

O 7: Metal substrates: Adsorption of organic / bio molecules I

Time: Monday 10:30–13:00

Location: A 053

O 7.1 Mon 10:30 A 053

Order or disorder? The adsorption of NTCDA on Ag(111) investigated by VT-STM — ●HOLGER WETZSTEIN^{1,2}, SEBASTIAN FIEDLER^{1,2}, JEREMIAS WEINRICH^{1,2}, MARTIN WINNERLEIN^{1,2}, ACHIM SCHÖLL^{1,2}, and FRIEDRICH REINERT^{1,2} — ¹Physikalisches Institut, Experimentelle Physik VII und Wilhelm Conrad Röntgen Research Center for Complex Material Systems (RCCM), Universität Würzburg, D-97074 Würzburg — ²Gemeinschaftslabor für Nanoanalytik, Karlsruher Institut für Technologie KIT, D-76021 Karlsruhe

The adsorption of organic molecules on single crystalline substrates results in a wealth of structural arrangements. This polymorphism is due to the interplay between lateral and vertical interactions and strongly depends on coverage, temperature and preparation. We investigated the adsorption of NTCDA on Ag(111) surfaces at different temperatures with the help of variable temperature scanning tunneling microscopy and low energy electron diffraction to analyze the structural and electronic properties. This systems shows various adsorbate superstructures and a particularly interesting reversible order-disordering transition upon cooling, so called inverse melting. While some thermodynamic parameters of this transition have already been derived, the driving force for this ordering phenomenon as well as the geometric arrangement of the molecules in the disordered phase has not yet been accessed. Our STM data shows various ordered and disordered structural phases at different temperatures. By correlating our new results with already existing data we intend to shed light on the mechanism involved in the ordering of organic molecules on metal substrates.

O 7.2 Mon 10:45 A 053

Observing Structural Phase Dynamics and Molecular Aggregation in Real Time: Dispersive NEXAFS Applied to Organic Films — ●MARKUS SCHOLZ^{1,2}, CHRISTOPH SAUER^{1,2}, MICHAEL WIESSNER^{1,2}, HOLGER WETZSTEIN^{1,2}, ACHIM SCHÖLL^{1,2}, and FRIEDRICH REINERT^{1,2} — ¹Physikalisches Institut, Experimentelle Physik VII und Wilhelm Conrad Röntgen Research Center for Complex Material Systems (RCCM), Universität Würzburg, D-97074 Würzburg — ²Gemeinschaftslabor für Nanoanalytik, Karlsruher Institut für Technologie KIT, D-76021 Karlsruhe

We present a novel experimental approach which allows following structural and electronic changes in organic films by quick near edge X-ray absorption fine-structure spectroscopy (QNXAFS). This technique utilizes the energy-dispersive mode of the BESSY UE52-PGM beamline and allows NEXAFS with about one second time resolution. We show the potential of the method on the example of thin films of the organic molecule 1,4,5,8-naphthalene-tetracarboxylicacid-dianhydride (NTCDA). The time-evolution of the NEXAFS signal recorded at different temperatures allows distinguishing between different processes that are involved in the reorganization of the film. Moreover, since the technique also monitors spectroscopic details we are able to study the interplay between film morphology, molecular orientation, and intermolecular interaction in real time. In a meta-stable phase we observe aggregated molecules that exhibit coherent coupling. The signature change of the vibronic progression and of the peak width allow us to quantify the coherent length of the electronic excitation.

O 7.3 Mon 11:00 A 053

Ultrathin heterostructures and mixed layers of the organic semiconductors NTCDA and PTCDA on Ag(111) — ●GREGOR ÖHL, CAROLIN R. BRAATZ, and PETER JAKOB — Philipps-Universität, Marburg, Germany

Heterostructures as well as mixed layers of the organic semiconductors PTCDA and NTCDA have been grown on Ag(111) and their thermal evolution (temperature range 80 - 550 K) investigated *in situ* using FT-IRAS, SPA-LEED and TDS. Specifically, the influence of the long range order within the first monolayer on the stacking and the thermal evolution of the heterolayers will be discussed. The high spectral resolution of IRAS thereby allows a clear discrimination of the two molecular species and of the various phases of the layered NTCDA/PTCDA system. Effects such as orientational changes, lateral ordering, dewetting and interlayer exchange become accessible this way. Depending on the stacking order of the PTCDA and NTCDA layers and on the amount of deposited material, the relevance of the individual processes is found to vary substantially. For the mixed PTCDA/NTCDA mono-

layers on Ag(111), results on the thermal evolution are presented.

O 7.4 Mon 11:15 A 053

Dissecting an organic-metal bond by molecular manipulation — ●CHRISTIAN WAGNER, NORMAN FOURNIER, CHRISTIAN WEISS, RUSLAN TEMIROV, and F. STEFAN TAUTZ — Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany and JARA-Fundamentals of Future Information Technology

Scanning probe microscopy with a dynamic AFM has been able to answer some fundamental questions of surface science, like the force necessary to move an atom[1]. Recently, we demonstrated the gradual removal of a single 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA) molecule from Ag(111) using a dynamic AFM [2]. The continuous force gradient measurement allowed the structural control over the junction. Here, we show how to extract details of the molecule-surface bonding (physisorption, chemisorption, bonding via functional groups) from such an experiment. The importance of a full-fledged simulation of the lifting -including tip oscillation- is emphasized. We point out the necessity of, and fundamental problems related to, a curved tip trajectory. We study PTCDA on Au(111) and Ag(111) and find qualitatively and quantitatively different binding potentials and adsorption energies. The data represents a good benchmark for existing and future ab-initio calculations on these systems. Our method should be applicable to various substrate-adsorbate systems and hence has the potential to answer many open questions in the field.

[1] M. Ternes et al., *Science* **319**, 1066 (2008)[2] N. Fournier et al., *Phys. Rev. B* **84**, 035435 (2011)

O 7.5 Mon 11:30 A 053

Force-controlled lifting of molecular wires — ●NORMAN FOURNIER^{1,2}, CHRISTIAN WAGNER^{1,2}, CHRISTIAN WEISS^{1,2}, RUSLAN TEMIROV^{1,2}, and F. STEFAN TAUTZ^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — ²JARA-Fundamentals of Future Information Technology

Understanding of the charge transport on a single-molecule level is vital for the future success of molecular electronics. Often, however, this understanding is hindered by the lack of data obtained under well-controlled experimental conditions. Recently, we have shown that a low-temperature dynamic atomic force microscope (AFM) can be used to perform well-controlled and tunable single molecule transport studies [1]. In this experiment a single 3,4,9,10-perylene-tetracarboxylicacid-dianhydride (PTCDA) molecule is lifted from a metal surface, while the stiffness of the junction is recorded along with the conductivity. Here, we compare lifting of PTCDA from Au(111) and from Ag(111), i.e., two situations where PTCDA is either connected to gold or to silver electrodes. We find clear differences in the conductivity and the stiffness in both cases that we attribute to the different character of the molecule-metal bond.

[1] N. Fournier et al. *Phys. Rev. B* **84**, 035435 (2011)

O 7.6 Mon 11:45 A 053

Importance of electron correlations for π -conjugated organic molecules on metal substrates — ●CHRISTOPH SAUER^{1,2}, FLORIAN BRUCKNER^{1,2}, HOLGER WETZSTEIN^{1,2}, SINA GUSENLEITNER^{1,2}, ACHIM SCHÖLL^{1,2}, and FRIEDRICH REINERT^{1,2} — ¹Physikalisches Institut, Experimentelle Physik VII und Wilhelm Conrad Röntgen Research Center for Complex Material Systems (RCCM), Universität Würzburg, D-97074 Würzburg — ²Gemeinschaftslabor für Nanoanalytik, Karlsruher Institut für Technologie KIT, D-76021 Karlsruhe

We demonstrate that electron correlations play an important role for the energy balance when the adsorption of π -conjugated molecules on metal substrates leads to charge transfer into the former lowest unoccupied molecular orbital (LUMO). By annealing an organic heterostructure of tin-phthalocyanine (SnPc) on top of a Ag(111) surface pre-covered with one monolayer (ML) of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) we produce a pure ML of SnPc on Ag(111). Therefore our high resolution photoemission spectroscopy (PES) analysis proves that the adsorption of SnPc is energetically favoured over PTCDA on Ag(111). We identify that this behavior is a consequence of a smaller Coulomb repulsion (U_C) between the electron in the former LUMO and the electrons in the other molecular orbitals for SnPc. The difference in U_C for SnPc and PTCDA is demonstrated by a com-

parison of PES and inverse PES data from multilayer and ML samples and values in the order of 1 eV are found. Hence U_C is not negligible for the adsorption energy balance.

O 7.7 Mon 12:00 A 053

Modification of the PTCDA/Ag(111) interaction by the formation of a hetero-organic interface with CuPc — •BENJAMIN STADTMÜLLER^{1,2}, TOMOKI SUEYOSHI^{1,2}, SERGUEI SOUBATCH^{1,2}, F. STEFAN TAUTZ^{1,2}, and CHRISTIAN KUMPF^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — ²Jülich-Aachen Research Alliance - Fundamentals of Future Information Technology

In recent years the adsorption of large organic molecules on noble metal surfaces has been studied in great detail. One key aspect in these studies was the characterization of the interaction between the organic adsorbates and the metal substrate. Based on these studies we have now started to investigate hetero-organic systems consisting of more than one molecular species. Here we present a X-Ray Standing Waves (XSW) and photoelectron spectroscopy (UPS) study of the adsorption behavior of CuPc on one closed layer of PTCDA on Ag(111). The CuPc molecules adsorb on top of the closed PTCDA layer and form a disordered CuPc layer at submonolayer coverages and room temperature, which condenses into the commensurate 'stacked bilayer'-structure upon cooling below 160K. XSW reveals an adsorption height of CuPc on PTCDA which is significantly smaller than the sum of the van der Waals radii of the atomic species. Even more interestingly, for this system the vertical adsorption geometry of the underlying PTCDA molecule changes: The molecular backbone is pushed towards the silver surface. Furthermore, UPS experiments reveal a shift of the PTCDA F-LUMO. These results clearly indicate a modified interaction between PTCDA and the silver surface by the adsorption of CuPc.

O 7.8 Mon 12:15 A 053

Electronic and geometric structure of organic overlayers from angle-resolved UPS and DFT calculations — •MATUS MILKO¹, SOPHIA HUPPMANN^{2,3}, MARKUS SCHOLZ^{2,3}, WIESSNER MICHAEL^{2,3}, ACHIM SCHÖLL^{2,3}, FRIEDRICH REINERT^{2,3}, and PETER PUSCHNIG¹ — ¹Chair of Atomistic Modelling and Design of Materials, Montanuniversität Leoben, Austria — ²Experimentelle Physik VII und Wilhelm Conrad Roentgen Research Center for Complex Material Systems, Universität Würzburg, Germany — ³Gemeinschaftslabor für Nanoanalytik, Karlsruher Institut für Technologie KIT, Germany

We present a combined experimental and theoretical study on the electronic and geometric structure of metal-free phthalocyanine (H₂Pc) and copper phthalocyanine (CuPc) adsorbed on Au(110). Experimentally, mono-layers of the molecules were analyzed by low energy electron diffraction (LEED) revealing ordered superstructures. Then, angular resolved photoelectron spectroscopy (ARPES) was employed to

examine the valence electronic structure. Theoretically, we computed the electronic structure within the framework of density functional theory corrected for many body effects which leads to correct ordering of orbitals. Moreover, using ARPES orbital maps of the highest occupied molecular orbitals in reciprocal space were obtained which we could directly compare to our *ab initio* results. We demonstrate, how one can extract information about the azimuthal orientation of the molecules on the substrate by this approach. Thus in combination with LEED we can provide a complete two-dimensional structure determination.

O 7.9 Mon 12:30 A 053

Low Temperature Scanning Tunneling Microscopy Study of Co-Phthalocyanine Molecules on Au(111) and Graphene/Ir (111) — •SAMUEL BOUVRON, PHILIPP ERLER, STEFAN AMBRUS, UDO DEHM, DAVID HEESE, ELIZABETA ČAVAR, and MIKHAIL FONIN — Fachbereich Physik, Universität Konstanz

Metal-phthalocyanines have attracted substantial attention due to their possible applications in molecular electronic devices. Since it may affect the electronic structure and magnetic properties of the molecule, the interaction between a molecule and a substrate is of crucial importance. Furthermore, the adsorption behavior of molecules on surfaces is decisive in a bottom up approach to build molecular electronics. For a better understanding of the interaction between Cobalt-Phthalocyanine molecules (CoPc) and surfaces, we investigated CoPc molecules deposited on Au(111) and Graphene/Ir(111) at different coverages by means of low-temperature scanning tunneling microscopy (STM) and near-edge xray absorption spectroscopy (NEXAFS). The possible use of the graphene layer to decouple the CoPc molecule from a metallic substrate will be discussed.

O 7.10 Mon 12:45 A 053

Naphthalocyanine on Au(100) – adsorption and structural formation at submonolayer coverage — •PATRICK MEHRING, AXEL BEIMBORN, TOBIAS LÜHR, and CARSTEN WESTPHAL — Technische Universität Dortmund, Experimentelle Physik 1, Germany

The formation of metal-free naphthalocyanine (H₂Nc) structures on Au(100) is investigated by means of room temperature scanning tunneling microscopy at submonolayer coverage. The molecules adsorb with their plane parallel to the surface and arrange in two types of ordered domain structures. A striped phase with an orientation perpendicular to the ridge of the Au(100)_{hex} reconstruction and a densely packed phase with an unequal distribution along the high-symmetry surface directions is found. In the densely packed domains only one configuration of H₂Nc is observed. Subsequent annealing induces a phase transformation of the adlayer. The number and size of H₂Nc domains arranged in the striped phase decreases and the molecular sequence within the densely packed domain structure is changed.