O 52: Metal substrates: Adsorption of organic / bio molecules VII

Time: Thursday 15:00–19:15 Location: SCH A118

O 52.1 Thu 15:00 SCH A118

Understanding the electronic transport across single phthalocyanine molecules — •Annika Bork[1], Albert F. Takács[1,2], Florian Witt[1], Stefan Schmaus[1,2], Timofey Balashov[1], Martin Bowen[3], Eric Beaurepaire[3], and Wulf Wulfhekel[1,2] — [1]Physikalisches Institut, Universität Karlsruhe (TH) — [2]CFN-DFG Centrum für Funktionelle Nanostrukturen — [3]Institut de Physique et Chimie des Matériaux de Strasbourg

Regarding the increasing miniaturization of electronic devices, molecular electronics is a field of growing interest. Here, we present STM and STS results on hydrogen (H_2Pc), cobalt (CoPc) and manganese (MnPc) phthalocyanines deposited on a clean Cu(111) surface as well as on bilayer cobalt islands on Cu(111). By laterally positioning the STM tip over a single molecule and approaching the tip towards the surface we were able to investigate the conductance of the molecules. Our results show that the molecules tend to lift from the surface and jump into contact with the STM tip. On Cu(111) we found that the conductance through H_2Pc, CoPc and MnPc is about $0.1\,G_0$ whereas the conductance of H_2Pc and CoPc on the cobalt islands is about 3 times higher. By performing STS measurements the orbitals of the H_2Pc and CoPc can be obtained. In both cases we can observe a shift of the HOMO to the Fermi edge, which explains the increased conductance on the cobalt islands. Further, inelastic STS revealed a soft phonon excitation located on the sidegroups, that is the underlying mechanism of the jump into contact.

O 52.2 Thu 15:15 SCH A118

Systematic study of phthalocyanine (sub-)monolayer phases by high-resolution PES and NEXAFS — •M. Häming[1], C. Scheuermann[1], E. Umbach[1,2], A. Schöll[1], and F. Reinert[1,2] — [1]Universität Würzburg, Experimentelle Physik II — [2]Forschungszentrum Karlsruhe, 76021 Karlsruhe

The interaction at metal-organic interfaces is crucial for electronic devices, since it influences the morphology and the electronic structure at the interface, and consequently the charge transport through metal-organic contacts. Therefore we investigate the interaction and interplay between the geometric and electronic structure at a metal-organic model interface. We study systematically various (sub-)monolayers phases of flat lying phthalocyanine on the Ag(111) surface by high-resolution photoemission spectroscopy (PES) and near edge x-ray absorption fine structure spectroscopy (NEXAFS). We observe evidence for chemisorption of the molecules in all spectra (valence band, NEXAFS and core levels). Moreover, already small differences in the adsorption geometry between the different phases change the respective spectra and the work function significantly. For example, an increase in coverage leads to a weaker interface bond. Consistent changes in the valence band and NEXAFS spectra indicate that consequently the occupation of the former molecular LUMO level, which is partly occupied due to the chemisorption, is altered. Our investigation demonstrates that the electronic structure at interfaces is very sensitive to relatively small changes in the interaction, and that high-resolution PES and NEXAFS are powerful techniques to study these correlations.

O 52.3 Thu 15:30 SCH A118

Temperature and thickness dependent adsorption studies of azobenzene molecules on Cu(100) — •Alex Krüger, Marten Piantek, Cristina Navio, Jorge Miguel, Matthias Bernien, and Wolfgang Kuch — Institut für Experimentalphysik, Freie Universität Berlin

Here we present a study of the influence of temperature and coverage on the ordering of dimetacyano-azobenzene (DMC) ultrathin layers adsorbed on Cu(001). Near-edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS) provided information on the molecular geometry relative to the substrate and on the nature of molecule adsorption to the surface, respectively. From XPS data we determine that DMC molecules evaporated onto Cu(001) at room temperature are chemisorbed, but a dramatic change in the angle-dependent C- and N-K edge NEXAFS between 0.5 and 1 ML (monolayer) indicates that strong intermolecular interactions provoke a conformational change. On a second step, we studied the temperature dependence of 1 ML DMC on Cu(001). At 150 K, about half of the molecules are physisorbed in a planar conformation parallel to the surface. As the temperature increases, the NEXAFS data shows a strong change in the molecular conformation at 230 K, concurrent with the formation of a bond between one of the azo nitrogen atoms to the surface, as seen by XPS. These results are supported by density functional theory calculations. We conclude that both intermolecular and molecule-substrate interactions can give rise to the observed conformational change.

O 52.4 Thu 15:45 SCH A118

Adsorption energy and geometry of adsorbed organic molecules on Au(111) probed by surface-state photoemission — •Johannes Ziroff[1], Frank Forster[1], and Friedrich Reinert[1,2] — [1]Universität Würzburg, Experimentelle Physik II , D-97074 Würzburg, Germany — [2]Forschungszentrum Karlsruhe, Gemeinschaftslabor für Nanoanalytik, D-76021 Karlsruhe, Germany

The modification of the Au(111) surface states by an adsorbed monolayer of large π-conjugated molecules (PTCDA, NTCDA, CuPc) was investigated by high-resolution angle-resolved photoelectron spectroscopy. We determined binding energy, band mass, and Rashba-splitting and discuss the results in the context of rare-gas adsorption on noble metals. This comparison allows the determination of the bonding strength of the adsorbates, found to be physisorptive with derived binding energies per molecule of 2.0 eV for PTCDA and 1.5 eV for NTCDA. We will also present a superstructure model for the NTCDA/Au(111) system, deduced from low energy electron diffraction images in combination with band-backfolding of the Tamm and Shockley states. The coverage dependent evolution of the surface states was also investigated for the three molecules, giving evidence for a dilute-phase growth of the CuPc molecule on the Au(111) surface.

O 52.5 Thu 16:00 SCH A118

Investigation of meso-Tetraphenylporphyrin Molecules using Scanning Tunneling Microscopy — •Vinícius Claudio Zoldan[1,2], Khalil Zakeri[1], Chunlei Gao[1], André Avelino Pasa[2], and Jürgen Kirschner[1] — [1]Max Planck Institute of Microstructure Physics, Halle, Germany — [2]Laboratório de Filmes Finos e Superfícies, Universidade Federal de Santa Catarina, Brazil

Due to their distinct physicochemical properties and potential for molecular architecture, porphyrins represent a group of molecules which has attracted a great technological and fundamental interest. The meso-Tetraphenylporphyrin (H_2-TPP) and meso-Tetraphenylporphyrin-Cobalt II (Co-TPP) molecules were grown on Ag(111) and $Cu_3Au(100)$ substrates. In the case of Ag(111), self-organized monolayer was observed, as has been reported [1]. The growth of single molecules were achived on $Cu_3Au(100)$ at room temperature. The chemical sensitivity through bias-dependent imaging of both molecules has been measured using low temperature Scanning Tunneling Microscopy/Spectroscopy (STM/STS). The STS results show one characteristic peak near 0.6 eV for H_2-TPP molecules, whereas for the Co-TPP molecules two peaks were observed at energies of -0.5 and -1.1 eV. Moreover, the dehydrogenation of the individual H_2-TPP and Co-TPP molecules was realized with a local ramp-voltage from the STM tip. The energy needed for the dehydrogenation is found to be 2.0 and 3.5 eV for H_2-TPP and Co-TPP, respectively.

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O 52.6 Thu 16:15 SCH A118

Interaction between coordinated metal ions and a metal substrate: Differently substituted cobalt porphyrins on Ag(111) — •Yun Bai, Florian Buchner, Martin Schmid, Ina Kellner, Florian Vollnhals, Hubertus Marbach, Hans-Peter Steinrück, and J. Michael Gottfried — Universität Erlangen-Nürnberg, Lehrstuhl für Physikalische Chemie II, Egerlandstr. 3, 91058 Erlangen, Germany

Adsorbed metalloporphyrins are of increasing interest due to their potential applications in heterogeneous catalysis and in sensor systems. Previous studies from our group have suggested the existence of an electronic interaction between the metal centers of the adsorbed porphyrin complexes of iron and cobalt and the underlying substrate surface, which plays an important role in modifying the electronic structure and, thereby, the reactivity of these metal centers.[1,2] However, with the previously used tetraphenylporphyrin (TPP) ligands, the adsorbed complexes undergo saddle-shape distortion, which could also influence the electronic structure. To separate the effects of distortion on the one hand and the coupling to the substrate on the other, we have studied cobalt octaethylporphyrin, which adsorbs in a flat, undistorted conformation on Ag(111). Comparison of our XPS, UPS, and STM results with previous CoTPP data [1,2] confirms that indeed the metal center plays an essential role in the electronic interaction between the porphyrin complexes and the substrate. Supported by the DFG through SFB 583.

1. T. Lukasczyk et al., J. Phys. Chem. C 111 (2007) 3090.
2. K. Flechtner et al., J. Am. Chem. Soc. 129 (2007) 12110.

O 52.7 Thu 16:30 SCH A118

Electronic and magnetic coupling of iron and copper phthalocyanine to ferromagnetic Co(100) surfaces — ●Felix Schmidt[1], Jens Sauther[1], Ehesan Ali[2], Stefan Lach[1], Peter Oppeneer[2], and Christiane Ziegler[1] — [1]Department of Physics, University of Kaiserslautern, Erwin Schrödinger Str. 56, D-67663 Kaiserslautern, Germany — [2]Department of Physics and Materials Science, Box 530, Uppsala University, S-75121 Uppsala, Sweden

Metallo-phthalocyanines are organic semiconductors which show in certain cases promising magnetic properties, advertising them for use in organic spintronics. Here, copper (CuPc) and iron phthalocyanine (FePc) were grown on ultra thin layers of Co(100) substrates with well known highly spin-polarized electron injection capability. Photoelectron spectroscopy (XPS) reveals different interactions between the pyrolic nitrogen atoms and the cobalt surface for the two phthalocyanines. The analysis of the different multiplet structures appearing for the nitrogen core levels in the submonolayer regime and UPS investigations of the valence band electronic structure of the Co dominated region near the Fermi level indicates a particularly electronic coupling and a rehybridisation of the molecular orbitals with the cobalt orbitals. In order to clarify the influence of the two different central atoms on the electronic- and subsequently the magnetic coupling to the Co substrate, theoretical calculations using the GGA and GGA+U methodologies on a structure of Fe/Cu-phthalocyanine adsorbed on a 3-layered cobalt surface were performed indicating a ferromagnetic coupling between FePc and Co.

O 52.8 Thu 16:45 SCH A118

Investigation of the electronic structure of CuPc on Cu(100) interfaces using ARUPS with polarized light — ●Michael Wiessner[1], Marc Haeming[1], Frank Forster[1], Achim Schöll[1], and Friedrich Reinert[1,2] — [1]Universität Würzburg, Experimentelle Physik II, D-97074 Würzburg — [2]Forschungszentrum Karlsruhe, Gemeinschaftslabor für Nanoanalytik, D-76021 Karlsruhe

The understanding of the electronic structure at metal-organic interfaces is crucial for electronic devices since it determines the charge transport through metal-organic contacts. Particularly if chemical interaction occurs, as it is the case between most aromatic organic molecules and metals, the hybridization of molecule and metal wave functions effects both the energy position and the symmetry of the involved orbitals. Consequently, the dipole matrix element, i.e. the intensity of a photoemission signal, will be influenced. This phenomenon can thus be utilized as a sensitive probe for the interfacial interaction and the character of the involved molecular and metal states.

We report on an investigation of the adsorption of ultra-thin Cu-phthalocyanine films on Cu(100) surfaces by means of angular resolved photoemission spectroscopy (ARPES) with polarized light. By using a monochromatized HeI_α source with a high degree of polarization and with variable polarization direction we observe polarization-dependent intensities for signals from the substrate, from the adsorbate molecules, and from interface states which are generated due to the chemisorption. The evaluation of these variations in intensity shows that the applied method is a usefull tool for understanding the interaction mechanisms.

O 52.9 Thu 17:00 SCH A118

Fingerprints of large organic molecules: on the interior of tetraphenyl-porphyrins in scanning tunneling microscopy — Florian Buchner[1,3], Karl-Georg Warnick[2,3], Thorsten Wölfle[2,3], Wolfgang Hieringer[2,3], Andreas Görling[2,3], Hans-Peter Steinrück[1,3], and ●Hubertus Marbach[1,3] — [1]Lehrstuhl für Physikalische Chemie II — [2]Lehrstuhl für Theoretische Chemie — [3]Interdisciplinary Center of Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91056 Erlangen

The appearance of a constant current scanning tunneling microscopy (STM) image is determined by both the topography and the electronic structure of the investigated object. The discrimination of these effects and the understanding of the bias dependent appearance of different adsorbed species represents a major challenge. We investigate an intermixed tetraphenylporphyrin (TPP) layer consisting of 2HTPP, CoTPP and FeTPP molecules on Ag(111), to allow for a direct in situ comparison. By a combined experimental and theoretical analysis, we find that at lower bias voltages the appearance of CoTPP in the STM image is dominated by electronic effects, while at high bias a combination of both electronic and topographic effects is observed. For 2HTPP and FeTPP the images are dominated by topographic effects. The detailed interpretation of the bias dependence is performed by means of high quality density-functional calculations, which allow to reproduce the experimentally observed STM images with very high accuracy and to trace back the observed features to individual molecular orbitals. Supported by the DFG through SFB 583.

O 52.10 Thu 17:15 SCH A118

Portrait of a potential barrier: electron tunneling at metal-organic interfaces — ●Lucia Vitali[1], Giacomo Levita[2], Robin Ohmann[1], Alessio Comisso[3], Alessandro De Vita[3], and Klaus Kern[1] — [1]Max-Planck Institute for Solid State Research, Stuttgart, Germany — [2]INFM Democritos, University of Trieste, Italy — [3]Physics Department, King s College, London

Organic semiconductors constitute the basis of a fast developing microelectronics and are successfully making the first steps towards high performance nanoscale devices. Further improvements and the design of new molecular-based electronic circuits require a better understanding of the charge transport and injection mechanisms. At present, one of the major constrains is given by the electron potential barrier forming at the molecule-metal interface. Here, by means of a low temperature scanning tunneling microscope (STM), we visualize this metal-molecule interface on a local scale. We found that the molecular interaction with the substrate leads to the formation of a potential barrier which is non-uniform across the molecule. This reflects the relation between the chemical composition and the interaction with the metal surface.

O 52.11 Thu 17:30 SCH A118

Adsorption of metal-phthalocyanines on the Ag(111) surface — ●Ingo Kröger[1], Christoph Stadler[1], Patrick Bayersdorfer[1], Florian Pollinger[1], Abdreas Stahl[1], Felix Erfurth[1], Benjamin Stadtmüller[1], Christian Kumpf[1,2], and Friedrich Reinert[1,3] — [1]Universität Würzburg, Experimentelle Physik II, 97074 Würzburg — [2]Forschungszentrum Jülich GmbH, IBN-3, D-52425 Jülich — [3]Forschungszentrum Karlsruhe GmbH, Gemeinschaftslabor für Nanoanalytik, D-76021 Karlsruhe

The sub-monolayer growth of metal-phthalocyanines (MePc) on the Ag(111) surface exhibits a rich phase diagram consisting of 2D gas-like phases, commensurate phases and - most interestingly - continuous series of phases with point-on-line coincidence with the substrate. The latter are caused by a repulsive molecule-molecule interaction which can be tuned (and even suppressed) by changing coverage and/or temperature. Therefore these adsorbate systems represent model systems for investigating the interplay of molecule-molecule and molecule-substrate interaction as well as geometric and electronic structure.In this talk we present an overview of the phase diagrams for CuPc, SnPc, TiOPc and H2Pc. The data was obtained using spot profile analysis low energy electron diffraction (SPA-LEED) and X-ray standing waves (XSW). Comparing these systems gives insight in the molecular adsorption geometry as well as the influence of the central metal atom on the molecule-substrate and the molecule-molecule interactions.

O 52.12 Thu 17:45 SCH A118

STM and STS study of F_{16}CoPc adsorbed onto Ag(110) surface — ●Marius Toader[1], Thiruvancheril G. Gopakumar[2], Mahmoud Abdel-Hafiez[1], and Michael Hietschold[1] — [1]Chemnitz University of Technology, Solid Surfaces Analysis Group, D-09107 Chemnitz, Germany — [2]Christian-Albrechts-Universität zu Kiel, Institute of Experimental and Applied Physics, D-24118 Kiel, Germany

In this work the adsorption of cobalt(II) hexadecafluorophthalocyanine (F_{16}CoPc), one of the few organic n-type semiconductors, onto silver (110) surface prepared by OMBD is investigated using UHV VT-STM from Omicron operating at 40 K. The asymmetry of the metal substrate is found to act as a template for the organic adlayer which grows preferentially along the [1-10] crystallographic axis leading to a commensurate structure with well defined pinning centers. The proposed structural model is strongly sustained by the molecular self assembly at the defects proximity and especially at the domain boundaries where a mirror structure is induced. The perturbed electronic properties like HOMO-LUMO gap, induced new states close to the Fermi level are illustrated using STS. Single molecule DFT calculations are implemented to understand the mechanism responsible for the organic-metal interface formation from STS.

O 52.13 Thu 18:00 SCH A118

Dimerization Boosts One-Dimensional Mobility of Conformationally Adapted Porphyrins on a Hexagonal Surface Atomic Lattice — •Maximilian Eichberger[1], Matthias Marschall[2], Joachim Reichert[2], Alexander Weber-Bargioni[1], Willi Auwärter[2], Richard L. C. Wang[3], Hans J. Kreuzer[3], Yan Pennec[1], Agustin Schiffrim[1,2], and Johannes V. Barth[2] — [1]Department of Physics & Astronomy, University of British Columbia, Vancouver, Canada — [2]Physik Department, TU München, Germany — [3]Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Canada

We employed temperature-controlled fast-scanning tunneling microscopy to monitor the diffusion of tetrapyridylporphyrin molecules on the Cu(111) surface. The data reveal unidirectional thermal migration of conformationally adapted monomers in the 300-360 K temperature range. Surprisingly equally oriented molecules spontaneously form dimers that feature a drastically increased one-dimensional diffusivity. The analysis of the bonding and mobility characteristics indicates that this boost is driven by a collective transport mechanism of a metallosupramolecular complex.

O 52.14 Thu 18:15 SCH A118

The Adsorption of Porphine on Copper (110) — •Matthew Stephen Dyer, Abel Robin, Sam Haq, Rasmita Raval, and Mats Persson — University of Liverpool, Liverpool, U. K.

Porphyrin molecules and related phthalocyanines have come under a lot of interest in recent years as potential components for molecular-scale devices with various applications. By studying the simplest porphyrin, porphine (H_2-P), and its interaction with a clean copper surface we obtain physical insight relevant for larger, more complicated systems.

We present the results of scanning tunnelling microscopy (STM) and reflection absorption infrared spectroscopy (RAIRS) experiments, along with density functional theory (DFT) calculations, which show that H_2-P is chemisorbed on Cu(110) with the centre above the short-bridge site. Considerable charge transfer occurs upon adsorption from the metal into the unoccupied orbitals of the molecule.

An unexpected and very interesting result is that copper adatoms are observed to reside in the vicinity of H_2-P molecules in STM images. DFT calculations show that there is an energetic preference of about 25 meV for copper adatoms to reside in certain sites on the surface close to H_2-P molecules. There is no chemical bond formed between the molecule and the adatom, rather the attraction is probably due to a substrate-mediated interaction.

O 52.15 Thu 18:30 SCH A118

Adsorption Geometry of Non-Planar Phthalocyanines on Cu(111): Orientation of the Electric Dipole Moment — •A. Gerlach[1], S. Duhm[2], T. Hosokai[1], F. Schreiber[1], N. Koch[2], O. Hofmann[3], E. Zojer[3], T.-L. Lee[4], and J. Zegenhagen[4] — [1]Institut für Angewandte Physik, Universität Tübingen, Germany — [2]Institut für Physik, Humboldt-Universität zu Berlin, Germany — [3]Institut für Festkörperphysik, Technische Universität Graz, Austria — [4]European Synchrotron Radiation Facility, Grenoble, France

The orientation of polar organic molecules on metal surfaces has important implications for the electronic properties of the first molecular layer. We have studied the orientational ordering of chlorogallium phthalocyanines (GaClPc) on Cu(111) using the X-ray standing wave technique, photoelectron spectroscopy and DFT calculations.

The XSW data indicate that for low coverages the majority of GaClPc molecules adsorb in a 'Cl-down' configuration with a chlorine bonding distance of 1.88 Å. Since the gallium atoms are located at 4.21 Å, we find a Ga-Cl bond length close to the gas phase value. For higher coverages the XSW data indicate a co-existence of the 'Cl-down' and 'Cl-up' configuration on Cu(111).

Due to the alignment of the GaClPc molecules in the sub-monolayer regime their dipole moments are expected to contribute to the decrease of the work function. The non-monotonic change of the work function with increasing GaClPc coverage observed in UPS measurements can be traced back to the different adsorption geometries of GaClPc. The analysis is further supported by quantum chemical calculations.

O 52.16 Thu 18:45 SCH A118

High-resolution ARUPS study of thin CuPc films on noble-metal (111) surfaces — •Mario Kochler[1], Johannes Ziroff[1], Frank Forster[1], Hatice Karacuban[2], and Friedrich Reinert[1,3] — [1]Universität Würzburg, Experimentelle Physik II, Am Hubland, D-97074 Würzburg, Germany — [2]Universität Duisburg Essen, Fachbereich Physik, D-47057 Duisburg, Germany — [3]Forschungszentrum Karlsruhe, Gemeinschaftslabor für Nanoanalytik, D-76021 Karlsruhe, Germany

The large π-conjugated organic molecule copper phthalocyanine (CuPc) is widely applied in the promising field of organic electronics, for instance as donor material in solar cells. For these applications the electronic structure of the organo-metallic interface is of particular interest. We present high-resolution ARUPS data of epitaxial CuPc films on Au, Ag and Cu (111). The valence band features, i.e. the highest occupied molecular orbital (HOMO), the former lowest unoccupied molecular orbital (F-LUMO) and a sharp resonance right at the Fermi level, are specific for each substrate. The differences in the electronic structure are a result of the increasing interaction strength between the molecules and the substrate, ranging from physisorption on Au to strong chemisorption on Cu. We correlate the coverage dependent change of the HOMO binding energy to the individual adsorption strength. The intermediate bonding strength on Ag (111) causes a partially filled F-LUMO that gives rise to the sharp resonance at the Fermi level. We will discuss these features on the background of the different growth modes of CuPc on noble metal surfaces.

O 52.17 Thu 19:00 SCH A118

STM observations of the interaction of NO and CO with adsorbed metalloporphyrin molecules — •Knud Seufert, Willi Auwärter, Joachim Reichert, and Johannes V. Barth — Physik Department, TU München, Germany

The reactivity of metalloporphyrins towards small gas molecules is of fundamental interest as it plays for example a key role in the transport of respiratory gases in biological systems. Here we present a comparative low temperature STM and STS study of the interaction of CO and NO with Cobalt-tetraphenylporphyrins (CoTPP) anchored on a Ag(111) surface. The response of CoTPP to the exposure of CO and NO is clearly different: In the CO case, the CoTPP can be dressed by one or two CO ligands. Hereby, the geometric and electronic structure of CoTPP is mostly preserved. The attachment of NO to CoTPP drastically modifies the topographic appearance of CoTPP. The two-fold symmetry of CoTPP resulting from an adsorption-induced distortion is lost upon NO coordination. These experiments were systematically extended to further metalloporphyrins and a Cu(111) surface, to get more information on the underlying bond characteristics.