Theory of Chemical Bonds in Metalloenzymes

—Manganese Oxides Clusters in the Oxygen Evolution Center—

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Abstract

Our theoretical descriptions of strongly correlated electron systems (SCES) have been reviewed from the viewpoint 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 dσ-pσ and dπ-pπ bonds. It has been concluded that high-valent M=O species such as Mn(VI)=O exhibit the electrophilic property in a sharp contrast with the nucleophilic one of low-valent M=O bonds: M(II)/O2-. and closed-shell dπ-pπ bonds often suffer the triplet-instability, giving rise to open-shell (BS) configurations with significant metal-diradical (MDR) character: •M-O•: 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: 2H2O -> O2 + 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), Mn(X)(µ-O)Mn(X)(2), Mn(X)(µ-O)=Mn(X)(3), O=Mn(X)(µ-O)=Mn(X)(4), O=Mn(X)(µ-O)=Mn(X)(5), Mn(X)(µ-O)2Mn(X)(6) and CaMn₄(X)O₆(7). These calculations have elucidated that high-valent Mn(X) =O(X=IV, V) bonds in 1-7 exhibit intermediate MDR character (γ=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.