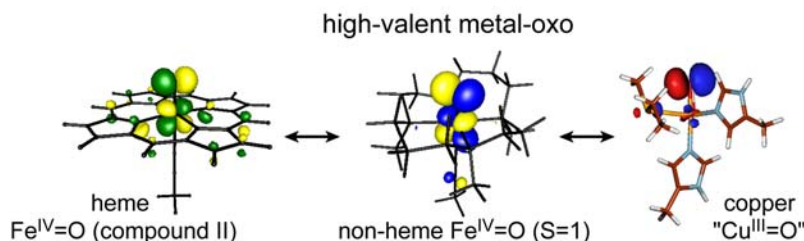
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Mononuclear non-heme iron enzymes catalyze a variety of biological reactions requiring the binding and activation of dioxygen. Using spectroscopic methods and density functional calculations, the geometric and electronic structures of the oxygen intermediates and their reactivities are being defined to understand the catalytic mechanisms on a molecular level.

A key intermediate is the Fe(IV)=O species. We present a detailed description of the electronic structure and Fe-O bonding of a non-heme Fe(IV)=O S=1 model complex and correlate these results to S=2 species, the ground state of non-heme enzyme intermediates [1].

In addition, the electronic structures of Fe(IV)=O S=1 heme and non-heme species are compared, with focus on the effects of the porphyrin  $\pi$ -system on the Fe-O bond, and their relative reactivities toward H-atom abstraction reactions are evaluated [2].

Copper enzymes also play important roles in oxygen binding and activation, i.e. non-coupled binuclear Cu proteins can perform H-atom abstraction reactions. We contrast the electronic structures of the key oxygen intermediates in iron and copper enzymes, and assess how these differences can relate to different reactivities and preferred reaction mechanisms [3].



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[2] A. Decker, E.I. Solomon, *Angew. Chem.* 117 (2005) 2292-2295, *Int. Ed.* 44 (2005) 2252-2255

[3] A. Decker, E.I. Solomon, *Curr. Opin. Chem. Biol.* 9 (2005) 152-163.