

Vibrational excitation and relaxation at surfaces.

Ivan Andrianov, Stephanie Beyvers and Peter Saalfrank

*Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Str. 24-25,
D-14476 Potsdam-Golm, Germany*

Abstract

Vibrational relaxation and excitation of adsorbates near surfaces is an important determinant for reaction dynamics following excitations with lasers, electrons, holes, or ions. We illustrate some of the relevant processes on the following examples.

In the first part of the talk a perturbation theory study of vibrational lifetimes for the bending and stretching modes of hydrogen adsorbed on a Si(100) surface is presented. The hydrogen-silicon interaction is treated with a semiempirical bond-order potential. The finite lifetime is due to vibration-phonon coupling, which is assumed to be linear or bilinear in the phonon and nonlinear in the H-Si stretching and bending modes. Lifetimes and vibrational transition rates are evaluated with one- and two-phonon processes taken into account. Temperature effects are also discussed. In agreement with experiment and previous theoretical treatment it is found that the H-Si stretching vibration decays on a nanosecond timescale, whereas for the H-Si bending mode a picosecond timescale is predicted. For higher excited vibrations, simple scaling laws are found if the excitation energies are not too large. The relaxation mechanisms for the excited H-Si stretching and the H-Si bending modes are analyzed in detail. We also present preliminary results on the relaxation dynamics of the combined system-bath system with the help of the multi-configurational time-dependent Hartree (MCTDH) method.

The second part deals with the effect of vibrational pre-excitation by IR laser pulses on subsequent UV-control of photo"reactions" on surfaces like desorption or diffusion of the adsorbed species. For a model of the system CO/Cu(100), which considers three physically quite distinct vibrational modes of CO, state-selective excitations with shaped optimal IR-pulses in the picosecond-domain are presented. The dynamics of system-field dipole-coupling and dissipation due to energy flow from vibrational excited states of the adsorbate to electronic and phononic degrees of freedom of the bath are treated within the open-system density-matrix (Liouville-von-Neumann) model. Optimal pulses are found by a quantum optimal control scheme and are analysed by the application of Wigner and Husimi "quasi-probability" distributions which allow a resolution of pulse intensity in time and energy.