O 6: Metal substrates: Adsorption of organic / bio molecules I

Time: Monday 11:15–13:00 Location: H36

O 6.1 Mon 11:15 H36

Phase boundaries in organic adlayers – a quantitative video-STM study — •Michael Roos, Harry E. Hoster, and R. Jürgen Behm — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

Bis(terpyridine)derivatives (BTP) form highly ordered hydrogen-bonded networks on different substrates at solid surfaces [1,2]. Using time resolved scanning tunneling microscopy (STM), we have studied dynamic phenomena in such adlayers on Ag/Ru(0001) at room temperature. BTP molecules on Ag/Ru(0001) form coverage dependent networks with different hydrogen bonding configuration. At low coverages, a parallel chain structure (PCS) is formed in coexistence with a two-dimensional admolecule gas. At higher coverages, domains of a locally more densely packed quasi quadratic network (QQN) are formed [2]. Time resolved STM imaging at QQN|PCS phase boundaries reveals a continuous exchange of molecules between both phases as indicative for a dynamic equilibrium. Based on a statistical evaluation of the STM sequences, we show that the anisotropy of the molecule-molecule interactions is not only reflected in the periodic structures of the 2 adlayers, but also in the probability of different types of local rearrangements at the phase boundary.

[1] M. Roos et al., *Phys.Chem.Chem.Phys.* 9, **2007**, 5672.

[2] H. E. Hoster et al., *Langmuir* 23, **2007**, 11570.

O 6.2 Mon 11:30 H36

Adsorption of Bis(terpyridine) studied with DFT and Force Field Methods — •Daniela Künzel and Axel Gross — Institute for Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

Bis(terpyridine) (BTP) molecules can form a number of different ordered surface structures on metal and graphite substrates [1]. The structural variability in combination with easily modifiable properties turn the BTP molecules into interesting candidates for theoretical and experimental studies.

Both DFT and force field methods are used to study the formation and modification of 3,3'-BTP and 2,4'-BTP surface structures. Self-assembling into ordered monolayers is directed by the formation of weak intermolecular C-H$\cdots$N hydrogen bonds and by van-der-Waals and π-π interactions with the surface. Depending on the BTP isomer, substrate and adsorption conditions, different phases can be observed and their stability estimated. The modification of the surface structures by the formation of host-guest systems or by the interaction with additional oxygen will also be addressed.

[1] C. Meier, M. Roos, D. Künzel, A. Breitruck, H.E. Hoster, K. Landfester, A. Groß, R. J. Behm and U. Ziener, J. Phys. Chem. C (2009), DOI: 10.1021/jp910029z.

O 6.3 Mon 11:45 H36

Alkali-Crown Ether Complexes at Metal Surfaces — •Nicha Thontasen[1], Giacomo Levita[2], Zhitao Deng[1], Nikola Malinowski[1,3], Stephan Rauschenbach[1], and Klaus Kern[1,4] — [1]Max Planck Institute for Solid State Research, Stuttgart, Germany — [2]University of Trieste, Trieste, Italy — [3]Bulgarian Academy of Sciences, Sofia, Bulgaria — [4]EPFL, Lausanne, Switzerland

Crown ethers are polycyclic ethers which, in solution, selectively bind cations depending on the size of the ring cavity. The study of a single host-guest complex is highly desirable in order to reveal the characteristics of these specific interactions at the atomic scale. Such detailed investigation is possible at the surface where high resolution imaging tools like scanning tunneling microscopy (STM) can be applied.

Here, electrospray ion beam deposition (ES-IBD) is employed for the deposition of Dibenzo-24-crown-8 (DB24C8)-H+, -Na+ and -Cs+ complexes on a solid surface in ultrahigh vacuum (UHV). Where other deposition techniques have not been successful, this deposition technique combines the advantages of solution based preparation of the complex ions with a highly clean and controlled deposition in UHV.

Single molecular structures and the cation-binding of DB24C8 at the surface are studied in situ by STM and MALDI-MS (matrix assisted laser desorption ionization mass spectrometry). The internal structure of the complex, i.e. ring and cavity, is observable only when alkali cations are incorporated. The BD24C8-H+ complex in contrast appears as a compact feature. This result is in good agreement with theoretical models based on density functional theory calculations

O 6.4 Mon 12:00 H36

STM/STS study of Spiro-DPO molecules on Au(111) — •Michael H. Waelsch[1], Tatjana Podlich[1], Melanie Klinke[1], Tobat P. I. Saragi[2], Josef Salbeck[2], and René Matzdorf[1] — [1]Universität Kassel, Experimentalphysik II, — [2]Universität Kassel, AG Makromolekulare Chemie und Molekulare Materialien, FB 18 Naturwissenschaften, Heinrich-Plett-Str. 40, 34132 Kassel

In the Spiro-DPO molecule an electron transport material (donor) is linked to a hole transport material (acceptor) via a Spiro-C-atom.

The arrangement of about 1/10 ML Spiro-DPO on a Au(111)-substrate has been investigated with respect to the molecular energy-levels by STM/STS in UHV at 4.8 K. We observed amorphous clusters of molecules, which showed obvious shifts in their HOMO- and LUMO-energies, if the sample was annealed above the glass transition temperature. The shifts may be due to screening by the surrounding molecules. Without annealing the molecules arrange in rings, double rows and chains, depending on the underlying Au(111)-herringbone-reconstruction. In these structures the HOMO/LUMO-levels measured with STS are less shifted than in the amorphous clusters.

O 6.5 Mon 12:15 H36

Charging and decharging single molecules — Dagmar Kreikemeyer-Lorenzo, Isabel Fernandez-Torrente, Anna Strozecka, •Katharina J. Franke, and Jose I. Pascual — Fachbereich Physik, Freie Universität Berlin, Germany

The charge state of molecules on surfaces crucially influences their reactivity, electronic transport properties and magnetic state. The mixture of the charge transfer compounds tetramethyl-tetrathiafulvalene (TMTTF) and tetracyanoquinodimethane (TCNQ) on a Au(111) surface leads to a self-assembled monolayer of homomolecular rows. In these structures, the majority of TCNQ becomes charged by accepting a single electron in its lowest unoccupied molecular orbital as evidenced by a Kondo resonance in STM transport experiments. Using the STM tip we can manipulate the charge state and thus its magnetic properties. The charging/decharging depends strongly on the position of the tip above the molecular structures and the applied bias voltage.

O 6.6 Mon 12:30 H36

An unusual approach to the description of bonding of chemisorbed conjugated molecules on noble metals — •Gerold M. Rangger[1], Lorenz Romaner[2], Oliver T. Hofmann[1], Michael G. Ramsey[3], and Egbert Zojer[1] — [1]Institut für Festkörperphysik, Technische Universität Graz, Austria — [2]Lehrstuhl für Atomistic Modeling and Design of Materials, Montanuniversität Leoben, Austria — [3]Institut für Physik, Karl-Franzens Universität Graz, Austria

The deposition of organic monolayers on metals has attracted significant interest as a tool to modify surfaces in the field of molecular electronics.

We present a theoretical study of the acceptor F4TCNQ on Ag(111) and the donor viologen on Au(111). There, experiments show pronounced changes in the UPS spectra of the molecules due to strong interactions with the surfaces. To understand the bonding mechanism, we use a projection of the density of states onto atomic and molecular orbitals in combination with a crystal orbital overlap type population analysis. This enables analyzing the molecular orbital occupation and the determination of bonding and anti-bonding contributions of molecular/atomic orbitals on the energy scale. Only a simultaneous examination of adsorption induced changes of the molecular geometry (including a bending of the molecule) and of the interaction between molecule and metal allows to arrive at a consistent picture for the investigated chemisorption processes.

O 6.7 Mon 12:45 H36

A new charge-transfer complex in UHV-deposited tetramethoxypyrene and TCNQ — •Katerina Medjanik[1], Sergej Nepijko[1], Gerd Schönhense[1], Milan Rudloff[2], Vita Solovyeva[2], Michael Huth[2], Shahab Naghavi[3], Claudia Felser[3], Martin Baumgarten[4], and Klaus Müllen[4] — [1]Institut für Physik, Johannes Gutenberg-Universität, 55099 Mainz, Germany — [2]Physikalisches Institut, Goethe-Universität, 60438 Frankfurt, Germany — [3]Institute für Analytische und Anorganische Chemie,

Johannes Gutenberg-Universität, 55099 Mainz, Germany — [4]Max-Planck-Institute for Polymer Research, 55128 Mainz, Germany

A study of the UHV-deposited mixed phase of tetramethoxypyrene (TMP) and TCNQ has been performed using UPS, X-ray-diffraction, and infrared spectroscopy. Formation of a new intermolecular compound is evident from the appearance of new reflexes in XRD (d_1=0.911 nm, d_2=0.684 nm). In UPS characteristic shifts of the level positions indicate a charge transfer from TMP to TCNQ, being suggested also by the softening of the CN stretching vibration of TCNQ visible in IR spectroscopy (shift by $7\,\mathrm{cm}^{-1}$). The size of the level shift is similar to shifts observed for the acceptor-donor pair hexaketo-/hexamethoxycoronene. In SEM and AFM micro crystals with sizes in the sub-micrometer range are visible, similarly as previously found for BEDT-TTF / TCNQ [1]. A DFT calculation serves as guideline for interpretation of the spectra. Project funded via Transregio SFB TR49 and Graduate School of Excellence MAINZ.

[1] V. Solovyeva *et al.*, Thin Solid Films **517**, 6671 (2009)