Hydrogen Evolution from Water via Metal Sulfide Cluster-based Catalysis

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Background Information

As the world uses more and more energy, there is a growing need to find a clean, sustainable source of energy. Hydrogen, as a high-energy carrier, is one of the top candidates for an alternative energy source because it produces minimal pollution as it undergoes combustion. However, H_2 is rarely found in its homonuclear form in nature.

$H_2O(l) \rightarrow \frac{1}{2}O_2(g) + H_2(g)$
ΔG=+237 kJ/mol

This reaction is highly endothermic and thermodynamically unfavorable!

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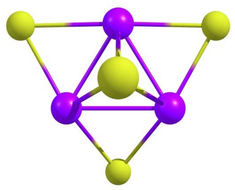
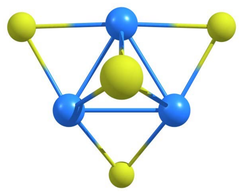
H_2O + photocatalyst + A → H_2 + AO + photocatalyst

Transition Metal Sulfides (TMS) as Photocatalysts

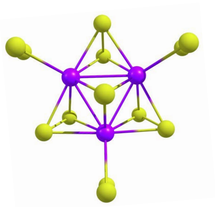
TMS molecules have high electrochemical activity and have smaller band gaps than their Transition Metal Oxide (TMO) analogues. Our molecules were chosen because of their structural similarity to edge sites of bulk MoS_2—known to be an efficient catalyst of the Hydrogen Evolution Reaction (HER)—and their similarity to the nitrogenase and hydrogenase enzymes, which are responsible for HER in a myriad of organisms.





Future Work

The search for a better catalyst:
Experimental studies have shown that $Mo_3S_{13}^-$ is an efficient catalyst of HER. We would like to investigate the mechanism by which this cluster catalyzes HER. Preliminary results indicate that the mechanism is different than the mechanism we've previously observed in other TMS and TMO clusters.

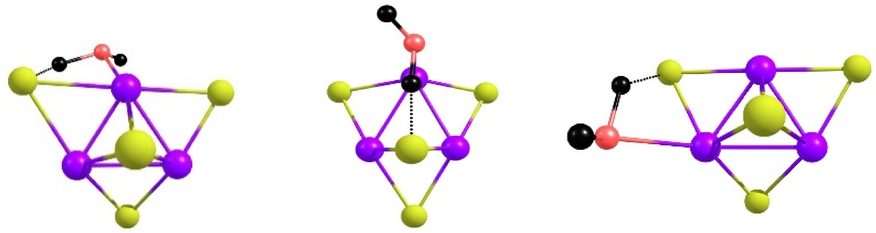


Working towards a catalytic cycle:
So far, the reaction that we've studied does not result in a full catalytic cycle. We have successfully generated H_2 but have not regenerated our catalyst molecule in its original form. We will now focus on designing a sacrificial reagent molecule (A) that will allow us to create a full catalytic cycle.

H_2O + photocatalyst + A → H_2 + AO + photocatalyst

The Reaction

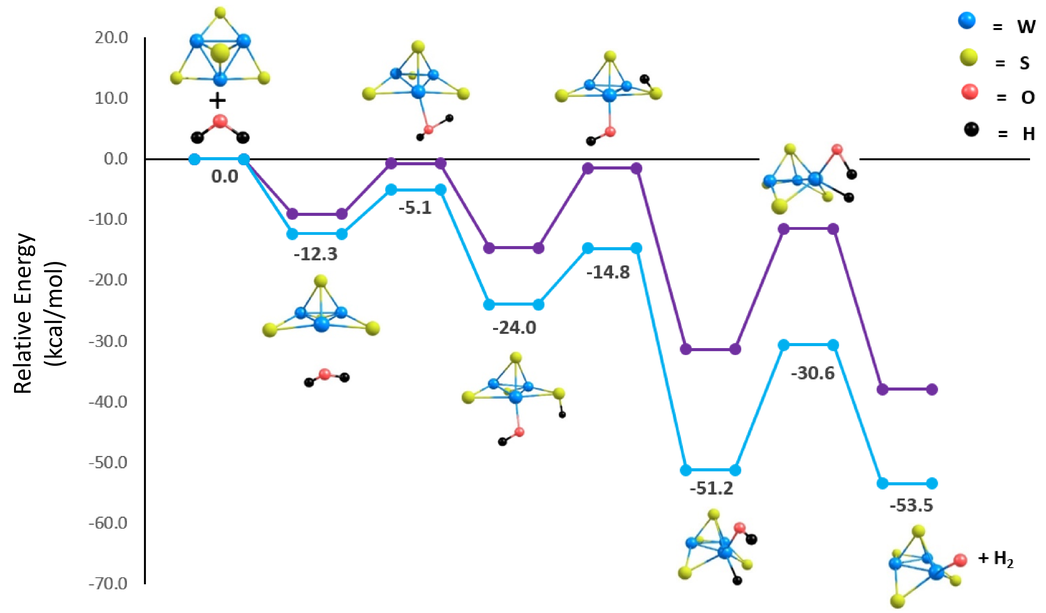
Step 1: The Attack of Water—The Rate-Determining Step (RDS):



Mode 1 Mode 2 Mode 3

The energetic barrier for Mode 1 was ~9.5 kcal/mol lower than Modes 2 and 3. Thus, Mode 1 was chosen for further investigation.

Potential Energy Profile:



The entire potential energy profile is below O kcal/mol. Therefore we expect the reaction to go to completion.

Acknowledgments