

Theory of Chemical Bonds in Metalloenzymes

—Manganese Oxides Clusters in the Oxygen Evolution Center—

Kizashi Yamaguchi[‡]¶, Mitsuo Shoji[‡], Toru Saitou[‡], Shusuke Yamanaka[†], Hiroshi Isobe[‡], Satoru Yamada[‡],
Takashi Kawakami[‡], Yasutaka Kitagawa[‡], Mitsutaka Okumura[‡],

[‡]*Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*

[†]*Protein Institute, Osaka University, Suita, Osaka 560-0871, Japan*

[¶]*Toyota Physical&Chemical Research Institute, Nagaute, Aichi 480-1192, Japan*

Abstract

Our theoretical descriptions of strongly correlated electron systems (**SCES**) have been reviewed from the view point of generalization of molecular orbitals (MO) concept; namely from broken-symmetry (BS) single reference (SR) MO theories to symmetry-adapted (SA) multi-reference (MR) MO theories through resonating BS MO configuration interaction (CI) method. Now a day, the BS MO method is a standard method for theoretical investigation of mono- and multi-nuclear transition metal complexes involved in metalloenzymes. In early 1980 we have initiated BS MO theoretical calculations of transition-metal oxo-species $M=O$ ($M=Cr, Mn, Fe, Ni, Cu$) to elucidate the nature of their $d\sigma-p\sigma$ and $d\pi-p\pi$ bonds. It has been concluded that high-valent $M=O$ species such as $Mn(V)=O$ and $Fe(IV)=O$ exhibit the electrophilic property in a sharp contrast with the nucleophilic one of low-valent $M=O$ bonds: $M(II)O^2-$, and closed-shell $d\pi-p\pi$ bonds often suffer the triplet-instability, giving rise to open-shell (BS) configurations with significant metal-diradical (MDR) character: $\bullet M-O\bullet$: note that these bonds are therefore regarded as typical examples of **SCES**. Because of the MDR character, 1,4-metal diradical mechanism was indeed preferable to four-centered mechanism in the case of addition reaction of naked $Mn(IV)=O$ to ethylene. Recently the manganese-oxo species have been receiving renewed interest in relation to catalytic cycle of oxygen evolution from water molecules in the photosynthesis II (PSII) systems: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.

Accumulated experimental results indicate that this process is catalyzed with four manganese oxide clusters with calcium ion. Past decade we have performed BS MO theoretical investigations of manganese oxide clusters related

to the complex: Mn(X)=O(1) , $\text{Mn(X)(}\mu\text{-O)Mn(X)(2)}$, $\text{Mn(X)(}\mu\text{-O)}_2\text{Mn(X)(3)}$, $\text{O=Mn(X)(}\mu\text{-O)}_2\text{Mn(X)(4)}$, $\text{O=Mn(X)(}\mu\text{-O)}_2\text{Mn(X)=O(5)}$, $\text{Mn(X)}_4\text{O}_y\text{(6)}$ and $\text{CaMn}_4\text{(X)O}_y\text{(7)}$. These calculations have elucidated that high-valent Mn(X)=O(X=IV,V) bonds in **1-7** exhibit intermediate MDR character ($y=50\%$) in the case of total low-spin (LS) configuration of **1-7** but the MDR character decrease with coordination of water molecules. While the MDR character of the Mn-oxo bonds becomes very high at the high-spin (HS) configuration. Our computational results enabled us to propose two possible mechanisms on the theoretical ground: (A) electrophilic (EP) mechanism and (B) radical coupling (RC) mechanism. These results indicate that the EP mechanism is preferable for the low-spin (LS) state in polar media like in the protein environments (oxygen evolution center (OEC)), whereas the RC mechanism is feasible at the high-spin (HS) states of in **1-7**. In my talk possibilities of EP and RC mechanisms are discussed in comparison with a lot of experimental results accumulated and theoretical results with several groups.