

O 4: Metal substrates: Adsorption of organic / bio molecules I

Time: Monday 11:15–13:00

Location: SCH A118

O 4.1 Mon 11:15 SCH A118

Molecule-substrate interactions of a strong charge-transfer molecule — ●DANIEL WEGNER¹, STEPHANE BEDWANI², ALAIN ROCHEFORT², and MICHAEL F. CROMMIE¹ — ¹University of California at Berkeley and Lawrence Berkeley National Laboratory, Berkeley, USA — ²Ecole Polytechnique de Montreal, Canada

Molecules containing multiple cyano groups such as tetracyanoethylene (TCNE) or tetracyanoquinodimethane (TCNQ) represent the archetype of strong electron acceptors. These molecules play a vital role in charge-transfer complexes and metal-organic coordination networks. Potential applications range from nanoscopic templating to molecular electronics and molecule-based magnetism. However, there is still a general lack of information on the properties of these molecules in contact with a conducting surface (e.g., the metallic leads of a single-molecule junction). We have performed scanning tunneling microscopy experiments and first-principles density functional theory calculations of the adsorption of TCNE on the Cu(100) surface. By comparing the experimental results with two different adsorption models, we show that the molecular self-assembly is caused by a strong structural modification of the Cu(100) surface rather than the formation of a coordination network via diffusing Cu adatoms. Surface atoms become highly buckled, and the chemisorption of TCNE is accompanied by a partial charge transfer due to a bonding-backbonding process.

O 4.2 Mon 11:30 SCH A118

Perpendicular Interaction between Donor and Acceptor Molecules — GAYANI PERERA¹, RYOTA MISHIMA^{1,2}, and ●SAW-WAI HLA¹ — ¹Ohio University, Physics and Astronomy Department, Athens, Ohio 45701, USA. — ²Division of Material Physics, Graduate School of Engineering Science, Osaka University, Japan.

The capability to modify the electronic properties of materials by the interaction between donor and acceptor molecules plays a significant role in molecular electronics. Formation of molecular charge transfer complexes have been observed for different donor acceptor system in a lateral configuration [1]. Here, we present the structural and electronic properties of decamethylmanganocene (Mn(C5Me5)2) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) molecules on a Au(111) surface at 4.6K using low temperature scanning tunneling microscopy to investigate the perpendicular interaction between the molecules. The molecular complexes are formed by depositing Mn(C5Me5)2 on predeposited TCNQ on Au(111) surface. TCNQ formed well ordered self assembled domains of molecules. Perpendicular interaction between the Mn(C5Me5)2 and TCNQ were determined by means of conductance tunneling spectroscopy. This work is supported by the Ohio University BNNT, National Science Foundation NSF-DMR 0304314, NSF-PIRE: OISE 0730257, and the United States Department of Energy, DE-FG02-02ER46012 grants. [1] F. Jackel, U.G.E. Perera, V. Iancu, K.-F. Braun, N. Koch, J.P. Rabe and S.-W. Hla, Phys. Rev. Lett. 100 (2008) 126102.

O 4.3 Mon 11:45 SCH A118

Layer growth and desorption kinetics of organic acceptor molecules on Au(111) — PAUL FRANK¹, NORBERT KOCH², RALPH RIEGLER³, KLAUS MÜLLEN³, and ●ADOLF WINKLER¹ — ¹Institute of Solid State Physics, Graz University of Technology, Graz, Austria — ²Institute of Physics, Humboldt University Berlin, Germany — ³Max Planck Institute of Polymer Research, Mainz, Germany

The layer growth and desorption kinetics of the organic acceptor molecules hexaazatriphenylene-hexacarbonitrile (HAT-CN) on Au(111) surfaces has been studied by TDS, XPS and AFM. Ultra-thin films of HAT-CN show a quite unexpected thermal stability. The first two layers are wetting the surface. They desorb at 460 K (2nd layer) and 610 K (1st layer), respectively. For higher initial coverage a layer like film forms at and below room temperature, which transforms into a Stranski-Krastanov film upon heating at ca. 400 K. Interestingly, during this transformation also the 2nd wetting layer is incorporated into the nascent islands which then desorb at a higher temperature of ca. 490 K. At even higher initial coverage eventually the 1st monolayer becomes incorporated into the islands during heating and all the molecules desorb already at ca. 500 K. This shows that the two wetting layers are meta-stable and depend on the initial coverage and the temperature. The reason for this unusual behavior can be identified by

the evaluation of the desorption spectra for the individual desorption peaks. It turns out that the desorption energies for all layers are rather similar, but that the pre-exponential factors (in particular for the 1st layer) differ by many orders of magnitude.

O 4.4 Mon 12:00 SCH A118

Electronic Structure of the Hexaketo- and Hexamethoxy-Substituted Coronene Nanographenes on Au — ●MEDJANIK K.¹, NAGHAVI S.², RIEGER R.³, KUTNYAKHOV D.¹, NEPIJKO S.A.¹, SCHÖNHENSE G.¹, ALIJANI V.², FELSER C.², BAUMGARTEN M.³, and MUELLEN K.³ — ¹Institut für Physik, Universität Mainz — ²Institute for Analytic and Anorganic Chemistry Univ. Mainz — ³Max-Planck-Institute for Polymer Research, Mainz

The electronic structure of the donor hexamethoxycoronene and the acceptor coronene-hexaone adsorbed on gold surfaces has been studied by UPS. There substituted nanographenes are synthesized by a novel route described in [1]. A special evaporation system has been developed that is suitable for milligram amounts of evaporant materials. The electronic structure of the keto- and methoxy-species is substantially different because the ligands strongly influence the aromatic system. The keto-species exhibits a significant energetic level shift in the first monolayer with the HOMO being shifted by 1.5 eV towards lower binding energies. The transition from monolayer to multilayer is accompanied by a characteristic variation of the work function that exhibits a sharp minimum. The methoxy species, in contrast, shows constant peak positions throughout the coverage range (along with a continuous drop of the work function) but already for thin layers strong charging sets in. An ab-initio calculation (Gaussian03) has been performed that shows good agreement.

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[1] R. Rieger et al., Chem. Eur. J. 14 (2008) 6322

O 4.5 Mon 12:15 SCH A118

Electronic structure of FeTPC on Cu(111) vs Cu(100) investigated with STM and STS — ●STEFAN KUCK, LEONID LICHTENSTEIN, GERMAR HOFFMANN, and ROLAND WIESENDANGER — Institute of Applied Physics, University of Hamburg, Hamburg, Germany

The investigation of organic molecular systems on metallic surfaces is of great interest due to the manifold applications derived from this combination. However, complications arise from the hybridization of molecule and substrate states at the molecule-substrate interface. Here we locally address the interface of corrole molecules and copper surfaces. In a recent STM study we could show the influence of the substrate on the geometry of iron triphenylcorrole (FeTPC) molecules inducing a bending into a saddle conformation [1]. Molecules are completely asymmetric on the copper substrate which results in a very peculiar electronic structure. We present the influence of the different facets of the copper substrate on the appearance of molecular orbitals spatially resolved in maps of differential conductance.

[1] S. Kuck *et al.*, J. Am. Chem. Soc. **2008**, 130, 14072

O 4.6 Mon 12:30 SCH A118

Ring opening reaction of spiropyran on a Au(111) surface — ●MARTEN PIANTEK, CRISTINA NAVIO, ALEX KRÜGER, MATTHIAS BERNIEN, JORGE MIGUEL, and WOLFGANG KUCH — Institut für Experimentalphysik, Freie Universität Berlin

Molecules that exhibit a photon-induced reversible transition between two isomeric states entail an enormous potential for applications in electronics, photonics, and computing. 1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indole](BIPS) undergoes such a photochromic process involving a heterolytic cleavage of the C–O bond in the pyran ring which goes along with a drastic change of the molecular electronic properties. In the gas phase, in solution, and in the crystalline form, this ring opening/closing mechanism is well understood.

Here we present a temperature-dependent adsorption study of one monolayer of BIPS on a Au(111) single crystal surface. By means of angle-dependent near edge X-ray absorption fine structure (NEXAFS) and X-ray photoemission spectroscopy (XPS) we obtained information about the adsorption geometry and the electronic properties. The simulation of NEXAFS by means of DFT calculations was used for the interpretation of the experimental data. We find that the BIPS molecules deposited at 150 K are in the closed-ring configuration. While the illu-

mination with UV-light had no effect on the monolayer, during heating the sample up to 330 K the molecules transform to the ring opened configuration. Since we did not find a back transformation by cooling back to 150 K, the opened-ring geometry is the preferred conformation on the the surface, in contrast to gas phase and solution.

O 4.7 Mon 12:45 SCH A118

Electron induced conformational changes of an imine-based molecular switch on a Au(111) surface — •CHRISTIAN LOTZE¹, NILS HENNINGSEN¹, KATHARINA FRANKE¹, GUNNAR SCHULZE¹, YING LUO², RAINER HAAG², and JOSE IGNACIO PASCUAL¹ — ¹Inst. f. Experimentalphysik, Freie Universität Berlin, Germany — ²Inst. f. organische Chemie, Freie Universität Berlin, Germany

Azobenzene-based molecules exhibit a cis-trans configurational photoisomerisation in solution. Recently, the adsorption properties of azobenzene derivatives have been investigated on different metal surfaces in order to explore the possible changes in the film properties

induced by external stimuli. In azobenzene, the diazo-bridge is a key group for the isomerization process. Its interaction with a metal surface is dominated through the N lone-pair electrons [1], which reduces the efficiency of the conformational change. In order to reduce the molecule-surface interaction, we explore an alternative molecular architecture by substituting the diazo-bridge (-N=N-) of azobenzene by an imine-group (-N=CH-). We have investigated the imine-based compound para-carboxyl-di-benzene-imine (PCI) adsorbed on a Au(111) surface. The carboxylic terminations mediates the formation of strongly bonded molecular dimers, which align in ordered rows preferentially following the fcc regions of the Au(111) herringbone reconstruction. Low temperature scanning tunneling microscopy was used to induce conformational changes between trans and cis state of individual molecules in a molecular monolayer. [1] N. Henningsen, R. Ruruli, K. J. Franke, I. Fernández-Torrente, and J. I. Pascual, Appl. Phys. A 93, 241 (2008)