

## O 38 Adsorption V

Time: Thursday 15:00–18:00

Room: TRE Phys

O 38.1 Thu 15:00 TRE Phys

**Scanning Tunneling Microscopy and Spectroscopy of Cobalt Pthalocyanine on Cu(111)** — ●XIN GE, CARLOS MANZANO, and RICHARD BERNDT — Institute für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, D-24908 Kiel, Germany

The adsorption morphology and electronic properties of Cobalt Pthalocyanine (CoPc) adsorbed on Cu(111) substrate were investigated by scanning tunneling microscopy and spectroscopy (STM/STS) at 5 K in ultrahigh vacuum. While CoPc has four fold symmetry in the gas phase, STM images acquired at submonolayer coverages show that two opposite lobes of a molecule appear higher than the other two, and they are oriented along the close-packed (110) directions. Tunneling spectra recorded over center and lobes of the molecule are different. Four different CoPc superstructures were observed at  $\sim 1$  ML coverage. Spectral features of CoPc in the superstructures are observed to differ with respect to those of single adsorbed CoPc. We discuss these findings in terms of the different adsorption geometries and intermolecular interactions.

O 38.2 Thu 15:15 TRE Phys

**Toward direct structure determination of adsorbed molecules: D and L cysteine on Cu(17 11 9)<sup>s</sup>** — ●RICHARD SCHILLINGER<sup>1,2</sup> und THOMAS GREBER<sup>1</sup> — <sup>1</sup>Universität Zürich, Winterthurerstrasse 190, CH 8057 Zürich, Schweiz — <sup>2</sup>Paul Scherrer Institut, CH 5232 Villigen PSI, Schweiz

Adsorption of biomolecules on metal surfaces finds an increasing number of applications from biocompatibility to chemical sensing.

The Cu(17 11 9) is a chiral vicinal (111) surface with 14 atoms in the unit cell. Upon adsorption of cysteine already in the monolayer (coverage 4 to 5 molecules per unit cell) find we hints for a change in conformation or ordering of the molecules from core level shifts and from angle scanned X-ray photoelectron diffraction (XPD). Further on, the XPD data point toward a pairing of the molecules in the (17 11 9) unit cell. This finding is in contrast to the situation on the also chiral Au(17 11 9)<sup>s</sup> surface, where we observe ordered single orientation adsorption with a different conformation for the D and L enantiomer. In the monolayer cysteine takes the neutral acidic (SCH<sub>2</sub>CH(NH<sub>2</sub>)-COOH) state. Upon multilayer formation the molecule takes the zwitterionic (HSCH<sub>2</sub>CH(NH<sub>3</sub><sup>+</sup>)-COO<sup>-</sup>) state, identified by appearance of the respective components in the C1s, N1s, S2p, and O1s core level spectra. The experiments were performed on enantiopure systems i.e. only D or L cysteine was evaporated at one time.

O 38.3 Thu 15:30 TRE Phys

**STM-manipulation of HB-HPB molecules: transport of adatoms and rotation along the edge of a molecular island** — ●FRANCESCA MORESCO, LEO GROSS, FRANCO CHIARAVALLI, and KARL-HEINZ RIEDER — Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

A specially designed six-legs molecule called HB-HPB (hexa-tert-butylhexaphenylbenzene), is manipulated on the Cu(111) surface by Scanning Tunneling Microscopy (STM) at low temperature. The molecule is able to aggregate and move Cu adatoms when moved with a STM tip. A single molecule accommodates up to six copper adatoms forming a 2D cluster. The molecule-atoms complex is then further STM manipulated on the surface to bring the Cu freight to a chosen position on the surface and the atoms alone can be released [2]. Moreover, the molecules form well-ordered monolayer structures by self-organisation on Cu(111) [3]. The manipulation of the molecules along the edge of such molecular ordered islands results in the movement between stable positions within the molecular monolayer structure. By marking one of the six molecular legs by substituting a phenyl side ring by a pyrimidine ring, we demonstrate that the molecule rotates along the edge of the monolayer in 60° steps.

[1] L. Gross, K.-H. Rieder, F. Moresco, S. Stojkovic, A. Gourdon, C. Joachim, Nature Materials, in press

[2] L. Gross, F. Moresco, P. Ruffieux, A. Gourdon, C. Joachim, K.-H. Rieder, Phys. Rev. B 71, 165428 (2005)

O 38.4 Thu 15:45 TRE Phys

**Absorption of  $\pi$ -conjugated molecules on Cu(111) studied by X-ray standing waves** — ●A. GERLACH<sup>1</sup>, S. SELLNER<sup>1,2</sup>, F. SCHREIBER<sup>1</sup>, N. KOCH<sup>3</sup>, T.-L. LEE<sup>4</sup>, and J. ZEGENHAGEN<sup>4</sup> — <sup>1</sup>Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany — <sup>2</sup>Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, 70569 Stuttgart, Germany — <sup>3</sup>Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany — <sup>4</sup>ESRF, Rue Jules Horowitz, B.P. 220, 38043 Grenoble Cedex 9, France

We study the adsorption of different aromatic molecules such as pthalocyanines and perylene derivatives on Cu(111) using the X-ray standing wave (XSW) technique. Element specific structural information of high precision is derived from the analysis of XSW yield measurements. Using the C(1s), N(1s), and F(1s) photoelectron signals we show that the molecules adsorb in a lying-down configuration, but with different distances relative to the metal substrate.

The binding distances between the aromatic ring structure and the metal substrate is generally found to be larger than covalent bond lengths. Furthermore, we discuss more subtle effects as e.g. deformations of the adsorbed molecules that are related to the charge (re)distribution at the interface.

[1] A. Gerlach, F. Schreiber, S. Sellner, H. Dosch, I. A. Vartanyants, B. C. C. Cowie, T.-L. Lee, J. Zegenhagen, Phys. Rev. B 71 (2005) 205425

[2] M. Preuss, W. G. Schmidt, and F. Bechstedt, Phys. Rev. Lett. 94, 236102 (2005)

O 38.5 Thu 16:00 TRE Phys

**Fullerene nanowires on a vicinal gold surface** — ●NÉEL NICOLAS, KRÖGER JÖRG, and BERNDT RICHARD — Institut für Experimentelle und Angewandte Physik, CAU Kiel

Submonolayer coverages of fullerene molecules on vicinal gold surface were investigated by low-temperature scanning tunneling microscopy. Straight fullerene stripes of few nanometers width and extending over hundreds of nanometers have been fabricated on the gold surface by utilizing faceting of Au(433) substrates upon C<sub>60</sub> adsorption and subsequent annealing. The observed step bunching is attributed to a lowering of the facet free energy. This surface morphology is a promising template candidate for subsequent deposition of functional units.

O 38.6 Thu 16:15 TRE Phys

**Probing and Modifying Locally the Intrinsic Electronic Structure and the Conformation of Supported Non-Planar Molecules** — ●WOLF-DIETER SCHNEIDER, MARIE-CHRISTINE BLÜM, MARINA PIVETTA, and FRANÇOIS PATHEY — Institut de Physique des Nanostructures, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

The supramolecular self-assembly of rubrene (C<sub>42</sub>H<sub>28</sub>) on Au(111) results in different adsorption conformations of the physisorbed molecules. Owing to the three-dimensional geometry of the molecule providing an inherent decoupling of the molecular  $\pi$ -states from the substrate, the conformers are distinguished by their submolecular appearance in the scanning tunneling microscopy (STM) images and by the corresponding position of the highest occupied molecular orbital (HOMO) in the differential conductance ( $dI/dV$ ) spectra. The application of an electric field induces an irreversible switching of the electronic and geometric conformation of the self-assembled molecules.

O 38.7 Thu 16:30 TRE Phys

**Adsorbate Properties of single PTCDA-Molecules on Ag(111)** — ●ROLF ÖTTKING<sup>1</sup>, WERNER A. HOFER<sup>2</sup>, WICHARD J.D. BEENKEN<sup>1</sup>, ERICH RUNGE<sup>1</sup>, and JUERGEN A. SCHAEFER<sup>1</sup> — <sup>1</sup>Institut für Physik und Zentrum für Mikro- und Nanotechnologien, Technische Universität Ilmenau Postfach 100565, 98684 Ilmenau — <sup>2</sup>Surface Science Research Centre, The University of Liverpool, Liverpool L69 3BX

We present structural, charge and bonding properties of the initial adsorption state of the organic molecule (3,4,9,10)-perylene-tetracarboxylic dianhydride (PTCDA) on highly coordinated silver Ag(111) surfaces derived from first-principles- (DFT-) calculations using projector-augmented waves (PAW-) pseudopotentials and a plane wave basis set. The substrate was taken to be a 11.5Å×20.0Å 4-layer

slab with the PTCDA- adsorbate with dimensions of  $\sim 11.3\text{\AA} \times 6.8\text{\AA}$  planar placed on top. After structural relaxation, performed along the Hellmann-Feynman-Forces, the molecule shows a bent structure with radius of curvature of  $\sim 20\text{\AA}$ . The oxygen-atoms point downwards with a height difference of  $\sim 0.17\text{\AA}$  to the silver surface plane between the carboxylic (corner) and the anhydride oxygen atoms. From a Bader analysis we derive a net charge transfer of  $\sim 1$  electron charge from delocalised states of the two topmost silver layers into the adsorbate LUMO. In addition, binding orbitals and Ag  $3d_{5/2}$  core level shifts were determined.

O 38.8 Thu 16:45 TRE Phys

**Robust hydrogen bonding plus molecular backbone flexibility: step-crossing allowed!** — ●JOACHIM SCHNADT<sup>1,2</sup>, EVA RAULS<sup>1</sup>, WEI XU<sup>1</sup>, JAN KNUDSEN<sup>1</sup>, RONNIE T. VANG<sup>1</sup>, BJØRK HAMMER<sup>1</sup>, and FLEMMING BESENBACHER<sup>1</sup> — <sup>1</sup>Interdisciplinary Nanoscience Center and Department of Physics, University of Aarhus, Building 1520, Ny Munkegade, 8000 Aarhus C, Denmark — <sup>2</sup>Department of Synchrotron Radiation Research, Lund University, Box 118, 221 00 Lund, Sweden

On perfect single crystal surfaces small organic molecules can self-assemble to form extended one- or two-dimensional networks using hydrogen bonding as the network-determining interaction. Real surfaces, however, are defect-afflicted and often it will be desirable that the self-assembled structures are tolerant with respect to the defects, a subject which has not been explored in detail to-date.

We have studied the self-assembly of 2,6-naphthalene-dicarboxylic acid (NDCA) on a Ag(110) surface by STM and XPS. We find that NDCA forms macroscopic-scale one-dimensional hydrogen-bonded structures up to the  $\mu\text{m}$  range. These structures extend over the step edges, which can be regarded as surface defects. We have used DFT to investigate the detailed structure of the assembly on both the terraces and at the step edges. The results show that NDCA indeed can form hydrogen bonds across the step edges, with the assembly having similar binding energies and geometries on the terraces and at the step edges. This behaviour can be traced back to an appropriate balance of the different interactions as well as a combination of molecular backbone flexibility and directionality of the hydrogen bonds.

O 38.9 Thu 17:00 TRE Phys

**Complex formation and proton transfer between formic acid and water on Au(111) surfaces under UHV conditions** — ●MICHEL KAZEMPOOR and GERHARD PIRUG — Institut für Schichten und Grenzflächen (ISG3), Forschungszentrum Jülich GmbH, 52425 Jülich

The coadsorption of formic acid (HCOOH) and water (H<sub>2</sub>O) on Au(111) single crystal surfaces has been investigated by means of vibrational spectroscopy (HREELS), photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). Formic acid adsorbs at 90 K molecularly with vibrational modes characteristic for flat lying zig-zag chains and solid formic acid in the monolayer and physisorbed multilayer regime, respectively. Annealing results in a complete desorption at 190 K without any detectable formation of intermediates like formates. Sequential adsorption of formic acid and water at 90 K shows no significant chemical interaction in the vibrational signatures and the core level photoelectron binding energies. Upon annealing the coadsorbed layer to 140 K new vibrational losses appear in the HREEL-spectrum at 190, 590 and 1000  $\text{cm}^{-1}$ . Using isotopically labelled adsorbates such as D<sub>2</sub>O and H<sup>13</sup>COOD we were able to identify a hydrogen-bonded complex between formic acid and water with a molecular ratio of one. Upon further annealing this complex decomposes leaving only molecularly adsorbed formic acid on the surface at 160 K. This process is accompanied by a proton exchange between formic acid and water. The results will be discussed in the light of recent findings for the electrochemical oxidation of formic acid on Au surfaces.

O 38.10 Thu 17:15 TRE Phys

**Isomerization of an azobenzene derivative on Au(111) by scanning tunneling microscopy** — ●MICOL ALEMANI, LEONHARD GRILL, KARL HEINZ RIEDER, and FRANCESCA MORESCO — Inst. für Exp.physik, FU Berlin, Arnimallee 14, D-14195 Berlin

Azobenzene molecules are of great interest because they have in the gas phase two stable isomers (cis and trans) and can switch reversibly from one configuration to the other by photo-excitation. An azobenzene derivative, equipped with four tert-butyl groups, has been investigated on Au(111) with a scanning tunnelling microscope (STM) at low tem-

perature (5K).

The molecules result mobile after preparation at room temperature and form islands. From the STM images, the exact molecular orientation and configuration have been extracted. All the molecule are found in the trans configuration, as it is in the gas phase the more energetically favoured one.

By applying voltage pulses with the STM tip on molecular islands, the isomerization of single molecules from the trans configuration to the cis and backwards has been realized. The process is characterized by changing the applied voltage. A model is proposed for the cis isomer adsorbed on the surface which is in accordance with its chemical properties.

O 38.11 Thu 17:30 TRE Phys

**Porous Network Structure of Octacyano-metal free Phthalocyanine on HOPG Surface** — ●THIRUVANCHERIL G. GOPAKUMAR<sup>1</sup>, WERNER R. THIEL<sup>2</sup>, and MICHAEL HIETSCHOLD<sup>1</sup> — <sup>1</sup>Chemnitz University of Technology, Institute of Physics, Solid Surfaces Analysis Group, D-09107 Chemnitz, Germany. — <sup>2</sup>Technical University Kaiserslautern, Department of Chemistry, Inorganic Chemistry, D-67663 Kaiserslautern, Germany.

The molecule-molecule interaction in the thin films of Phthalocyanine is the reversible weak van der Waals interaction. The use of functional groups in these molecular systems open the possibility to introduce strong molecule-molecule interaction and thereby a supra-molecular engineering. In this work we report the porous-network structure formation in Octacyano-metal free Phthalocyanine (H<sub>2</sub>Pc(CN)<sub>8</sub>) on HOPG surface. The molecular layers forming quadratic packing with one void per unit cell with an average void area of 2 nm<sup>2</sup>. Simple molecular dynamics calculation of different type of quadratic molecular unit cells shows the minimum energy structure has only one void per unit cell and show good agreement with the experiments. Beyond these porous structures there has been observed another phase of molecules, where highly close packed structures were found. Moreover typical point defects of filling of pore-structures are found which suggest this molecular layer to be used as a template for other organic molecules to elaborate the understanding of co-adsorption, site-selectivity, sensing etc. Finally we show that these defects can be induced and repaired by a tip-induced process.

O 38.12 Thu 17:45 TRE Phys

**In-situ Alteration of Bimolecular Hydrogen-bond Networks** — ●LORENZ KAMPSCHULTE<sup>1,2</sup>, MARKUS LACKINGER<sup>1</sup>, TOVA ADLERSTEIN<sup>2</sup>, STEFAN GRIESSL<sup>1</sup>, GEORGE W. FLYNN<sup>2</sup>, and WOLFGANG M. HECKL<sup>1,3</sup> — <sup>1</sup>Dept. Earth and Environmental Sciences, LMU München, Theresienstr. 41, 80333 Munich, Germany — <sup>2</sup>Dept. of Chemistry, Columbia University, New York, New York 10027, USA — <sup>3</sup>Deutsches Museum, Museumsinsel 1, 80538 Munich, Germany

Bimolecular monolayers were grown by spontaneous self-assembly from solution at the liquid-solid interface and subsequently investigated by Scanning Tunneling Microscopy (STM). The co-adsorption of two different molecules, BTB (1,3,5-benzenetribenzoic acid) and TMA (trimesic acid) in open (loosely packed) networks was studied in two different solvents (heptanoic and nonanoic acid). Altering the absolute and relative concentrations of the two compounds in binary solutions resulted in phases with six different structures. Their cavity size ranges from 1.1 nm for a structure solely composed of the smaller TMA molecules up to 2.8 nm for a pure BTB network. All structures are stabilized by twofold intermolecular hydrogen bonding between the carboxylic acid head groups. Moreover, in-situ dilution of liquid mixtures induced phase transitions of the monolayer structures, accompanied by an alteration of the size and shape of cavity voids in the 2-dimensional molecular assembly.