A Valence Bond Study of the a nd B onds of Transition Metal Dioxyen Dications

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The transition metal dioxygen dication σ and π bonds of all first row transition metals ($[TM\text{-}O_2]^{2+}$ TM= Sc – Zn) have been studied using valence bond theory (VB). Geometries were first optimized at the B3LYP/LANL2DZ level of theory (including an extra oxygen *d*-type polarization function) using the GAUSSIAN03 program package. Then CASSCF calculations with a 9 orbital active space were used to determine the ground electronic states. Knowing the geometric and electronic ground states, VB calculations were preformed using the XMVB program. Structural weights and bond energies have been determined for the σ and π systems separately first, and then combined. This work is a precursor for a study of first row TM-porphyrin systems. To this end, we plan to study the σ and π bonds of [tetraamine-TM- O_2]$^{2+}$ by holding the amine-TM geometric parameters constant at their TM-porphyrin B3LYP/LANL2DZ optimized values followed by CASSCF and VB calculations as described above.