

Abstract

This thesis reports the structure determination of the local adsorption geometry of three model molecules on low index single crystal surfaces by means of photoelectron diffraction (PhD) in the scanned-energy mode. This technique is based on the analysis of the intensity variations, as a function of the photoelectron kinetic energy and the emission angle, of a core-level photoemission peak from the atom under study. All the data presented in this work were collected at the BESSY II synchrotron facility in Berlin, Germany.

The local adsorption geometry of the weakly chemisorbed Ni(100) $c(2 \times 2)$ -N₂ phase was determined by N 1s chemical shift scanned-energy photoelectron diffraction. We found that the N₂ molecules adopt an atop Ni site with the Ni-N spacing of 1.81 ± 0.02 Å and the N-N intramolecular distance of 1.13 ± 0.03 Å. This result contrasts strongly with the results of an earlier ARPEFS investigation and is in contradiction with the general idea that associates long bond lengths to weak bonds. Analysis of the PhD modulations of the N 1s photoemission satellite peak show that these are formally consistent with a previous assumption based on a XPD study that the satellite peak is separable into components fully localised on the two inequivalent atoms.

PhD data from the O 1s and C 1s photoemission were used to determine the local structure of the surface species produced on the rutile TiO₂(110) surface after room temperature exposure to formic acid. The results show clear evidence for the coexistence of formate, HCOO⁻, and hydroxyl, OH surface species. The formate species is aligned along the [001], bridging an adjacent pair of surface 5-fold-coordinated Ti atoms with the formate O atoms near-atop the Ti atoms and a Ti-O bondlength of 2.08 ± 0.03 Å. The hydroxyl species are formed by H attachment to the surface bridging O atoms and have a Ti-O bondlength of 2.02 ± 0.05 Å. Our results exclude the possibility of a large (~33%) fractional occupation by the formate species of a second site azimuthally rotated by 90° and bonded to a surface oxygen vacancy site, as proposed in some earlier infrared and X-ray absorption spectroscopic studies.

The local adsorption structure of the S-enantiomer of the simplest chiral amino acid, α -alanine (NH₂CH₃HCOOH), on Cu(110) has been investigated. The analysis of the PhD data from the N 1s and O 1s photoemission signals indicates that a tri-dentate bonding is involved through the amino N atom and the two O atoms of the carboxylate of the deprotonated alaninate (NH₂CH₃HCOO⁻) species. The N atoms are close to atop surface layer Cu atoms, while the O atoms occupy off-atop sites due to the mismatch of the O-N distances in the molecule to the Cu-Cu distance in the [001] surface direction. In the vicinity of the alaninate O atoms, substrate Cu atoms reconstruct along the [1 $\bar{1}$ 0] direction, shortening the Cu-Cu distance by an 11%.

Measurements of the C 1s photoemission spectrum from both S- and R-alaninate using circularly polarised incident radiation with opposite polarisations shown circular dichroism in the angular dependence (CDAD). The possibility of using this effect to distinguish between adsorbed enantiomers of chiral substances is briefly discussed here.