A Computational Study of Metalloporphyrin-Oxygen Systems

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Transition metal (TM) porphyrins can bind to O_2 in a variety of biological and catalytic systems, most notably heme. However, a definitive understanding of the TM-O_2 bonding does not exist despite extensive computational work. As a starting point for metalloporphyrin studies, $[TM\text{-}O_2]^{2+}$ molecules have been investigated (the 2+ results from the absence of the 2- porphyrin ligand). For all first-row TM's, optimized geometric parameters were first obtained at the B2LYP level with the LANL2DZ basis set, augmented with a set of d-type polarization functions on the oxygen atoms. Subsequent CASSCF energy points were obtained in order to account for the possibility of various spin states. Once trends in the $[TM\text{-}O_2]^{2+}$ system are established, various ligands will be added to the TM in order to ultimately shed light on TM-O_2 bonding in metalloporphyrins.