

Hydrogen Adsorbed on Flat, Stepped and Adatom Decorated Copper Surfaces.

Abstract

This thesis deals with spectroscopic studies regarding weak adsorption of molecular hydrogen on copper surfaces exposing different structural situations, including surface steps and surface adatoms. The aim is to understand, mostly from rotational and vibrational spectra, how the molecule-surface interaction is influenced by the coordination of the surface atoms.

The experiments were performed in an ultra-high vacuum (UHV) system at a base pressure in the 10^{-11} Torr range. The system is equipped with a separate evaporation chamber for adatom deposition. Adsorbate rotations and vibrations are induced and monitored by electron energy loss spectroscopy (EELS), where the spectrometer used has an optimum energy resolution of about 1 meV. The sample holder is He-cooled and hydrogen adsorption and EELS measurements were performed at temperatures around 10 K.

On the flat Cu(100) surface the hydrogen molecules are physisorbed in a free-particle like 3-D rotor state. This adsorption state is also found on the terraces of the stepped Cu(510) surface, but at the step edge sites of this surface a weakly adsorbed 2-D rotor state is observed. Calculations reveal that the molecule is weakly chemisorbed in a potential well which confines it to rotate in two dimensions. The 2-D rotor state is found to be responsible for dramatic enrichment of adsorbed ortho- H_2 at elevated surface temperatures and hydrogen pressures.

When low concentrations of Cu and Au adatoms are present on the Cu(100) surface, the adsorbed hydrogen molecules tend to form dense 2-D clusters around the adatoms. The molecules are physisorbed and behave like 3-D rotors, but with a revealing signature, a pronounced dipole activity associated with the rotational motion. In general the physisorbed molecules acquire weak polarisation induced dipole moments which make their vibrational and rotational motion in the physisorption potential well dipole active. A striking consequence of this dipole activity is the observation of infrared photodesorption of the physisorbed molecules. Calculations reveal that this occurs via a direct bound-state continuum transition. Infrared photodesorption also occurs but with an order of magnitude larger probability for the weakly chemisorbed molecules at the Cu(510) step sites.