

Institutsseminar

Influence of Solvation and Dynamic Hydrogen Bonding on the Reactivity of Reductive Electron Transfer and Hydrogen Evolution

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Water molecules are ubiquitous in chemical systems and play a crucial role in stabilizing polar species through hydrogen bonding. They also facilitate numerous reactions, including electron transfer in metal-ion complexes. The interplay between water solvation and hydrogen bonding critically governs the energetics and dynamics of these reactions, thereby influencing both electron and proton transfer processes. Given the pivotal role of water in promoting reductive electron transfer, this study aims to investigate the solvation dynamics of water molecules in the reductive electron transfer of dimethyl disulfide (DMDS) using hydrated electron clusters, as well as proton transfer in aluminum hydride–hydroxide complexes related to molecular hydrogen production. Using the CP2K/Quickstep framework with revPBE-D3 functional and MOLOPT basis sets, we characterized the reaction trajectories of CH_3SSCH_3 interacting with hydrated electrons and the hydrogen evolution in $[\text{HAIOH}(\text{H}_2\text{O})_{n-1}]^+$ clusters. The simulations reveal that hydrogen bonding to the sulfur atom is crucial for facilitating electron transfer, primarily due to the large solvation energy released during the process. Interestingly, this solvation energy serves as the main driving force for electron transfer and compensates for the intrinsic redox potential. The reductive electron transfer leads to a frustrated solvent cavity, which is energetically unfavorable; consequently, the surrounding water molecules close this cavity by forming additional hydrogen bonds before solvent migration occurs. In the hydrated aluminum hydride–hydroxide complex, hydrogen-bond solvation at the hydride site can be categorized into single and dual hydrogen-bond configurations. The single hydrogen-bonded structure is energetically less stable than the dual hydrogen-bonded one in larger clusters. However, despite its lower energy, the dual hydrogen-bonded structure exhibits a higher activation barrier for Al–H bond dissociation and molecular hydrogen generation. Therefore, hydrogen-bond formation at the hydride site suppresses H_2 production in larger water clusters. These findings underscore the dynamic and competing roles of hydrogen bonding in governing reductive electron transfer and proton transfer processes.

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