Stephan Blankenburg,
Theory of the creation of self-assembled molecular structures on metall surfaces,
PhD Thesis, Department of Physics, Faculty of Science, University of Paderborn (2009).
159 pages, 76 figures, 7 tables.

Abstract

With the help of ab-intio methods the present work analyzes the creation of self-assembled molecular structures on metal surfaces for the production of highly-ordered structures in the context of the nanotechnology. This key technology of the 21th century needs a high reproducibility and thus a deep understanding of molecular interactions for the industrial manufacturing process.

Density functional theory (DFT) calculations are used for the theoretical analysis while the inclusion of van der Waals interactions is performed with the help of a semiempirical approach based on the London dispersion formula. Bader's topological paradigm helps to characterize hydrogen bonds (H-bonds) and scanning tunneling microscopy (STM) images are calculated with the Tersoff-Hamann approach. Additionally, Monte Carlo simulations allow the temperature dependent analysis of the structure stability while the molecular linear combination of atomic orbitals (MO-LCAO) theory reveals the relation between molecular rows and Friedel oscillations.

In this context, the adsorption of phenylglycine and adenine on copper (110) surface is a particularly impressive example for molecular self-assambly and thus represents a motivating experiment. While the STM images show that adsorbed adenine forms ordered one-dimensional dimer chains, the coadsorption of phenylglycine and the following decoration of the adenine chains mainly result in to effects. On the one hand the interaction between the two molecules leads to an enantiomeric effect, on the other hand there exist namely two highly ordered phenylglycine rows with a distinct separation.

The theoretical analysis of the afore mentioned system traces the enantiomeric effect back to substrate-mediated Coulomb repulsion due to substrate-molecule charge transfers as well as template effects arising from the surface. Thus, these facts expand the 'three-point contact model" from Easson and Stedman for enantiomeric interactions. Friedel oscillations resulting from screening effects explain the highly-ordered phenylglycine double rows, while indirect elastic interactions give only a minor contribution to the effect. The calculations of glutamic acid rows on silver (110) strengthen this explanation model whereas, in contrast to the phenylglycine rows, the indirect elastic interactions are also important to reproduce the experimental findings. Additionally, the analysis of the influence of the alkyl-side chains from the rosette molecules diethylbarbituric (DEB) and butylcyanuric acid (BuCYA) adsorbed on gold (111) on the structural ordering, shows the necessity of special types of H-bonds and van-der-Waals interactions.