

O 18: Metal substrates: Adsorption of organic / bio molecules III

Time: Tuesday 10:30–12:45

Location: SCH A118

O 18.1 Tue 10:30 SCH A118

Probing Orientation and Conformation of α -Helix and β -Sheet Model Peptides on Self-Assembled Monolayers with SFG and NEXAFS Spectroscopy — ●TOBIAS WEIDNER¹, JULIA APTE, LARA J. GAMBLE, and DAVID G. CASTNER — National ESCA and Surface Analysis Center for Biomedical Problems, University of Washington, Seattle, USA

Understanding the interaction of proteins and peptides with engineered surfaces from first principles is essential for the design of biomaterials applications. In this study we characterized amphiphilic α -helix and β -strand model peptides on self-assembled monolayers (SAMs) on Au in situ using sum frequency generation (SFG) spectroscopy and ex situ using near edge X-ray absorption fine structure (NEXAFS) spectroscopy. The α -helix peptide is a 14-mer and the β -strand is a 15-mer composed of hydrophilic lysine (K) and hydrophobic leucine (L) residues. SAMs having either carboxylic acid or methyl terminal groups were used as charged and hydrophobic model surfaces, respectively. SFG peptide spectra on methyl SAMs exhibited peaks near 2965 cm^{-1} and 2875 cm^{-1} related to ordered leucine side chains. A relative phase of 0 rad for both peptides showed, that the leucines were oriented towards the interface. Features near 3200 cm^{-1} and 3400 cm^{-1} related to bound water were also observed. The spectra on carboxylic acid SAMs were dominated by a peak near 3300 cm^{-1} , indicating substantial lysine-surface interactions. The linear dichroism of the amide π^* orbital near 400.1 eV observed in the NEXAFS spectra proves the peptides are oriented parallel to the interface on both SAMs.

O 18.2 Tue 10:45 SCH A118

Irradiation-promoted exchange reaction as a tool for Chemical Lithography — NIRMALYA BALLAV¹, ANDREAS TERFORT², and ●MICHAEL ZHARNIKOV¹ — ¹Angewandte Physikalische Chemie, Universität Heidelberg, D-69120 Heidelberg, Germany — ²Institut für Anorganische und Analytische Chemie, Goethe-Universität Frankfurt, 60438 Frankfurt, Germany

The development of novel approaches for the fabrication of nanostructures and, in particular, chemical and biological patterns is an important technological and scientific challenge. One of the perspective methods applies a modification of chemisorbed monomolecular films - self-assembled monolayers (SAMs), which are well-ordered 2D-assemblies of long-chain molecules attached to a suitable substrate. A flexible molecular architecture of the SAM constituents allows one to use a wide range of substrates, whereas the molecular size of these constituents makes SAMs an ideal platform for the fabrication of micro- and nanostructures. We present here a new approach for the fabrication of chemical patterns with aliphatic SAMs as templates. The approach relies upon electron beam or X-ray lithography, but requires much lower patterning dose as compared to already available methods. The technique is based on so-called irradiation-promoted exchange reaction (IPER) between the primary SAM template and potential molecular substituent and can utilize a broad variety of commercially available molecules. The preparation of chemical patterns occurs similar to photography: in the first step the pattern is written by electrons, and in the second step it is developed in the solution of the substituent.

O 18.3 Tue 11:00 SCH A118

Embedded dipoles in monomolecular films: physical and electronic structure effects — ●MICHAEL ZHARNIKOV¹, ORLANDO M. CABARCOS², TOBIAS WEIDNER¹, SUNDARARAJAN UPPILI², LINDA S. DAKE³, and DAVID L. ALLARA² — ¹Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany — ²Department of Chemistry and the Materials Research Institute, Pennsylvania State University, University Park, PA 16802, USA — ³Department of Physics, Utica College, Utica, NY 13502, USA

Ester moiety was imbedded into the molecular chain of alkanethiolate self-assembled monolayers (SAMs) on Au(111), with the length of the segments below and above the ester moiety being varied. The bottom segments of the alkyl chain were found to be better ordered than the upper ones. The presence of the ester moiety leads to the formation of a strong electric dipole layer with a component of 1.05 Debye normal to the surface. This dipole layer exhibits a strong electrostatic effect on the XPS spectra in which the C 1s photoelectron kinetic en-

ergies are consistently shifted by 0.85 eV between the top and bottom alkyl chain segments, regardless of relative lengths. This shift correlates, within error, with the value of 0.81 eV predicted via classical electrostatics due to the presence of the ester dipole layer. Overall, these data show that SAMs assembled from molecules with appropriately selected internal groups can be used to prepare internally layered structures with highly controlled electrical characteristics and further demonstrate that simple XPS shifts in core level energies can be used to derived accurate molecular dipole values in structured thin films.

O 18.4 Tue 11:15 SCH A118

Differences in Self Assembly of Linear Dicarboxylic Acids — ●CHRISTOPH HEININGER¹, LORENZ KAMPSCHULTE^{1,2}, MARKUS LACKINGER¹, and WOLFGANG HECKL^{1,2} — ¹Ludwig-Maximilians-University and Center for NanoScience, Theresienstrasse 41, 80333 München — ²Deutsches Museum, Museumsinsel 1, 80538 München

Self-assembly at the liquid solid interface into two-dimensionally ordered supramolecular structures of three aromatic dicarboxylic acids; 2,6-naphthalenedicarboxylic acid (NDA), 4,4'-biphenyldicarboxylic acid (BPDA), and 4,4'-stilbenedicarboxylic acid (SDA) is studied by scanning tunneling microscopy. The structure of the compounds is very similar and consists of two interconnected aromatic moieties and functionalization through two carboxylic groups in linear configuration. For all molecules, ordered monolayers were observed on a graphite substrate, and the resulting structures can be described as a dense packing of one-dimensionally hydrogen-bonded rows. Concerning the stability of the adsorbate layers, the average domain size, and the degree of order, distinct differences were noticed. Supported by density functional theory (DFT) calculations, these differences are analyzed and explained as a consequence of molecular structure, adsorption geometry, and adsorption energy.

O 18.5 Tue 11:30 SCH A118

N,N'-di(n-butyl)quinacridone monolayer on Ag(110): a DFT study with semiempirical dispersion corrections — ●JÖRN-HOLGER FRANKE¹, VASILE CACIUC², LIFENG CHI¹, and HARALD FUCHS¹ — ¹Physikalisches Institut, WWU Münster, Germany — ²Forschungszentrum Jülich, Germany

We studied the adsorption of N,N'-di(n-butyl)quinacridone (DBQA) on Ag(110) by DFT including semiempirical dispersion corrections. 4 different adsorption geometries are studied, the most stable one showing a binding of molecular oxygen to first layer Ag atoms and butyl chains folded away from the substrate. The charge redistribution upon adsorption is governed by charge donation to the molecular LUMO and the push-back effect, yielding a lowering of calculated work functions by up to 0.85 eV. The semi-empirical dispersion corrections introduce a large non-site specific binding energy gain for all configurations and induce an approach of the molecule to the substrate for weakly bound ones.

[1] J.-H. Franke, V. Caciuc, L.F. Chi, and H. Fuchs, PRB, 78, 165432

O 18.6 Tue 11:45 SCH A118

Chemical versus van der Waals Interaction: The Role of the Heteroatom — ●NICOLAE ATODIRESEI, VASILE CACIUC, PREDRAG LAZIĆ, and STEFAN BLÜGEL — Institut für Festkörperforschung (IFF), Forschungszentrum Jülich, 52425 Jülich, Germany

We performed first-principles calculations aimed to investigate the role of an heteroatom like N in the chemical and the long-range van der Waals (vdW) interactions for a flat adsorption of several π -conjugated molecules on the Cu(110) surface. To evaluate the dispersion effects we used an *ab initio* as well as a semiempirical method. A key result of our study is that a state of the art investigation of the bonding mechanism leading to a flat molecule-substrate adsorption geometry requires the use of both methods to correctly describe the geometry, the electronic structure and the correlation effects of the molecule-surface interface. Our study reveals that the molecule-surface vdW interactions involve not only π -like orbitals which are perpendicular to the molecular plane but also σ -like orbitals delocalized in the molecular plane.

Ref.

1. N. Atodiresei, V. Caciuc, H.-J. Franke and S. Blügel, Phys. Rev. B **78**, 045411 (2008).
2. N. Atodiresei, V. Caciuc, P. Lažić, and S. Blügel,

arXiv:0811.3082.

O 18.7 Tue 12:00 SCH A118

Theoretical Investigation of Bis(terpyridine)-based Surface Structures — •DANIELA KÜNZEL and AXEL GROSS — Institute for Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

Ordered organic layers of bis(terpyridine)-derived molecules (BTPs) adsorbed on graphite show a number of interesting properties that can easily be varied by slight modifications of the system such as the coverage [1]. In order to understand this dependence, structures of 3,3'-BTP and 2,4'-BTP on graphite were investigated using density functional theory (DFT) and several force field methods such as COMPASS, UFF, CVFF and Dreiding.

These calculations confirm that the formation of weak C-H...N hydrogen bonds controls the self-assembled adsorption of BTP molecules into ordered surface structures. Modifications with different surface coverages and surface structures can be obtained, depending on BTP isomer and adsorption conditions. In addition, chemical modifications of the adsorbate molecules and their consequences on structure formation have been addressed.

Due to its large cavities, the hexagonal structure of 3,3'-BTP is of special interest. These cavities can be used as a template for the adsorption of guest molecules such as phthalocyanine derivatives. At room temperature, the guest molecules can rotate within the cavities, as both STM experiments and force field calculations of the rotational barriers demonstrate [1]. Furthermore, the dependence of the rotational barriers on the size of the guest molecules will be discussed.

[1] C. Meier *et al.*, *Angew. Chem. Int. Ed.* **47**, 3821 (2008).

O 18.8 Tue 12:15 SCH A118

First-principles and semi-empirical van der Waals studies of pyridine and thymine on the Cu(110) surface — •V. CACIUC¹, N. ATODIRESEI¹, P. LAZIC¹, J.-H. FRANKE², Y. MORIKAWA³, and S. BLÜGEL¹ — ¹Institut für Festkörperforschung, Theorie I, Forschungszentrum Jülich, D-52425 Jülich, Germany — ²Physikalisches Institut, Westfälische Wilhelms Universität Münster, Wilhelm-Klemm-Str. 10, D-48149 Münster, Germany — ³The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki Osaka, 567-0047 Japan

We performed density functional calculations aimed to investigate

the adsorption geometry and bonding mechanism of a single pyridine (C₅H₅N) and thymine (C₅H₆N₂O₂) molecule on the Cu(110) surface. In the ground state, the pyridine molecule adsorbs with its molecular plane perpendicular to the substrate and is oriented along the [001]-direction while the thymine is aligned along the [1 $\bar{1}$ 0]-direction. For this adsorption configuration, the bonding mechanism of these molecules involves a strong hybridization between the highest occupied molecular orbitals (HOMOs) and the *d*-states of the substrate. However, when the molecular plane is parallel to surface, the long-range van der Waals interactions play an important role on both the molecule-surface geometry and the adsorption energy. Their specific role was analyzed by means of a semi-empirical and the seamless methods. In particular, for a planar configuration, the inclusion of the dispersion effects can dramatically change the character of the adsorption process from physisorption to chemisorption.

O 18.9 Tue 12:30 SCH A118

Molecular Switches at Surfaces: The Role of Van Der Waals Interactions — •ERIK MCNELLIS, JOERG MEYER, and KARSTEN REUTER — Fritz-Haber-Institut, Faradayweg 4-6, 14195 Berlin

Molecules that by external stimuli may be reversibly switched between different defined states are envisioned as a key component of a future molecular nanotechnology. For the latter, it is particularly the molecular function when the switch is stabilized at a solid surface that is of key interest. Using density-functional theory (DFT) with a gradient-corrected (GGA) functional we carry out a detailed characterization of the metastable structures of the prototypical molecular switch azobenzene at close-packed coinage metal surfaces. We obtain a range of switch-surface interactions that goes from weak physisorption at Au(111) to a reversal in the stability of the gas-phase cis and trans molecular conformations at Cu(111). In view of the known inadequacies of present-day GGA functionals in the description of long-range van der Waals interactions, we check on these findings considering corrections from semi-empirical pair potential schemes. While corrections to the gradient are small enough to leave adsorbate geometries essentially unchanged, the obtained adsorption energy corrections are substantial, in certain cases significantly altering the pure DFT picture. We discuss this, and the discomfiting differences obtained between the employed semi-empirical schemes in the greater context of molecular adsorption at metal surfaces.