

Theory of Chemical Bonds in Metalloenzymes XI: CAS-DFT study of transition metal-oxo species

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Chemical-bonding of transition metal oxo species (M=O) has been attracted much attention in relation with catalytic reactions in enzymes. In order to trace the correct catalytic cycle, it is needed to describe various low-lying spin states correctly. Previously, Shoji et al. investigated electronic structures of reaction center of P450 [1] using the hybrid DFT approach to elucidate mechanism of the catalytic cycle. They discuss the reaction path of P450 in analogy with the model reaction [2]: ^3O or $^1\text{O} + \text{CH}_4$, suggesting that the reactions at the ground and excited state proceed via abstraction (^3O -model) and insertion mechanisms (^1O -model), respectively.

In this study, we investigate chemical bonding between transition-metal (M; M=Fe, Cu, Mn) ion and oxygen (O) using CAS-DFT approach [3]. The relative stabilities among low-lying spin states for potential surfaces of M-O will be examined with and without point charges that coordinate to M, and, M-O with porphrin environment. The computational results will be discussed in analogy with chemical bonding of singlet and triplet molecular oxygen.

[1] Shoji, M. et al., Int J Quantum Chem. in press.

[2] Yamaguchi, K.; Takahara, Y.; Fueno, T. in: Smith Jr., V. H.; Scheaffer III, H. F.; Morokuma, K.; (Eds.), Applied Quantum Chemistry, D. Reidel, Boston, 1986, p. 155.; Yamaguchi, K. Singlet Oxygen III (Frimer A. A. Ed. CRC press, 1985), p237; Yamaguchi, K.; Takahara, Y.; Fueno, T. in: W. Ando and Y. Morooka, Eds, The Role of Oxygen in Chemistry and Biochemistry, Elsevier: Amsterdam, 1988, 33,263.

[3] K. Nakata, et al. Int J Quantum Chem 106, 3325, 2006; Yamanaka, S. et al. Chem Lett 35, 242, 2006; Ukai, T. et al. Mol Phys, in press.