
Electron Transfer and Molecular Dynamics at Metal Surfaces

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Abstract

This thesis covers key aspects of the interaction between a molecule and a metal surface. The effect of electron transfer on dynamical phenomena, such as initial sticking and desorption, is of special interest. From a fundamental point of view these questions require information about the electronic structure and potential-energy surfaces of the molecule-metal system for both ground and excited states. The ground-state information is obtained within the framework of density-functional theory (DFT). However, today's theoretical tools for calculation of excited states are difficult to apply to such extended systems as the metal surface represents. This shortcoming is one of the issues that are addressed in this thesis.

A DFT-based method is introduced to calculate electronically excited states of molecules close to the metal surface with a working accuracy. It is tested on a number of systems and phenomena, such as photodissociation of NaCl and LiCl, surface chemiluminescence that occurs when halogen molecules collide with alkali metals, and vertical excitation energies for adsorbed molecules. The results are then compared with those obtained from experiments and other available theoretical methods, in order to confirm the usefulness of our method.

Extensive adsorption studies of various diatomic molecules on the Al(111) surface elucidate the need to account for electronically excited states. Only within a diabatic electron-transfer model that is based on electronically excited states the sticking behavior of several of the studied molecules can be explained. Electronegativity is identified as a key parameter in determining whether an adiabatic or a diabatic picture should be used to describe the dynamics of the impinging molecules. Together with such concepts as bond order, Pauli-repulsion, and asymmetry, it can be used to categorize sticking and adsorption properties for the considered molecules. In particular, an explanation is given for the longstanding problem of the observed energy dependence of the initial sticking probability of O₂ on Al(111).

The theoretical study of NO desorption from the Pt(111) surface, caused by femtosecond laser pulses, is initiated by experimental observations that internal degrees of freedom of the adsorbate play an important role in the desorption dynamics. A model calculation, based on the hot-electron mechanism for surface photochemistry, suggests that the behavior of the temperature associated with rotational motion might be affected by the substrate-induced electron structure of the adsorbed NO molecule.

The effect of mass asymmetry and dipole polarization, experienced by a hydrogen molecule physisorbed on the clean Cu(100) surface is also studied with a multidimensional pseudo-potential wavepacket method.

Keywords: surface dynamics, density-functional theory, potential-energy surfaces, excited states, electron transfer, wavepacket, sticking, photodesorption.
