Controlled Self-Assembly, Switching, and Catalysis: Ab-Initio Insights into Stimulated Chemistry on Surfaces

A fundamental understanding of molecular structure and chemical reactivity at complex interfaces is key to many technological applications ranging from single molecule electronics to functionalized surfaces. Realistic applications will require the ability to manipulate single molecules in well-defined chemical environments. We develop electronic structure methods that accurately describe the structure, spectroscopy, and reactivity of complex molecular adsorbates and apply them to prototypical model systems such as azobenzene [1], porphyrine [2], and retinoic acid [3] derivatives adsorbed on well-defined surfaces. Hereby we focus on the effects of key design parameters such as molecule functionalization, substrate reactivity, finite-temperature, and surface coverage on experimentally accessible structural and electronic properties of adsorbates. We do this by directly simulating observables from experiments such as Temperature Programmed Desorption and X-ray Photoemission spectroscopy. On the example of photo-induced isomerization of azobenzene, key parameters and molecular design principles will be discussed that govern molecular function on metallic surfaces. We address the detailed non-adiabatic dynamics of molecular reactions on surfaces using our recently developed methods to sample adsorbate configurations [4], study electronic excited states and vibrational energy dissipation [5].