

1 Abstract

This thesis deals with the conformational properties of adsorbed molecules. The behavior of molecules with a C=C double bond adsorbed on semiconductor and metal surfaces is investigated and the manifestation of handedness of intrinsically achiral and chiral molecules upon adsorption is reported on.

With its two phenyl groups connected via a C=C double bond bridge, stilbene is a prototype molecule for a photochromic “molecular switch”. It was investigated mainly using near edge x-ray absorption fine structure spectroscopy (NEXAFS) in the gas phase and adsorbed on Si(100) and Cu(110) surfaces. NEXAFS shows a characteristic and unambiguous lineshape in the π^* -resonance for the cis- and trans-stilbene, which allows the clear identification of the isomers. Upon adsorption on a surface, the bonding takes place at the C=C bridge through substrate-bridge- π interactions. Depending on the properties of the substrate, the isomerisation capability known from gas phase is changed. On Si(100) with its directed bonds, the stilbene molecules adsorb on the Si dimers. The interaction between the Si atoms and the molecular π -system is rather strong. Angle resolved NEXAFS spectra reveal that both isomers adsorb through the C=C bridge and in both isomers the phenyl rings are twisted away from the surface, in the originally flat trans- less than in the cis-isomer. Since the interaction between substrate and π -system is strong, the photoinduced isomerisation is inhibited. On Cu(110) with its diffuse bonding characteristics the substrate-adsorbate interactions are weaker. Thus the photoinduced cis-to-trans isomerisation can be performed with an overall conversion of about 25% and does not depend on surface coverage. A trans-to-cis reaction is not detected. In order to improve the isomerisation capability the interaction between stilbene molecules and surfaces has to be tailored. This can be done using substituents with defined bonding functions.

In stilbene substituted with two carboxylic groups at either end of the molecule, bonding to Cu takes place only through these functional groups. Such a stilbene derivative, namely 4,4'-stilbene-dicarboxylic acid (DCSB), adsorbs on Cu(110) with the C=C double bond oriented either to the left or to the right with respect to the stilbene backbone. It can assume two adsorption sites, along or across the Cu rows. Long range ordered supramolecular structures consist of combinations of these four “building blocks”. STM images show that two handed adsorption phases are formed: the herringbone phase *H*

and the parquet phase P . While the former one is a racemic mixture of the same number of left- and right handed adsorption isomers, the latter one is enantiomerically pure, i.e. with either only left- or only right handed molecules. Both phases show an identical unit cell and indications exist that they are also energetically equivalent. At low temperatures all phases can be simultaneously detected on the surface. After thermal activation only the herringbone phase is present.

In the last part of my thesis I report on a method that allows to determine directly the handedness (chirality) of adsorbed chiral molecules. In $C1s$ core level spectroscopy the emission from the chiral centers exhibit an intensity difference for left- and right circular polarized light. This circular dichroism is angular dependent. Right handed molecules have a negative asymmetry at negative emission angles and vice versa.