

384b Theoretical Insights into Chemistry and Catalysis at the Aqueous Metal Interface

Matthew Neurock

The metal-solution interface is important in controlling a number of relevant processes including catalysis, electrocatalysis, and corrosion chemistry. Relatively little, however, is known about the structure and dynamics of the metal solution interface and its impact on elementary physicochemical surface processes, including adsorption, diffusion, and reaction. Density functional theory and ab initio molecular dynamic methods have been used to analyze the effects of aqueous media on the mechanism and the kinetics of different surface processes. The presence of protic solutions on well-defined metal substrates leads to a wealth of interesting surface behavior. Hydrogen bonding can modify the structure of adsorbed intermediates, alter the strength of the adsorbate surface-bond, stabilize charged intermediates, enhance surface kinetics and even provide new mechanistic pathways in which the solution directly participates.

We describe the direct, as well as the indirect, effects of solution on different surface processes including the heterolytic dissolution of organic and inorganic intermediates, molecular and dissociative adsorption and desorption of organic intermediates over well-defined metal surfaces, surface reactivity, and diffusion. There are many cases where the solution can directly participate in these mechanisms by directly participating in proton transfer processes.