

## O 47: Metal substrates: Adsorption of organic / bio molecules V

Time: Wednesday 10:30–13:00

Location: H36

O 47.1 Wed 10:30 H36

**Adsorption behaviour of Phthalocyanine molecules on a Au(110) surface** — •TOBIAS PERTRAM<sup>1</sup>, JAN-MARKUS ESSEN<sup>1</sup>, SÉVERINE LE MOAL<sup>2</sup>, MARCO MOORS<sup>1</sup>, MICHAEL PEINTINGER<sup>1</sup>, CONRAD BECKER<sup>2</sup>, THOMAS BREDOW<sup>1</sup> und KLAUS WANDEL<sup>1</sup> — <sup>1</sup>Institute of Physical and Theoretical Chemistry, Wegelerstr. 12, D-53115 Bonn, Germany — <sup>2</sup>CINAM - CNRS - UPR 3118, Campus de Luminy - Case 913, F-13288 Marseille, France

The {110} surfaces of fcc metals contain an intrinsic anisotropy due to their rectangular surface unit cell. This anisotropy is even more pronounced in case of the (1 × 2) missing row reconstruction, which is typical for the Au(110) surface. We have used this reconstructed surface as a substrate for the deposition of phthalocyanine molecules. In our STM and LEED study we found the formation of molecular double rows which are aligned with the closed packed rows of the reconstructed Au(110) surface. In addition to a coverage dependence of the length of the double rows, we found that the presence of these rows also influences the type of the reconstruction of the Au(110) surface. Whereas at uncovered regions the (1 × 2) reconstruction could be observed, at regions covered with phthalocyanine double rows a (1 × 3) reconstruction was found. The formation of double rows on the (1 × 3) reconstructed Au(110) surface is triggered by both a strong molecule–molecule interaction and a strong molecule–substrate interaction. In contrast only a weak interaction between adjacent dimmers along the rows could be observed, the closest distance between them equals six times the Au lattice constant.

O 47.2 Wed 10:45 H36

**Diffusion of phthalocyanine on Ag(100) investigated by STM** — •GRAZYNA ANTczAK<sup>1,2</sup> and KARINA MORGENSTERN<sup>1</sup> — <sup>1</sup>Leibniz University, Hannover, Germany — <sup>2</sup>University of Wrocław, Wrocław, Poland

Information about the thermal stability of phthalocyanine as well as how the molecule binds to surfaces are crucial in a bottom up approach to build molecular electronics. Phthalocyanine is already widely used in technology, for example in laser printers, CDs, colorants and so on. How do these organic molecules move over a surface? In contrast to the well studied diffusion of individual atoms, molecules exhibit more motional degrees of freedom that make their movement much more complicated. It is likely that concerted mechanisms will play an important role in their diffusion. Such concerted movements were already proven to be present for movement of close-packed metallic clusters. We have carried out a study of phthalocyanine motion on the Ag(100) surface in low-temperature scanning tunneling microscopy in the temperature range 50–80 K. We will show that phthalocyanine starts thermal movement over the surface at 55 K and follows an Arrhenius relation at least up to 80 K. From the Arrhenius plot of diffusivity the activation energy of 116 meV for the movement of single molecules was obtained. The prefactor of diffusivity will also be discussed.

O 47.3 Wed 11:00 H36

**XSW experiments on Copper(II)-Phthalocyanine submonolayer films on noble metal surfaces** — •INGO KRÖGER<sup>1</sup>, CHRISTOPH STADLER<sup>2</sup>, BENJAMIN STADTMÜLLER<sup>1</sup>, CHRISTOPH KLEIMANN<sup>1</sup>, GIUSEPPE MERCURIO<sup>1</sup>, PATRICK BAYERSDORFER<sup>2</sup>, FLORIAN POLLINGER<sup>2</sup>, and CHRISTIAN KUMPF<sup>1</sup> — <sup>1</sup>Institute of Bio- and Nanosystems 3 (IBN-3), Forschungszentrum Jülich & JARA-FIT — <sup>2</sup>Experimentelle Physik II, Universität Würzburg

The adsorption of large pi-conjugated molecules on noble metal surfaces is in the focus of recent experimental and theoretical investigations. The basic bonding mechanisms are of particular interest, as well as their influence on crucial parameters like workfunctions and the alignment of molecular levels with respect to the substrate Fermi level. Geometric parameters are also of high interest. However, the most prominent and fundamental parameter, the adsorption height, is generally overestimated in state of the art DFT calculations. We present a series of X-ray standing wave measurements of the bonding distances for the model system Copper(II)-Phthalocyanine in different submonolayer phases on Ag(111), Au(111) and Cu(111). It is shown that the adsorption height does not only depend on the substrate, but also on the lateral structure of the molecular thin film which is very sensitive to small changes in the coverage [1]. The data are compared with

the results of other techniques (see also contributions of C. Kleimann and B. Stadtmüller) and discussed in terms of the interaction strength. [1] Stadler et al., Nature Physics 5, 153 (2009)

O 47.4 Wed 11:15 H36

**Sub-monolayer growth of CuPc on Cu(111)** — •BENJAMIN STADTMÜLLER<sup>1,2</sup>, INGO KRÖGER<sup>1</sup>, FRIEDRICH REINERT<sup>2</sup>, and CHRISTIAN KUMPF<sup>1</sup> — <sup>1</sup>Forschungszentrum Jülich (IBN-3) & JARA-FIT — <sup>2</sup>Exp. Physik II, Univ. Würzburg

The geometric arrangement of organic molecules within the first monolayer adsorbed on a metal surface has crucial influence on the interface properties as well as on the growth behavior of the following molecular layers. We studied the sub-monolayer growth of the model system copper-II-phthalocyanine (CuPc) on the Cu(111) surface using high resolution low energy electron diffraction (SPA-LEED) and photoelectron spectroscopy (UPS). This system is of highest interest since phthalocyanine molecules show an unusual intermolecular repulsion upon adsorption on the Ag(111) surface [1]. This is also discussed in the contributions of I. Kröger and C. Kleimann. On Cu(111), however, the alignment of the molecules indicates an attractive intermolecular interaction at sub-monolayer coverages. At low coverages the molecules align in linear chains of different length. At higher coverages they start to form islands having a commensurate structure. UPS-measurements show a new electronic state close to the Fermi level which indicates charge transfer (i.e. chemical interaction) between the molecules and the substrate. This breaks the 4-fold symmetry of the molecule and consequently influences the molecular order. From the comparison of results found for CuPc on Cu(111), Ag(111) and Au(111) we gain insight the influence of the substrate on the intermolecular interaction. [1] Stadler et al., Nature Physics 5, 153 (2009)

O 47.5 Wed 11:30 H36

**Selective bonding and apparent symmetry of single Cobalt-Phthalocyanine on a Cu(111) surface** — •DEUNG-JANG CHOI<sup>1</sup>, BENJAMIN W. HEINRICH<sup>1</sup>, CRISTIAN IACOVITA<sup>1</sup>, THOMAS BRUMME<sup>2,3</sup>, LAURENT LIMOT<sup>1</sup>, MIRCEA V. RASTEI<sup>1</sup>, JENS KORTUS<sup>2</sup>, WERNER A. HOFER<sup>4</sup>, and JEAN-PIERRE BUCHER<sup>1</sup> — <sup>1</sup>IPCMS(CNRS), UMR 7504, Université de Strasbourg, France — <sup>2</sup>Institut für Theoretische Physik, TU Bergakademie Freiberg, Germany — <sup>3</sup>Institute for Materials Science and Max Bergmann Center of Biomaterials, Dresden University of Technology, Germany — <sup>4</sup>Surface Science Research Centre, University of Liverpool, United Kingdom

Low-temperature scanning tunneling microscopy and spectroscopy are combined with *ab initio* calculations to study isolated CoPc molecules on a Cu(111) surface. Tip-assisted manipulation and constant-height scans are employed to resolve the adsorption geometry of the molecule and to obtain high-resolution maps of the intramolecular conductance. We show that nitrogen atoms play a central role in the adsorption and the conductance of the molecule on Cu(111). The preferential adsorption of nitrogen on top of surface atoms centers CoPc on a bridge site of the Cu lattice and anchors the molecule to the surface with an adsorption energy estimated at 6.9 eV. Furthermore, we show that the *p*-orbitals of the nitrogen atoms along with the *d*-orbitals of cobalt govern the molecular conductance, the former contribution being responsible for the symmetry of CoPc on the surface. The symmetry is seen to change at selected biases due to electronic effects, which are discussed in detail.

O 47.6 Wed 11:45 H36

**Modification of magnetic properties of a manganese phthalocyanine by axial coordination of CO molecule** — •ANNA STROZECKA and JOSE IGNACIO PASCUAL — Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

The coordination of small molecules, like NO, CO or O<sub>2</sub>, to transition metal phthalocyanines can substantially modify properties of these complexes and their interaction with the underlying substrate. We investigated the effect of coadsorption of CO molecules on magnetic properties of manganese phthalocyanines (MnPc) adsorbed on Bi(110) surface. STM experiments reveal that the Kondo resonance observed for unligated MnPc molecules changes upon bonding of CO to a central metal ion. The increase in the Kondo temperature of the complex indicates the enhancement of spin-electron coupling. The

original magnetic state of MnPc is recovered after selective desorption of CO molecules.

O 47.7 Wed 12:00 H36

**Effect of fluorination on the adsorption geometry and electronic structure of Zn-phthalocyanine molecules** — ●A. GERLACH<sup>1</sup>, T. HOSOKAI<sup>1</sup>, F. SCHREIBER<sup>1</sup>, S. DUHM<sup>2</sup>, N. KOCH<sup>2</sup>, H. YAMANE<sup>3</sup>, Y. TANAKA<sup>3</sup>, Y. MI<sup>4</sup>, and J. ZEGENHAGEN.<sup>4</sup> — <sup>1</sup>Institut für Angewandte Physik, Universität Tübingen, Tübingen, Germany — <sup>2</sup>Institut für Physik, Humboldt-Universität, Berlin, Germany — <sup>3</sup>Institute for Molecular Science, Okazaki, Japan — <sup>4</sup>European Synchrotron Radiation Facility, Grenoble, France

Using the X-ray standing wave (XSW) technique and angle-resolved UPS (ARUPS) we studied the structural and electronic properties of Zn-phthalocyanine (ZnPc) and perfluorinated Zn-phthalocyanine (F<sub>16</sub>ZnPc) molecules on Cu(111).

The element specific bonding distances of ZnPc and F<sub>16</sub>ZnPc derived by XSW show that the molecule-substrate interaction depends significantly on the chemical structure of the adsorbate. Compared to its perfluorinated derivative ZnPc shows a surprisingly small bonding distance ( $d(C) = 2.49 \text{ \AA}$ ), which reflects the strong interaction of the molecules with the copper substrate. Moreover, the XSW data reveal different distortions of these molecules that can be related to their specific bonding mechanism: Relative to the molecular plane the central zinc atom of ZnPc is pulled  $0.25 \text{ \AA}$  towards the substrate, whereas the fluorine atoms of F<sub>16</sub>ZnPc are pushed  $0.15 \text{ \AA}$  towards the vacuum side. We show that these adsorption induced changes of the molecular geometry are reflected in electronic structure of both systems.

O 47.8 Wed 12:15 H36

**SnPc on Ag(111) investigated by STM** — ●CHRISTOPH KLEIMANN, INGO KRÖGER, CHRISTIAN WEISS, CHRISTA ELSAESSER, and CHRISTIAN KUMPF — Institut für Bio- und Nanosysteme (IBN3), FZ Jülich & JARA-FIT

The investigation of interfaces between thin organic films and metal surfaces is a field of highest interest because it represents the basis for future applications of organic electronic devices. In this context, phthalocyanines are of particular interest since repulsive intermolecular interaction was found recently for this group of organic molecules [1]. Tin(II)-phthalocyanine (SnPc) is non-planar and can adsorb in two different geometries: with the Sn atom pointing downwards (Sn down) or upwards (Sn up). In our group different Pc molecules have previously been studied using several experimental techniques like SPA-LEED or XSW (see also contributions by I. Kröger and B. Stadtmüller). Here we present STM studies of SnPc on Ag(111), taken at different coverages and temperatures, and discuss the results in the context of our previous findings. At low coverages the formation of chains can be observed for Sn down molecules while Sn up molecules tend to stay separated. This originates from a strong interaction with the substrate which leads to a broken symmetry of the SnPc molecules. Measurements at higher coverages show large ordered areas of Sn down molecules which are oriented along the different domains of the silver surface. The combination of STM and LEED in our setup allows to precisely correct the STM images for distortions and therefore enables a quantitative

analysis of the adsorption geometry. [1] Nat. Phys. 5, pp 153-158 (2009)

O 47.9 Wed 12:30 H36

**STM and STS study at the organic-metal interface: Adsorption of CoPc on Ag(111) surface** — ●MARIUS TOADER, PAVEL SHUKRYNAU, and MICHAEL HIETSCHOLD — Chemnitz University of Technology, Institute of Physics, Solid Surfaces Analysis Group, D-09107 Chemnitz, Germany

In this work, we have studied the interface effects which arise upon adsorption of cobalt(II)-phthalocyanine (CoPc) on a silver (111) surface, in terms of morphology and electronic properties. The organic ultra-thin film corresponding to a slightly sub-monolayer coverage has been prepared using OMBD and investigated with an UHV VT-STM from Omicron. A strong molecule-substrate coupling is emphasized by template-guided molecular arrangements of single molecules, molecular nanochains and extended molecular domains. Therefore, the reported highly-oriented adlayer structures, like pseudo-square and superstructures with different molecular appearance, have to be discussed. The electronic properties at the organic-metal interface, are discussed based on voltage polarity-dependent STM imaging and tip-sample distance-dependent scanning tunneling spectroscopy. A molecular HOMO-LUMO gap narrowing has been reported with decreasing tip-sample distance. Moreover, the features in the superstructure exhibit slightly different electronic properties. For a better understanding of the interface effects, single molecule DFT calculations were also employed and compared with STS data.

O 47.10 Wed 12:45 H36

**Electronic structure of ultra thin organic hetero-interfaces - SnPc/PTCDA/Ag(111)** — ●ACHIM SCHÖLL<sup>1</sup>, MARC HÄMING<sup>1</sup>, MICHAEL GREIF<sup>1</sup>, MICHAEL WIESSNER<sup>1</sup>, and FRIEDRICH REINERT<sup>1,2</sup> — <sup>1</sup>Universität Würzburg, Experimentelle Physik VII, D-97074 Würzburg, Germany — <sup>2</sup>Karlsruhe Institute of Technology, Gemeinschaftslabor für Nanoanalytik, D-76021 Karlsruhe, Germany

While the interfaces of molecules to a substrate have been studied extensively, knowledge about the interface between different molecular compounds is still relatively scarce. This is to some extent caused by the fact that these interfaces, which are of great relevance for optoelectronic devices consisting out of multiple organic compounds, are more complicated to access experimentally. Structurally well defined model systems, which allow for a systematic and detailed investigation of the interface characteristics, are thus of great importance. In this work we provide data from x-ray absorption and photoelectron spectroscopy on the organic heterolayer system tin-phthalocyanine (SnPc) / perylen-tetracarboxylic acid dianhydride (PTCDA). We show, that SnPc, prepared on a Ag(111) surface precovered by a monolayer of PTCDA, forms a well defined interface with a closed first layer of flat lying molecules. Moreover, the bonding of the SnPc molecules to the PTCDA interlayer is clearly non-covalent and a detailed inspection of the valence spectra shows that the respective molecular signatures can be distinguished well. The SnPc/PTCDA/Ag(111) system is thus well suited for further investigations employing complicated techniques.