Theoretical Investigation of Photochemical Reactions on Surfaces from first principles

Thorsten Klüner
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of
Chemical Physics, Faradayweg 4-6, 14195 Berlin, Germany

Surface photochemistry occurs in many instances, including photocatalysis, laser induced desorption, and solar energy conversion. Despite its ubiquitous nature, a microscopic understanding of the underlying basic processes and elementary reactions remains a great challenge. In this talk, I will focus on the theoretical description of the simplest photochemical phenomenon on surfaces: the laser-induced desorption of small molecules.

Ab initio calculations of high dimensional potential energy surfaces (PES) for ground and excited states of the systems CO/Cr2O3(0001) and NO/NiO(100) will be presented. The surface model consists of a small cluster embedded in a semi-infinite array of point charges to simulate the electrostatic field above the surface. Based on Configuration Interaction (CI) calculations a reliable construction of global potential energy surfaces for the electronic ground state as well as for excited states of the adsorbate substrate system becomes feasible. Subsequent high-dimensional time-dependent wave packet studies using the calculated potential surfaces enable us to simulate quantum state resolved experiments. Detailed microscopic insight into the mechanism of the desorption process can be deduced on a first principles basis.