Theory of Chemical Bonds in Metalloenzymes X:
Full geometry optimization and vibration analysis of porphyrin iron-oxo species

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Abstract

An oxyferryl state, called compound I, is suggested as a reactive intermediate for some heme proteins such as P450, catalase and perosidase. Extensive experimental studies have been performed for these metalloproteins, however, direct experimental evidence for the intermediate state has not been reported yet. One of the differences among these heme proteins is an axial ligand at the iron center, which is cystein, tyrosine and histidine residue for P450, catalase and peroxidase, respectively (Fig. 1).

In previous papers of this series [1], we have studied electronic structures of some iron centers in metalloproteins and inorganic model complexes. We have recognized a necessary of precise analysis on the electronic structures for some low-lying states.

In this study, electronic and vibrational analysis on compound I models are performed at broken symmetry hybrid-density functional theory (BS-HDFT) level. Nature of chemical bonds is characterized by natural orbital analysis.

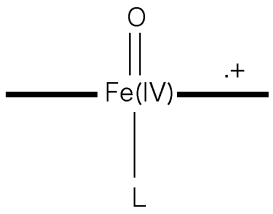

Figure 1. Structure of compound I model (Fe(IV)=O and porphyrin π cation radical)

[1] M. Shoji, et al, Int. J. Quantum Chem. 100, 887 (2004), 105, 628 (2005), 106, 3288 (2006), 107, 609 (2006), 107, 3250 (2007), 2008 in press.