

## ABSTRACT

The dynamics of atoms and molecules at surfaces is a topic of much scientific and technological interest, with application in, for instance, heterogeneous catalysis and epitaxial growth. The dynamics is governed by a multidimensional potential energy surface (PES), which is often characterized by the bound vibrational and rotational properties of the adsorbate. Comparisons between calculated and measured vibrational and rotational properties can yield a detailed description of the PES and the interaction behind the adsorption.

This thesis presents theoretical studies of the vibrational and rotational character of diatomic molecules at surfaces. Two and three-dimensional PESs have been constructed for non-dissociative adsorption of  $\text{H}_2$  and  $\text{N}_2$  on  $\text{Cu}(111)$  and for  $\text{H}_2$  on  $\text{Cu}(510)$ , using density functional theory (DFT). The adsorbate dynamics for these systems, and for  $\text{H}_2$  on  $\text{Cu}(100)$ , has been investigated using time-dependent wavepacket calculations, which are described in detail. For  $\text{CO}$  chemisorbed in the  $c(4 \times 2)$  structure on  $\text{Pt}(111)$ , the bound vibrational modes have been studied within the harmonic approximation, using DFT.

For  $\text{H}_2$  on flat  $\text{Cu}$  surfaces, calculated dipole activity for vibrational motion in the physisorption well, shows non-negligible intensities for transitions to continuum levels, indicating the possibility of direct photodesorption. Calculated rates for such a process agree well with measured rates of desorption, induced by infrared radiation from the walls of a UHV chamber. For  $\text{H}_2$  at the step edge of  $\text{Cu}(510)$ , calculations reveal the existence of states, in which the molecule is confined to perform two-dimensional quantum rotation. Rotational and vibrational transition energies of these states agree well with results from EELS measurements. Scattering calculations show that an observed large difference in the probability for rotational inelastic scattering of  $\text{D}_2$  and  $\text{N}_2$  from  $\text{Cu}(111)$ , is due to the difference in the rotational constant of the molecules. The calculated vibrational modes of  $c(4 \times 2)$   $\text{CO-Pt}(111)$  show small energy splittings among lateral modes that have previously been assumed to degenerate, based on the local adsorption symmetry, and a reassignment of previously measured vibrational energies to low-energy modes is suggested. Two modes which have previously been assumed to be dipole forbidden are found to be weakly dipole active.

**Keywords:** physisorption, chemisorption, photodesorption, surface scattering, potential energy surfaces, wavepacket calculations