

ELECTRONIC STRUCTURE ANALYSIS OF GROUND AND EXCITED STATES OF $\text{MO}^{2+/+/0/-}$ ($\text{M} = \text{Mo}, \text{Ru}$) AND THEIR WATER ACTIVATION STRENGTHS

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Production of H_2 gas via water splitting reactions facilitated by solar light harvesting, can be a solution to the constant increase of energy demand. Water splitting is an endothermic process which requires about 2.69 eV per water molecule. High endothermicity of this process can be overcome by exploiting the sun light and using a suitable catalyst. Transition metal oxide (MO) catalysts are promising candidates for this process because of their multiple low-lying electronic states.

The rate determining step in the water splitting reactions is often the activation of the O-H bonds. Here we have tested water activation strengths of several neutral and charged MOs computationally. The complicated electronic structures of these MOs forced us to perform multi-reference calculations. For these MOs the water activation process can be partitioned into three major processes. 1) Formation of the $\text{H}_2\text{O} \cdots \text{OM}$ interacting complex. 2) Surpass the transition state barrier which involve H-O bond cleavage of metal bound water. 3) HO-M-OH product formation.

Due to the multiple low-lying excited states of these species, spin crossovers and electron excitation from ground to higher states are expected. Among the considered $\text{H}_2\text{O} + [\text{MoO}]^{-/+ / 2+}$ reactions, the anionic system is the best candidate for the water activation, which has a lower activation energy barrier and create a more stabilized product than interacting complex. On the contrary, $\text{MoO}^{2+/+}$ stabilizes the $\text{MoO}^{2+/+} \cdots \text{H}_2\text{O}$ interacting complex over products. A similar pattern was observed for the $\text{H}_2\text{O} + [\text{RuO}]^{-/0/+ / 2+}$ reactions. The suitability of RuO species for the water activation vary in $\text{RuO}^{2+} < \text{RuO}^+ < \text{RuO} < \text{RuO}^-$ order.